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**DISTILLATION OF AQUEOUS SOLUTIONS OF
FORMALDEHYDE.**

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It is a well-known fact that when ordinary solutions of formaldehyde in water are exposed to the air and are allowed to evaporate spontaneously, there is left behind a solid polymer as a residue. Auerbach¹ states that when solutions of any strength of formaldehyde are distilled the distillate always becomes weaker and the residue stronger.

Since endeavors have been made to use mixtures of steam and formaldehyde vapor as a means of killing the spores on grain which is to be used for seed and since these mixtures are prepared by boiling solutions of formaldehyde in water, it is essential to know just what happens on boiling solutions of different concentrations of formaldehyde, that is, how the percentages of formaldehyde in the distillate and in the residue vary. That is the purpose of this investigation.

Method.

Solutions of various concentrations were prepared and placed in 1-liter round-bottom flasks and fractionally distilled with a Hempel distilling head and Liebig condenser. The original solution, the different portions

¹ Auerbach *Centr.*, 1905, II, p. 1081.

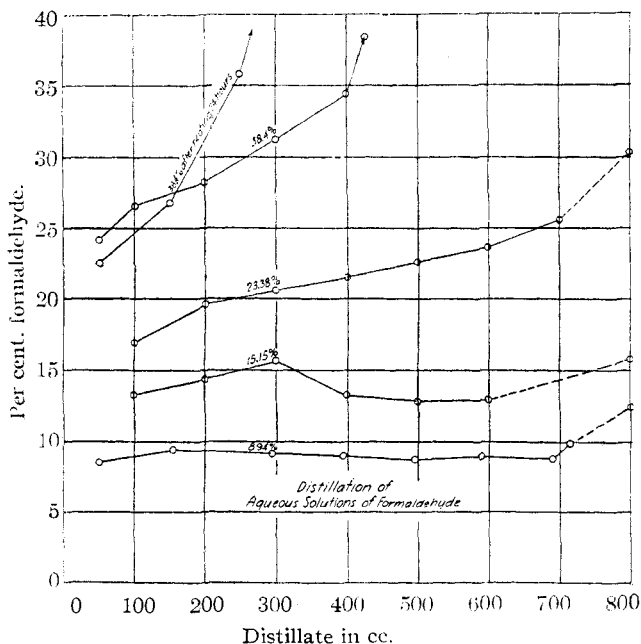
of the distillate and the residue were analyzed for formaldehyde. The temperature at the top of the distilling head was read at the beginning and at the end of each fraction. In the case of the strong solution fractional distillation under reduced pressure was tried.

Analysis.

The method of analysis used was that suggested by Blank and Finkenbeiner and modified by Haywood and Smith¹ in which the formaldehyde is oxidized with hydrogen peroxide in a known volume of standard alkali and the amount of formic acid formed determined by titrating the excess of alkali using litmus as the indicator. The method gives good check results even with the stronger solutions. The alkali solution is placed in the flask first, 25 to 50 cc. of the hydrogen peroxide added and then the sample introduced. The mixture is allowed to stand for a few minutes, then placed on the water-bath in contact with live steam for at least 15 minutes, cooled to the temperature of tap water and titrated.

Data.

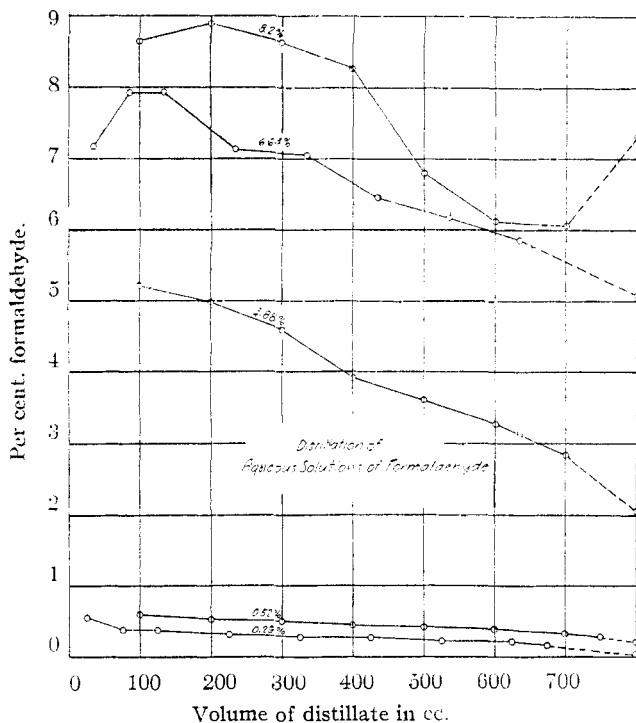
In most of the runs 800 cc. of solution was used for the distillation, but in the case of the stronger solution only 600 cc. was used. The results are shown graphically by the curves in which the percentages of formaldehyde present in the distillates are plotted as ordinates and the cc. of distillates as abscissas. The total volumes of distillate which came over



¹ Haywood and Smith, THIS JOURNAL, 27, 1183 (1905).

when this fraction was removed are plotted as cc. Each curve is marked with the percentage of formaldehyde present in the original solution which was distilled. For the sake of reference the percentage of formaldehyde present in the residue in each case is plotted and joined to the rest of the curve by a *dotted line*. When the residue went to a solid the curve is ended by an arrow at the point indicated by the last distillate.

In order to find whether prolonged heating of the formaldehyde solution would tend to form more of the polymer and thus cut down the vapor pressure still more and therefore lower the percentage in the distillate, a



solution of formalin containing 38.4% formaldehyde was heated with a reflux condenser for 24 hours and then fractionally distilled. As is shown, the distillation curve obtained is practically the same as that obtained from the same solution without previous heating.

The same solution was distilled under reduced pressure using a Pauli receiver. The formaldehyde in the first distillate was 14% when distilled under a pressure of from 11 to 12 cm. of mercury. The distillate had practically a constant composition until the residue in the flask started to solidify and then the concentration immediately went to 45%, and the solid polymer appeared in the distilling head and the receiver.

Discussion of Results.

As can be seen from the curves, the concentration of the formaldehyde in the distillates obtained from the higher concentrations follows the rule laid down by Auerbach¹ that the distillate is always weaker than the residue, but with a lower concentration the reverse is the case. With the medium concentrations (about 8%) the material distills over almost as a constant-boiling mixture, but not quite. The interesting parts of the curves are relationships between the original solutions and the first distillate, and between the last distillate and the residue.

Considering the original solution and the first distillate, it will be noted that with the 0.29% solution the first distillate is almost twice as concentrated as the original. With the 0.52% solution the same relation is shown, but is not so pronounced.

Smith² has developed an empirical method for the determination of formaldehyde, when used as a preservative for food, which is based on the assumption that $\frac{1}{3}$ of the total formaldehyde will distil over in the first fifth of the distillate. This agrees very well with the distillation of a 0.29% solution of which, starting with 775 cc. (2.25 g.), the first 175 cc., a little more than $\frac{1}{5}$ of the original, contained 0.70 g. or very close to $\frac{1}{3}$ of the original amount of formaldehyde.

The difference between the concentration of the original and that of the first distillate decreases continuously up to about 8% formaldehyde where there is practically no difference. Beyond this point the distillate is always weaker than the residue as Auerbach has said.

Now consider the relationship between the last distillate and the residue. With the 0.29% solution the residue is weaker than the last distillate, and the same thing is true up to about 10%; but beyond this point the residue is stronger, as Auerbach has said.

The percentages of formaldehyde in the solution at which the original and the first distillate have the same concentration and those where the last distillate and the residue have the same concentration, are different. The 8% original solution still gives a strong distillate for the first fraction and a stronger residue than the last fraction, but the 10% solution gives a weaker distillate. Several runs were made for concentrations between 8 and 10%, and the material was found to come over very much as a constant-boiling mixture, the first distillate being stronger than the original and the later ones being weaker than the original. The residues were always stronger than the last distillate. Owing to the difficulty in keeping the rate of distillation constant, curves with these concentrations tend to overlap and cross each other, and hence were not plotted.

In explaining these results there are three factors to be considered.

¹ Auerbach, *loc. cit.*

² Smith, *THIS JOURNAL*, 25, 1032 (1903).

First, formaldehyde is polymerized in solution in water, and the greater the concentration the greater the amount of polymerization that takes place.¹ Second, the vapor pressure of the polymer is much less than that of the simple form. Third, an equilibrium is reached in the solution between the polymerized and the simple form. The higher the temperature the less polymerization with any given concentration of formaldehyde. As can be seen, the first two factors are working against each other. The greater the concentration of the simple molecules the greater the vapor pressure. However, the greater the concentration of the total formaldehyde the greater the concentration of the polymer and this has a lower vapor pressure. The result is that at a high concentration of total formaldehyde most of it is present as the complex molecule and the vapor pressure is low if compared to what it would be in a solution of the same concentration but having the formaldehyde all present as the simple molecules.

Considering the low concentration curves, the material is present largely as simple molecules and distills over as such. Having a high vapor pressure, the percentage in the distillate will always be higher than in the original or the residue.

With the 6.64% solution the first distillate came over at 96.5° and the temperature rose rather rapidly up to 98° at the end of the third distillate. This increase in temperature was sufficient to increase the dissociation of the polymer into the simpler molecules and thus increase the vapor pressure and hence the percentage of formaldehyde in the distillate. After the third distillate the temperature stayed nearly constant at 98.1° until the end of the distillation. The rest of the curve is similar to those for the very dilute solutions where the temperature at which the distillates came over was nearly constant. The pressure during the distillation of the 6.64% solution was 742 mm.

With the 8.2% solution the same kind of a curve was obtained, the temperature rising from 96.5° to 98.1° in the first fractions and stayed constant at 98.5° for the rest of the distillation. The pressure here was 746.5 mm.

With the 9.77% solution the effect of the increase in concentration upon the amount of polymerization begins to be apparent as the first distillate is weaker than the original. The temperature rose quite rapidly from 96° to 97.3° with the first two distillates and then rose very slowly to 98.5° for the rest of the distillation. The pressure was 756 mm.

With the 15.15% solution the temperature rose very rapidly from 95.4° to 97.25° in the first four distillates and remained constant at 97.3° for the rest of the distillation. The pressure was 744 mm.

¹ Auerbach, *Centr.*, 1905, II, p. 1081.

With the higher concentration the effect of polymerization is very great in cutting down the vapor pressure, and the distillates are always weaker.

There is, therefore, a certain concentration of total formaldehyde at which the amount of simple molecules in equilibrium with the complex ones stays nearly constant with the slowly rising temperature, and since the vapor pressure is dependent almost entirely upon the simple molecules and not the polymer the vapor pressure will be constant and the material will distill over of a constant composition. With concentrations above 15% the formaldehyde is there chiefly as a polymerized form and therefore its vapor pressure is much lower than it would be if it were there as simple molecules. The result is as shown; the distillate is weaker than the original, although the total amount of formaldehyde present is large as shown by the high percentage in the residue.

Conclusions.

1. Distillation curves for solutions of various concentrations of formaldehyde in water have been determined.
2. With low concentrations (below 8%) the distillate is always *stronger* than the original, but with high concentrations the distillate is always *weaker*.
3. With low concentrations the residue is always weaker than the last distillate, but with high concentrations the residue is always stronger.
4. The difference is accounted for by the polymerization of the formaldehyde in water solutions into molecules having a low vapor pressure.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF AMHERST COLLEGE.]

TRIHALOGEN-METHYL REACTIONS. III. THE USE OF THE SILVER CATHODE IN ELECTRO-DEPOSITION OF COPPER.

BY HOWARD WATERS DOUGHTY AND BENJAMIN FREEMAN.¹

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The recent advances in the price of platinum, together with the numerous thefts of platinum from college and university laboratories, emphasize the desirability of substituting less expensive metals for it so far as may be practicable, and the writers therefore suggest the use of silver instead of platinum cathodes in the quantitative electro-deposition of copper. Silver cathodes have been used by students in this laboratory during the past year with entirely satisfactory results.

The use of silver cathodes has been suggested by various writers, but has not come into general practice, principally because of the difficulty in removing the deposit of copper after the analysis without also removing

¹ Presented before the Connecticut Valley Section of the American Chemical Society, November, 1920.