and methanol were collected. The residue from this fractionation weighed 141 grams and contained 17% by weight of formaldehyde. The conversion to formaldehyde and methanol was 80% and the yield 95% of theory.

COST OF RECOVERY

The chief items to be considered in the cost estimation of the present process are steam, cooling water, methanol, and formaldehyde. Methanol and formaldehyde are recoverable and, under ideal operating conditions, should not add much to the cost of recovery. Therefore, the economics of the present process, like those of distillation and extraction, depend on the consumption of cooling water and steam. Figure 1, a flow sheet for the recovery of glycerol from 3000 pounds of 3.5% glycerol beet, is shown here to allow comparison of this process with other processes on a similar scale.

ACKNOWLEDGMENT

The 2,3-butanediol-diol which was used throughout this work was supplied by J. J. Ruiter, now with W. S. Merrell Company, and by R. J. Hickey of the Bacteriological Research Division of Commercial Solvents Corporation.

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PREPARATION OF TECHNICAL DDT

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A study has been made of the effect of time, temperature, acid strength, and excess chlorobenzene on the condensation of chloral and chlorobenzene in the presence of sulfuric acid to give DDT. When 95-99.5% sulfuric acid is used with 4 moles of chlorobenzene per mole of chloral and at a temperature of approximately 15°C for 5 hours, 95-98% yields of DDT can be obtained.

DDT is most readily synthesized by some variation of the original Bayer condensation (1) used by Zöllner when the synthesis of this compound was first reported (29). Since then various experimental conditions have been described for this reaction:

\[ C_6H_5CHO + 2C_2H_5Cl \rightarrow C_6H_5CH \equiv C(\text{H})Cl_2 + HCl + H_2O \]

These appear in the Geigy patents (15) and, more recently, in articles by Darling (6), Bailes (3), Iris and Leyva (13), and Breckenridge (5). A survey of the literature prior to 1944 for other possible methods of preparing compounds such as DDT and for other catalysts such as aluminum chloride (9) did not reveal any promising alternative. Recently the use of chlorosulfonic acid as the condensing agent was described (11, 12, 16).

Thus the problem was to determine, first, the optimum conditions for the condensation of chloral and chlorobenzene with sulfuric acid to give DDT and, second, the best method of working up and purifying the reaction mixture. Our problem was not merely a matter of finding the conditions which would give a maximum yield of DDT, for these conditions might not be the most economical. This technical DDT can readily be obtained in 97-98% yields (based on chloral) by the use of a large excess of chlorobenzene and condensing acid.

CONDITIONS FOR CONDENSATION

Preliminary experiments showed that DDT was readily formed according to Equation 1 at temperatures ranging from below 0°C to above 85°C and with sulfuric acid concentrations from 90% to over 100%. At the lower temperatures the reaction rate was slow, and at the higher temperatures some decomposition occurred. This could be counteracted to some extent by using higher acid concentration at the lower temperatures and more dilute acid at the higher temperatures; at either low or high temperatures, however, extensive sulfonation of the chlorobenzene took place. Thus one of the primary problems seemed to be a determination of the temperature and acid concentration at which precipitation of DDT was at a maximum while sulfonation of the chlorobenzene was at a minimum, within the limits of reasonable reaction time and temperature.

In order that the different condensations could be accurately compared with one another, a standard method was devised for conducting the reaction and working up the product. The following section describes a typical run in which standard method A was employed for isolating the technical DDT. This standard method was not necessarily the best, but it gave reproducible results and required a minimum of operations which might result in loss of product or alteration in the properties of the product. The use of this standard procedure eliminated a number of variables and made it possible to study the effects of temperature and acid concentration on the DDT condensation. Since alterations of the additional variables, represented by mole ratios of chlorobenzene and chloral and by volume ratios of the condensing acid to both of these, would have expanded the work to an unmanageable extent, the mole ratio of chlorobenzene to chloral was standardized at 2.2 to 1.0 (10% molar excess of chlorobenzene), and a final volume of approximately 500 ml of sulfuric acid was used per mole of chloral. After the optimum temperature and acid concentration were determined under these conditions, the effect of altering the mole ratio of chlorobenzene and chloral, the excess sulfuric acid, and the reaction time were studied.

TYPICAL DDT CONDENSATION

A mixture of 200 grams of 99.5% sulfuric acid, 74 grams (0.5 mole) of chloral purified through the crystalline hydrate, and 124 grams (1.1 moles) of technical chlorobenzene were stirred rapidly
in a one-liter, three-necked flask, while 178 grams of 104% sulfuric acid were dropped into the reaction mixture over a period of 2.5 hours. During the addition the reaction was maintained at 20° C. by external cooling with cold water. After the addition the reaction mixture was stirred at the same temperature for 4.5 hours and the crude DDT isolated according to method A.

Method A. To the reaction mixture (0.5-mole run based on chloral), contained in a Pyrex separatory funnel, were added 250 ml. of n-hexane (Phillips Petroleum Company, 75% n-hexane, 25% methylcyclopentane, boiling point 68° C.). The crude DDT was extracted by stirring at 60° C. The sulfuric acid was dropped and the hexane solution washed successively, while maintained at 60° C., with 125 ml. of water, 125 ml. of 2% sodium carbonate solution, and 125 ml. of water. The resultant hexane solution was evaporated on the steam bath and the final solvent removed by heating for 15 minutes on the steam bath under a pressure of 35 mm. or less. The molten DDT was then drained into a porcelain dish to solidify. This gave 149 grams (84% of the theory based on the chloral taken) of a cream-colored solid which had a setting point (5) of 86.2° C. This was further crystallized from 500 ml. of hexane to give 84 grams, or 57% recovery, of a product melting at 106.5-107.5° C. A total of more than sixty runs were conducted in order to define the conditions reported in Figures 1 to 5.

**EFFECT OF TEMPERATURE**

Figure 1 records the results of experiments designed to show the effect of temperature on DDT condensation when 98% sulfuric acid was used as the condensing agent. All references in this paper to the acid concentration for a condensation mean calculated final acid concentration, on the assumption that the DDT condensation was 100% complete and no sulfonation took place.

All, or nearly all, of the chlorobenzene was consumed in the reaction either by condensation with the chloral or by sulfonation. Since the relative extent of each reaction was not known in advance, the true final acid concentration could not be calculated. Experimentally the acid concentration was kept approximately constant by the initial mixing of chloral, chlorobenzene, and an excess of the concentration of sulfuric acid being studied, and by the subsequent dropwise addition of a sufficient quantity of 104% sulfuric acid, as the reaction proceeded, to maintain the initial concentration of acid. In actual practice the final titrated acid concentrations were usually 6 to 12% below the calculated values.

It is apparent from Figure 1 that, for 98% sulfuric acid in the laboratory apparatus employed, a temperature of approximately 15° C. is optimum for the production of DDT. A temperature of 15-20° C. not only gave the highest yield under these specified conditions but also produced a product with the highest setting point. The setting point, an empirical determination conducted essentially as described by Fleck and Preston (8), was adopted by the Army Quartermaster Corps as a criteria of purity of technical DDT. It should be remembered that the pure DDT has a melting point of 108.5-109° C. (uncorrected) and a setting point of 108° C., whereas the crude DDT from the reaction mixture is contaminated with approximately 15% of the o,p'-isomer along with other by-products and has a setting point from 80-93° C. The melting point of a technical sample of DDT is somewhat higher than the setting point. Thus a sample of technical DDT with a setting point of 91° C. softens indefinitely from 65° to 80° C. but does not melt completely until 94° C. is reached.

The setting points are indicated by the dotted lines in Figures 1 to 5. These and subsequent curves would undoubtedly be different if such conditions as rate and length of stirring, amount of excess chlorobenzene, and weight and concentration of sulfuric acid were varied. If relatively large amounts of chlorobenzene are present in the crude DDT, this impurity is not completely removed by method A, and it is probable that the lower setting points corresponding to the lower yields in Figures 1 to 5 are due in part to unconsumed chlorobenzene contaminating the product.

The lower yields at the higher temperatures reported in Figure 1 would not be greater in shorter time, since warm sulfuric acid of concentrations less than 100% has little effect on DDT.

**EFFECT OF REACTION TIME**

It is possible that the causes for decrease in yields at lower temperatures (Figure 1) is incomplete reaction during the 6-hour stirring time specified. However, the effect of time on the reaction at 20° C. was studied, and the results (Figure 2) show that the reaction is virtually complete after 4 hours under the condi-
The reactions from which the data for Figure 2 were obtained were carried out as follows:

Simultaneous runs were performed using constant speed stirring (800 revolutions per minute) with a Hershberg-type stirrer while the temperature of the reaction was maintained at 19–21°C. Each of the 2-liter, three-necked flasks was charged with 73.7 grams (0.5 mole) of chloral and 125 grams (1.1 moles) of chlorobenzene. Over a 5-minute period 200 grams of 98% sulfuric acid were added to each reaction; then 200 grams of 104% sulfuric acid were added over a 55-minute period. Immediately upon completion of this addition, run 1 was worked up by stirring successively with 200 ml. each of water, 2% sodium carbonate solution, and water, and dried over calcium chloride; the solvent was then removed by heating on the steam bath in vacuo. The final heating under vacuum was continued 15 minutes beyond the time when the last bit of solvent was observed to distill over. Run 1 produced 107 grams of technical DDT, setting point 83.2–83.5°C. The other runs were identical except for the time interval allowed before the extraction was begun.

**EFFECT OF ACID CONCENTRATION**

It was not feasible to study the effect of varying the acid concentration over a wide temperature range; consequently a temperature of 20°C was chosen, and the yields and setting points of the DDT obtained were determined when acid concentrations of 95–104% were employed. The results are shown in Figure 3. The yields with 98–99% sulfuric acid were equally good; but as soon as the acid concentration reached 100%, the yields fell off sharply.

**SULFONATION OF CHLOROBENZENE**

Since the main limiting factor in the condensation is the extent of sulfonation, the sulfonation of chlorobenzene alone was studied. In forty experiments 56 grams of chlorobenzene and 200 grams of sulfuric acid of varying concentrations were allowed to react under controlled temperature conditions, for 5 hours with uniform stirring. These conditions approximate those found in the DDT condensation reaction. The resulting mixture was allowed to separate, the sulfuric acid layer drawn, and the extent of sulfonation under these specific conditions measured by determining the increase in weight of the sulfuric acid layer and decrease in weight of the chlorobenzene layer. The assumption was made that the disappearance of the chlorobenzene layer was a measure of the extent of sulfonation; the validity of this assumption was shown by isolation, in several cases, of a near-quantitative yield of p-chlorobenzenesulfonic acid as the ammonium salt. The results of these sulfonation experiments are recorded in Figure 6. The accuracy of the data on this graph is not more than ±3%; the values given are greatly dependent upon the efficiency and uniformity of stirring. In every case the acid concentration is the initial concentration; the final values were much less, depending upon the extent of sulfonation. It should be re-emphasized that this is the extent of sulfonation of chlorobenzene under specific conditions which approximate those found in the conventional DDT condensation.

In a typical example 56 grams of technical chlorobenzene were stirred rapidly with 200 grams of 102% sulfuric acid for 5 hours at 5°C. After this time the chlorobenzene layer weighed 13 grams (corresponding to 77% sulfonation) and the sulfuric acid layer weighed 241 grams (corresponding to 74% sulfonation). The sulfuric acid layer was diluted with approximately three volumes of ice and made basic with 50 ml. of concentrated ammonium hydroxide at 20°C. After standing one hour, the solution deposited crystals of the ammonium p-chlorobenzenesulfonate, which weighed 78 grams after filtering, washing with ether, and drying at 120°C for 3 hours. This is a 97.5% yield on the basis of the loss in weight of the chlorobenzene layer, and a 100.8% yield on the basis of the increase in weight of the sulfuric acid layer. On recrystallizing from 150 ml. of boiling water, these 78 grams gave 63 grams of pure ammonium p-chlorobenzenesulfonate (81% yield on the basis of the gain in weight of the sulfuric acid layer).

With the help of these sulfonation data, a study was undertaken of the DDT condensation. Acid concentrations were selected from Figure 6, which at the various temperatures possessed the same sulfonating strength toward chlorobenzene. A concentration of acid was arbitrarily chosen which resulted in 40% sulfonation of the chlorobenzene under the conditions of the DDT condensation but in the absence of chloral. These acid concentrations are represented by the intersections of the dotted line with the curves for the various temperatures in Figure 6.
The results of the condensations using these acid strengths and temperatures are represented in Figure 4. The results indicate that the highest crude DDT production with the smallest concomitant formation of p-chlorobenzenesulfonic acid probably occurs at a temperature in the neighborhood of 20°C and acid concentrations of 98-99%. The temperature is only optimum for the 6-hour reaction time allowed in these experiments. From the standpoint of the economy of time, however, it is probably not worth while to run the reaction longer for the sake of a slightly higher yield.

It is thus apparent that, in the condensation mixture of sulfuric acid, chlorobenzene, and chloral, two chief reactions compete—the sulfonation of chlorobenzene and the formation of DDT. In the absence of chloral the sulfonation of chlorobenzene is extensive at the same temperatures and concentrations commonly employed in the DDT condensation. In spite of this fact, the yield of DDT is excellent under conditions which, in the absence of chloral, result in a high percentage of sulfonation; this indicates that, of the two competitive reactions, the DDT condensation is much faster under properly chosen conditions. In addition, the data on the formation of DDT show that the temperature effect on the extent of sulfonation of chlorobenzene is larger than that on the extent of DDT formation. Thus the more concentrated acids with lower temperatures seem to favor DDT formation, whereas the higher temperatures with more dilute acids seem to favor sulfonation.

**EFFECT OF EXCESS CHLOROBENZENE**

Under controlled conditions of temperature (16°C), time (3 hours), stirring (800 r.p.m. with a Hershberg-type stirrer), and acid concentration (final calculated acid concentration 99%), six simultaneous condensations were conducted in which the variable was the amount of excess chlorobenzene. These runs were worked up by method A to give the results reported in Figure 5. The 15-minute heating on the steam bath ordinarily used in method A to remove the solvent was insufficient for the complete removal of excess chlorobenzene from the runs which used a 50% or greater molar excess of chlorobenzene. It was necessary to heat at 105°C and 2 mm. pressure for 15 minutes to remove the chlorobenzene completely from these runs. The 10% molar excess chlorobenzene used in the experiments represented by Figures 1 to 4 gave an 84% yield in this series. This indicates that the maximum yields in Figures 1 to 4 would be approximately 10-12% higher if 100% excess chlorobenzene had been employed.

Figure 5 shows that the increased yield makes it profitable to employ an excess chlorobenzene up to approximately 75% molar excess, but the increased yield of DDT beyond this point does not compensate for the large amount of chlorobenzene necessary.

**MAXIMUM YIELDS OF DDT**

A 97-98% yield of crude DDT of setting point 90°C was obtained when the condensation with chloral was carried out in a large volume of 98% sulfuric acid and 4-molar excess of chlorobenzene at 5-10°C for 8 hours, as described in the following experiment:

A mixture of 74 grams (0.5 mole) of pure chloral, 250 grams (2.2 moles) of technical chlorobenzene, and 1100 grams of 98% sulfuric acid was placed in a 2-liter, three-necked flask equipped with a dropping funnel, thermometer, and efficient stirrer. Since the reaction is heterogeneous, the efficiency of the stirring is important and should be such that the reaction is practically emulsified. While the reaction mixture was maintained at a temperature between 5° and 10°C, 1100 grams of 101% sulfuric acid were added over a period of 4 hours. The reaction mixture was stirred 4 more hours at the same temperature and then worked up by extracting with three 500-ml. portions of hexane solvent at 60°C. The sulfuric acid layer was discarded and the hexane layer washed with a 4% sodium carbonate solution and then with water. The solvent was removed from the product by heating on the steam bath, and the last traces were taken off by heating in a vacuum oven at 10 mm. pressure for 2 hours at 80°C. The yield was 171.9 grams or 97.0%; the setting point was 89.8°C, 90.0°C. A duplicate run gave 174.3 grams (98.4%), setting point 90.2°C, 90.5°C.

Although these proportions are not economically practical, they indicate the trends which lead to the best yields. There is obviously a point at which the increased cost of materials and decreased size of run (due to the increased volume of sulfuric acid used) outweighs the advantages of higher yields. This depends upon the particular conditions and equipment employed.

**COMPOSITION OF TECHNICAL DDT**

The composition of technical DDT has been extensively studied by Haller et al. (12). The approximate composition of the technical DDT obtained in the experiment described above was determined prior to their publication. The results are of interest because of the specifically defined conditions under which the technical DDT was prepared. The crude DDT, which was obtained in 97% yield and had a setting point of 90.0°C, was purified by a systematic fractional crystallization from hexane and a distillation of the residual oils, followed by further crystallizations to give approximately 77% pure p,p'-DDT, 15% o,p'-isomer of DDT, 1.5% of an oil, probably 2,2'-trichloro-1-p-chlorophenylethanol; the remaining 6.5% represents losses and unidentified residues which undoubtedly contain some more p,p'-DDT and its o,p'-isomer. It should be emphasized that the sample of technical DDT used here was prepared from chloral, purified through the crystalline hydrate; no impurity such as 1,1-dichloro-2,2-bis-(p-chlorophenyl)-ethane, DDD, should be present.

The 171.9 grams of DDT of setting point 90°C were put through a seven-step systematic fractional crystallization from hexane. Fractions 7, 7a, and 7b gave a total of 130 grams of purified DDT with a melting point above 105°C. Fractions 7c, 7d, and 7e gave a total of 24.5 grams of an oil which would not crystallize. These last three fractions were combined and distilled to give the following: fraction 1, 2.5 grams, boiling point 120-125°C (1 mm.); fraction 2, 24.6 grams, b.p. 172-175°C (0.5 mm.); fraction 3, 2.5 grams, b.p. 175-185°C (0.5 mm.); and a residue of 3.2 grams. The first fraction was not positively identified but was soluble in concentrated sulfuric acid, and its...
tematic crystallization was forked up to give 200 mg. of a solid 0,p'-dichlorobenzophenone in a similar manner to that reported solidified when seeded with the above crystals and melted at 70°. Obtained in crystalline form by cooling its hexane solution to crystallize many of the oils from previous runs. Fractions 2 and 3 resulted in the isolation of 92 mg. of the 0,p'-isomer of DDT which, after successive recrystallizations from hexane, ethanol, boiling point was the same as that reported (18) for 2-trichloro-1-p-chlorophenylethanol. A small sample of fraction 2 was finally obtained in crystalline form by cooling its hexane solution to -40°. Once the crystals were obtained, it was possible to crystallize many of the oils from previous runs. Fractions 2 and 3 solidified when seeded with the above crystals and melted at 63-70°. These two cuts were crystallized from hexane, in which they were very soluble, by cooling to -40°; they were then crystallized from ethanol and methanol to give a total of 17.2 grams melting at 73-74° C. (analysis of C₁₁H₇Cl₂ for Cl: calculated, 50.0; found, 49.3). This material was identified by oxidation to o,p'-dichlorobenzophenone in a similar manner to that reported by Haller et al. (18). The remaining fraction, 74, from the systematic crystallization was worked up to give 200 mg. of a solid which, after successive recrystallizations from hexane, ethanol, methanol, and acetone, still melted sharply at 53.0-55.5° C.

If it is a mixture, the other component cannot be simply p,p'-DDT, for the eutectic between p,p'-DDT and its o,p'-isomer melts at 59-60° C., as Figure 7 shows. Thus from the 171.9 grams of crude DDT obtained in 97% yield, the authors obtained 113 grams (77%) of pure p,p'-DDT, m.p. above 105° C.; 26.1 grams (15%) of crude o,p'-isomer of DDT, m.p. 63-70° C.; or 17.2 grams (10%) of purified o,p'-isomer; 2.5 grams (1.5%) of a crude material, probably 2-trichloro-1-p-chlorophenylethanol; 5 grams of oils and residues; and 0.2 gram of an unidentified material melting at 55.0-55.5° C. These findings are in complete agreement with those of Haller et al. (18) but differ somewhat from those of Gunther (11) reported for the material obtained by the Brothman process (12).

SYNTHETIC MIXTURES OF p,p'-DDT AND o,p'-DDT

Synthetic mixtures of pure DDT and its o,p'-isomer were prepared, and the melting points were taken in capillary tubes in an electrically heated aluminum block. The point at which the first liquid formed determined the lower curve, and the lowest temperature at which a completely clear melt could be obtained defined the upper line. The latter value was determined by allowing the temperature of the block to rise at a rate of not more than 1 degree every 3 minutes. The results are given in Figure 7. Similar mixtures, in which the setting points were determined, were studied by Fleck and Preston (8).

RELATIVE SOLUBILITIES OF DDT

The solubility of DDT in various solvents was reported by Gunther (10), Campbell and West (9), and Fleck and Haller (7). Figure 8 shows additional solubilities determined in two ways: (a) A known weight of p,p'-DDT was dissolved in the solvent, well above the saturation temperature being determined, and the solution allowed to cool slowly until crystallization commenced, as noted by the first separation of crystals and the leveling off of the cooling curve. The solubilities were carried out in a jacketed, tared test tube 2.5 × 18 cm., with constant speed mechanical agitation (180 2-inch strokes per minute) to prevent supercooling. After each determination the weight of the solvent was immediately determined. (b) This method was not applicable at or near the boiling points and, in these cases a solution of a known weight of p,p'-DDT in the desired solvent was adjusted to the saturation point in a tared flask. The flask was cooled immediately by immersion in a cold bath, the gross weight determined, and the weight of solvent determined by difference. The results of these solubility determinations are shown in Figure 8.

The solubility of DDT in sulfuric acid was also studied. DDT was found to be insolubly soluble in anything less than 100% sulfuric acid. Thus when 5.02 grams of DDT were heated at 90° C. for 10 hours with 390 grams of 98% sulfuric acid, 4.2 grams of the original DDT were recovered by filtration and washing. At room temperature all of the DDT was removed; but when 5.02 grams of DDT were heated for 10 hours at 90° C. with 390 grams of 100% sulfuric acid, only 0.4 gram was recovered and the sulfuric acid solution had turned black.

The o,p'-isomer of DDT is approximately twice as soluble as p,p'-DDT in 95% ethanol and three times as soluble in hexane at room temperature. It is apparent, then, as to why the crystallization from such a solvent greatly purifies the DDT and leaves most of the o,p'-isomer (the main impurity) in the mother liquor. Chlorobenzene and carbon tetrachloride, especially the former, show a high solubility for DDT at room temperature and are, therefore, good solvents for the cold extraction of DDT. If it is desirable to raise the melting point of the crude product a certain definite amount without the losses inherent in crystallization, partial purification can be achieved either by pouring the molten DDT into a definite amount of ethyl alcohol (or other solvents) or of a predetermined concentration of aqueous ethyl alcohol.
with vigorous stirring, or by wet grinding the product with such solvents. This produces, in addition to purification, a desirable granulation of the final product.

1-DICHLORO-2,2-BIS-(p-CHLOROPHENYL)-ETHANE

The preparation of chloral by the chlorination of ethanol according to the method outlined in Thorpe (18) usually produces a low boiling impurity because of incomplete chlorination. By fractionating this low boiling material through a sixty-plate column, the dichloroacetaldehyde (14) was separated which had a boiling point of 88° C. and an oxide melting point of 177-178° (analysis of C₇H₆Cl₂ for Cl: calculated, 62.78; found, 62.86-63.32). When this material was condensed with chloroacetaldyde, 300 grams of chlorobenzene, and 500 ml of 98% sulfuric acid were added to the stirred mixture over a 1-hour period. The reaction mixture was poured onto 1 kg of ice; the solvent layer was washed twice with 25% potassium carbonate solution and once with water; the solvent was evaporated to 500 ml, and the product was allowed to crystallize (weight 196 grams or 61%, m.p. 104-106° C.). This product was recrystallized from ligroin (155 grams, m.p. 108.5-109.5° C.) and recrystallized from 95% ethanol (135 grams, m.p. 110.5-111.0° C.). Further recrystallizations did not change this melting point. A mixed melting point determination between this DDD and pure DDT was approximately 85-90° C. (analysis of C₁₃H₁₁Cl₂ for Cl: calculated, 44.2; found, 43.8). Haller et al. (12) have shown that this is an impurity in technical DDT.

EFFECT OF IMPURE CHLORAL ON TECHNICAL DDT

The following two runs were identical with the exception of the starting chloral. In run C18 the chloral was pure; in run C19 the chloral was crude material used just as it was obtained by distilling a batch of chloral alcoholate from sulfuric acid under vacuum. This batch of chloral alcoholate had been chlorinated to a density of 1.5 at 20° C. The distillation of a sample of chloral from this chloral alcoholate gave 178 grams boiling below 96.5° C. and 498 grams boiling between 96.5° and 07.5° C. in an ordinary distilling flask.) The two condensations were conducted essentially as indicated in the description of a typical DDT condensation and were worked up as in method A. The results were: run C18 (pure chloral), 87% yield, 84.4° C. setting point; run C19 (crude chloral), 86% yield, 72.7° C. setting point. It is apparent that the low boiling impurity does not lower the crude yield appreciably but contributes greatly to the lower setting point of the crude product.

METHODS OF WORKING UP TECHNICAL DDT

Ten different methods of working up the DDT condensation mixture are compared in Table I. Method A is the standard against which all other variations were compared. In comparing any two methods, the same reaction mixture was used. This was accomplished by filtering the crude reaction mixture through glass cloth and dividing both the filtrate and precipitate into equal portions, recombining the separate portions of filtrate and precipitate, and working up one part by method A and the other part by the method being studied. In this way the starting reaction mixtures of the test and the standard methods were identical.

METHOD B. The product was filtered directly from the reaction mixture through glass cloth or a sintered glass filter. It was then washed by mechanical stirring with water, sodium carbonate solution, and water. The product was finally dried for six hours at 60° C.

METHOD C. The reaction mixture was diluted with an equal volume of water, and care was taken not to allow the temperature to rise above 60° C. The creamy reaction product was filtered and washed by mechanical stirring with sodium carbonate solution and water. It was finally dried as in method B.

METHOD D. Except that the product was subjected to a steaming process for 5 minutes in the molten state, this method was identical with the standard process. All of the water was removed by heating at 100° C. under vacuum until a clear melt was obtained; the melt was then drained onto a porcelain dish to crystallize.

METHOD E. This was identical with standard method A, except that chlorobenzene instead of hexane was used as the solvent.

METHOD F. The standard procedure was followed to the point where the solvent was evaporated. Here the total volume was reduced to 200-230 ml for a one-mole run and the DDT allowed to crystallize; it was then filtered and dried.

METHOD G. The reaction mixture was poured onto 1 kg of ice for each half mole of chloral used. The solution was stirred

![Figure 8. Solubility of DDT in Various Solvents](image-url)
TABLE II. COMPARISON OF METHODS FOR PURIFYING DDT

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<th>Recovery (%)</th>
<th>Setting Point, °C</th>
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<td>8</td>
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* This sample of crude DDT with setting point of 77°C was obtained by combining the crude DDT from several typical runs and the residues from some previous crystallizations. This sample, therefore, has an abnormally low setting point, and the percentage recovery on treatment is always lower than normal, whereas the increase in setting point is always higher than normal. All setting points were rounded off to the nearest degree.

** Decomposed, in attempting to distill this sample of DDT, when the temperature reached about 190°C, the amount of gas evolved was more than normal whereas the increase in setting point is always higher than normal. All setting points were rounded off to the nearest degree.

** This sample of crude DDT with a setting point of 86°C was purified by washing the solid free of acid and to dry the wet solid than it is to wash and dry the hexane solution as in method A.

mecanically until the ice had melted, the water decanted, and the solid DDT dried with a solid carbonic carbonate solution and next with water. The DDT was finally filtered and dried in an oven at 60°C for 6 hours.

Method H. Enough water was added directly to the reaction mixture to melt the DDT. The sulfuric acid layer was drawn from the flask and the molten DDT washed with a 2% sodium carbonate solution and with water while still molten. The DDT was finally dried by heating at 100°C under vacuum until clear.

Method I. The DDT was extracted from the reaction mixture with hexane. The sulfuric acid layer was separated, and the molten DDT was poured, with vigorous mechanical stirring, into 600 ml. of a 2% Triton B solution. The solution was not washed with water or carbonate solution, but the solvent was removed directly by heating under vacuum. The unpurified DDT was poured into a porcelain dish to crystallize.

Method J. Water was poured into the crude DDT reaction mixture until the DDT melted. The sulfuric acid layer was separated, and the molten DDT was poured, with vigorous mechanical stirring, into 600 ml. of a 2% Triton B solution (2% benzocyaninum hydroxide) solution. The solid, which was in the form of a finely granulated product, was washed with water, dried in air, and finally dried for 6 hours at 60°C.

Method K. gives a purer product but, as would be expected, the crude yield is lower. Pure DDT is almost completely insoluble in 96% sulfuric acid even at 65°C, whereas the expected contaminants, such as unreacted chloral, p-chlorobenzene-sulfonic acid, and 2-trichloro-1-phenylbenzeno, are soluble in concentrated sulfuric acid; thus method K. should result in a mixture containing only p,p'-DDT and its a.p'-isomer, if pure chloral has been employed.

Method M. was not used as the standard procedure, however, because the physical state in which the DDT is often precipitated from the reaction, particularly at higher temperatures, precludes its successful use. In addition, it is more difficult to wash the solid free of acid and to dry the wet solid than it is to wash and dry the hexane solution as in method A.

PURIFICATION OF TECHNICAL DDT

In addition to the various methods of working up the DDT condensation mixture, there are other obvious methods of treating the crude product in order to purify it. A description of some of these methods follows: the results obtained by the use of these methods are compared in Table II. The percentage yields and temperatures were rounded off to the nearest degree.

** Method 1a.** A 50-gm portion of crude DDT was triturated thoroughly in a mortar with 500 ml. of absolute ethanol at room temperature. This quantity of absolute ethanol should not dissolve more than 4 gm. of p,p'-DDT at this temperature.

** Method 1b.** This was identical with 1a except that 100 ml. of 96% ethanol were employed. This amount of ethanol dissolves only about 1 gm. of p,p'-DDT at this temperature.

** Method 1c.** This method was identical with 1a except 100 ml. of 60% ethanol were used.

** Method 2a.** Crude molten DDT (280 gm.) was poured with vigorous mechanical stirring into 300 ml. of 65% ethanol which had been warmed to 60°C. The ethanol was cooled to 15°C, and the product filtered and dried.

** Method 2b.** Crude molten DDT (60 gm.) was poured with vigorous mechanical stirring into 200 ml. of 90% ethanol at 30°C.

** Method 2c.** Crude molten DDT was poured with mechanical stirring into 100 ml. of 80% ethanol at room temperature.

** Method 3a.** Crude molten DDT was poured with vigorous mechanical stirring into 200 ml. of a 1% Triton B solution. The product, formed as a fluffylike mass which solidified on cooling and was readily broken up into a fine granular form. It was then filtered, washed, and dried at 60°C for 6 hours.

** Method 3b.** This was identical with method 3a except that 1% of a mixture of hexane mother liquors from a previous DDT crystallization was used.

** Method 4.** Crude DDT (50 gm.) was recrystallized from 200 ml. of 90% ethanol, cooled to 15°C, filtered, and dried.

** Method 5.** Crude DDT (50 gm.) was recrystallized from 125 grams of hexane mother liquors from a previous DDT crystallization.

** Method 6.** Crude DDT (50 gm.) was recrystallized from 100 ml. of methanol.

** Method 7.** Crude DDT was melted on the steam bath and steam-bubbled through the molten DDT for 5 minutes. The molten DDT was then heated under vacuum at 100°C until the water was removed, as indicated by a clear melt.

** Method 8.** Crude DDT (50 gm.) was thoroughly washed with 100 grams of concentrated sulfuric acid (96%) by mechanical stirring for 1 hour at a stirring temperature. The product was filtered through glass cloth, washed with sodium carbonate solution and then with water, and finally dried at 60°C for 6 hours.

** Method 9.** A sample of DDT having a setting point of 86°C was heated in a Claisen flask at 1 mm. pressure. Some liquid distilled, but when the temperature at the side arm reached 100°C, the evolution of gas was such that the vacuum could not be maintained; as a result the distillation was discontinued. However, when a sample of setting point 103°C was heated under vacuum, the product distilled smoothly at 210°C (1 mm. pressure).

** Method 11.** Crude DDT (68 gm.) was boiled for 2 hours with 200 ml. of water. The product was worked up by grinding the granules, which separated on cooling, with dry ice and drying the product at 65°C for 5 hours.

** Method 12.** The setting point may also be raised by blending with a purer grade of DDT. The data of Table III indicate how much the setting point is raised in a specific instance.

ACKNOWLEDGMENT

This work was undertaken April 15, 1944, at the request of the Office of Production Research and Development of the War Production Board under WPA Contract 180. The material presented here is taken from DDT Reports 44-1 through 44-12 which were distributed by the Office of Production Research and Development to various institutions and industries concerned with the production of DDT. The authors are greatly indebted to Frank C. Whitmore for his help and advice throughout this work.
Two new rules for change of latent heat of vaporization with temperatures are presented, and their derivations given. It is believed that the new rules have the advantages of simplicity and general applicability to all liquids.

Several investigators have reported results on the change of latent heat of vaporization with temperature (1, 2, 5, 7–18). This paper presents some new rules for calculating the change of latent heat of vaporization with temperature. The new rules are simple and seem to have general applicability to all liquids.

For vapor-liquid equilibria, the Clapeyron equation is

$$\frac{dp}{dT} = \frac{L}{T(V_v - V_f)}$$  \hspace{1cm} (1)

where

- $p =$ vapor pressure of a given liquid at temperature $T$
- $V_v, V_f =$ molal volumes of saturated vapor and liquid, respectively
- $L =$ latent heat of vaporization per mole
- $T =$ temperature

If we set

$$V_v = \mu \frac{RT}{p}, \quad \tau = \frac{V_f}{V_v}, \quad \text{and} \quad s = -\frac{d\ln p}{d\left(\frac{1}{T}\right)}$$

Equation 1 may be written as follows:

$$L = s \mu R(1 - \tau)$$  \hspace{1cm} (2)

Equation 2 contains, in addition to the gas constant, $R$, three factors—namely, the slope of the plot, $l$ in $p$ vs. $1/T$, for the change of vapor pressure of the liquid with temperature; the compressibility factor $\mu$ to account for the deviation of the vapor from the perfect gas law; and $\tau$, the ratio of volumes of liquid and vapor per unit mass.

The vapor pressure curve of log $p$ plotted against $1/T$ is nearly linear over wide ranges of temperature or pressure. Figure 1, presented a few years ago by the author (11), shows log $\tau$ vs. $1/\beta$ for twenty liquids, $\beta$ being the reduced pressure $(p/p_a)$ and $\theta$, reduced temperature $(T/T_c)$. All the vapor pressure data are from International Critical Tables (3) except the data on water, which were taken from the steam tables of Keenan and Kyes (4). The individual lines are surprisingly linear, but the slopes are fairly different from one another; that is, at equal reduced temperatures the reduced vapor pressures of various liquids are, in general, far from being equal to one another.

The compressibility factor $\mu$ changes with pressure as well as with temperature and was shown to be a function of $\tau$ and $\theta$ (6). The ratio, $r$, of liquid volume to vapor volume per unit mass plays an important role only near the critical point for, at low or moderate pressures, $r$ is small and $(1 - r)$ is nearly equal to 1.

The data are correlated as the ratio of two latent heats of vaporization at any two temperatures. The reduced temperature and pressure are used as temperature and pressure measures.

If we assume a reference temperature $\theta$ at this temperature Equation 1 becomes, for the same liquid,

$$L_\theta = s_\theta \mu R(1 - r_\theta)$$  \hspace{1cm} (3)

Dividing Equation 1 by Equation 3,

$$\frac{L}{L_\theta} = \frac{s_\theta \frac{\mu}{s} \left(1 - \frac{r}{1 - r_\theta}\right)}{s_\theta \mu}$$  \hspace{1cm} (4)

If the vapor pressure curve, in $p$ vs. $1/T$, for the given liquid is linear—that is, if $s = s_\theta = \text{constant}$—Equation 4 becomes

$$\frac{L}{L_\theta} = \frac{\mu}{s_\theta} \left(1 - \frac{r}{1 - r_\theta}\right)$$  \hspace{1cm} (5)

Case I. It is assumed that $L/L_\theta$ is a function of $\pi/\theta$, the latter being a measure of the reduced concentration of the saturated vapor over the liquid in question:

$$\frac{L}{L_\theta} = \frac{s_\theta}{s_\theta} s \left(1 - \frac{r}{1 - r_\theta}\right) = F\left(\pi/\theta\right)$$  \hspace{1cm} (6A)

or

$$\frac{L}{L_\theta} = \Psi, \quad \psi = F\left(\pi/\theta\right)$$  \hspace{1cm} (6B)

The reference state is arbitrarily chosen as that point at which the vapor conditions have the ratio

$$\pi_0/\theta_0 = 0.1$$

All latent heat values at other temperatures with respect to $L_\theta$ are then referred to the reference state.