

analyzed by a method¹ already devised for the benzene, toluol and solvent naphtha content.

The analysis showed on the basis of light oil recovered from the cracking of solvent naphtha the following percentages of aromatic hydrocarbons:

	Per cent
Refined Benzol.....	14.5
Refined Toluol.....	23.7
Refined Solvent Naphtha.....	19.8
Crude Heavy Naphtha.....	9.7
Dead Oil.....	14.0

On the basis of 100 gallons of solvent naphtha cracked the following percentage of aromatics can be recovered:

	Per cent
Refined Benzol.....	8.3
Refined Toluol.....	13.6
Refined Solvent Naphtha.....	11.2
Crude Heavy Naphtha.....	5.5
Dead Oil.....	8.0

In these critical times, with a high scarcity of toluol, no quicker method lends itself to adding to our toluol supply than the cracking of solvent naphtha in carbureted water-gas machines. This being due to the fact that there is more than a sufficient number of carbureted water-gas machines already in operation, which could be used at once without any change for the adding of 2,000,000 gallons of toluol to our much needed supply.

THE ESTIMATION OF PHENOL IN THE PRESENCE OF THE THREE CRESOLS²

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Of the many methods proposed for the estimation of phenol in the presence of the three cresols, only those based on the determination of physical constants of mixtures of these substances would have much practical value in the analysis of coal-tar distillates, for the reason that small amounts of xylenols and other impurities that are apt to be present in the final distillate would seriously affect the accuracy of any of the chemical methods.

Many methods of proximate analysis have been based on the determination of physical constants such as the specific gravity, index of refraction, solidifying point, optical rotation, etc., of the substance to be analyzed or a part of it that has been purified as much as possible. In the case of the determination of phenol in the presence of the cresols, advantage can be taken of variations in the solidifying points and specific gravities of the various constituents to determine the phenol.

Part of the problem of working out along these lines a really accurate method for the determination of phenol in the presence of the cresols was accomplished by Lowe,³ and also by Weiss.⁴ Very recently, Masse and Leroux⁵ and Weiss and Downs⁶ have in-

vestigated the problem further and have published methods in which they make use of the specific gravities and solidifying points or solidifying points alone obtained by them for certain mixtures of phenol and cresols.

The principal difficulty in working out a reliable and satisfactory method for the determination of phenol in the presence of cresols in coal-tar products lies in the fact that in coal-tar distillates there is no constant relation between the amounts present of any of the cresols, *i. e.*, any of the three cresols may be present in any amount varying over a very large range, and this is more particularly true now since *m*-cresol is being removed in some cases for making trinitrocresol. Attention has been called to this fact in the literature by Lunge,¹ Ihle,² Tiemann and Schotten,³ Wegen,⁴ Schulze⁵ and even Weiss and Downs.⁶ Nevertheless, the methods of Weiss and Downs and Masse and Leroux have been partly based on the arbitrary assumption that *m*-cresol and *p*-cresol occur in certain fixed proportions to each other in coal-tar distillates or crude tar acids. Weiss and Downs assumed this proportion to be 50 per cent of *m*- to 50 per cent of *p*-, and Masse and Leroux 60 per cent of *m*- to 40 per cent of *p*-cresol. Consequently, when the interproportion of *m*- to *p*-cresol present in the final distillate upon which the constants are determined is different from that upon which their methods are based, a condition very frequently met with in actual practice, the results obtained by the use of either of these methods are apt to be unreliable.

The following investigation was carried on in the hope of developing a method along similar lines that would eliminate this and other weaknesses in these methods, be capable of wider application, give more concordant results and be as short and concise as accuracy would permit.

EXPERIMENTAL

In order to accomplish this end it was necessary to obtain phenol, *o*-cresol, *p*-cresol and *m*-cresol in as pure a condition as possible and to work with as many samples from different sources as possible in order to study the effect produced by slight amounts of impurities on the constants of the different mixtures.

Various samples of the purest phenol obtainable were procured from different commercial sources. A large number of samples of the purest *o*-cresol made commercially was obtained from American sources and also from England. Most of the samples of phenol were synthetic, while the *o*-cresol was all obtained directly from coal tar. Some of the *m*-cresol used in the investigation was synthesized in this laboratory by the method of Staedel and Kolb,⁷ while some was of coal-tar origin obtained from commercial sources. Likewise some of the *p*-cresol used was

¹ Egloff, *Met. & Chem. Eng.*, **16** (1917), 259.

² Contributed with the permission of the Secretary of the Treasury and the U. S. Appraiser, Port of New York.

³ Lunge, "Coal Tar and Ammonia," 5th Ed., **1916**, 782.

⁴ *J. Franklin Inst.*, **1912**, 683.

⁵ *Compt. rend.*, **165** (1916), 361-3.

⁶ *This Journal*, **9** (1917), 569.

¹ "Coal Tar and Ammonia," 5th Ed., **1916**, 784.

² *J. prakt. Chem.*, [2], **14** (1876), 442.

³ *Ber.*, **11** (1878), 767.

⁴ *Z. angew. Chem.*, **1909**, p. 391.

⁵ *Ber.*, **20** (1887), 409.

⁶ *Loc. cit.*

⁷ *Ann.*, **259** (1890), 209.

synthesized in the laboratory by the method of Erdmann,¹ while the rest was bought from commercial houses, as having been obtained directly from coal tar. The specific gravities and solidifying points of these substances were determined by the methods and apparatus described later on. The various samples of phenol had solidifying points of from 40.4 to 40.7° C. and specific gravities of from 1.0640 to 1.0647 at 45° C./45° C. Those of *o*-cresol varied in solidifying point from 28.8 to 30.2° C. and in specific gravity (25° C./25° C.) from 1.0439 to 1.0451. The *p*-cresols varied in solidifying point from 31.9 to 34.4° C. and in specific gravity (25° C./25° C.) from 1.0334 to 1.0335, while the *m*-cresols varied from -3.3 to +3.0° C. in solidifying point and from 1.0248 to 1.0333 in specific gravity (25° C./25° C.). Of the various samples the following were selected as being either the purest or else freest from slight impurities that might introduce serious errors:

	Specific Gravity	Solidifying Point
Phenol.....	1.0647 at 45° C./45° C.	40.6° C.
<i>o</i> -Cresol.....	1.0439 at 25° C./25° C.	29.0° C.
<i>p</i> -Cresol.....	1.0335 at 25° C./25° C.	34.4° C.
<i>m</i> -Cresol.....	1.0333 at 25° C./25° C.	3.0° C.

These samples were selected after a considerable amount of preliminary work with mixtures of the various substances to determine the impurity present, if any, in each one. They represent as a rule those having the highest solidifying points, although this is not the case with the *o*-cresol. Another *o*-cresol sample had a solidifying point of 30.2° C. but was not selected because it appeared to contain 2 or 3 per cent of phenol.

The constants obtained by using these samples in making up the necessary mixtures were used in the final plotting of lines and calculation of formulae, while those obtained by the use of the other less pure samples were used for comparison and to study the effect of varying amounts of the different impurities.

The following mixtures of the pure substances mentioned above were made up and the constants of the mixtures determined and plotted on cross-section paper. Most of the constants obtained were checked by two or more chemists working independently in order to eliminate errors due to personal equation.

Mixtures of the *o*-cresol and the *p*-cresol were made containing varying quantities of *o*-cresol from 95 to 70 per cent by weight and *p*-cresol from 5 to 30 per cent by weight and the solidifying points and the specific gravities at 25° C./25° C. of these mixtures were obtained, using all precautions to have the data as accurate as possible. The values obtained were plotted using the specific gravities as abscissae and the solidifying points as ordinates. Other mixtures were made using varying proportions of *o*-cresol from 90 to 70 per cent by weight, *p*-cresol from 5 to 25 per cent by weight and phenol 5 per cent by weight in each mixture. Similar mixtures containing decreasingly proportionate amounts of *o*-cresol and *p*-cresol and increasing proportions of phenol in series of increments of 5 per cent were made up, the constants determined and the values plotted as before. The results are shown in Fig. I.

¹ *Anleitung Z. Därst. Org. Präp.*, 1894.

This process was repeated using the *m*-cresol in place of the *p*-cresol. The line representing mixtures of the *o*-cresol and the *m*-cresol and no phenol is shown in Fig. I, the lines representing those mixtures containing the increments of phenol being omitted to avoid confusion. Similar mixtures were made up using the other less pure samples of the different cresols and the constants determined and plotted. These results, being used only for comparison, were not plotted.

It was found that the tangent of the angle formed by the line representing mixtures of the purest *o*-cresol and the purest *p*-cresol and no phenol and a line drawn through the point representing 100 per cent *o*-cresol parallel to the axis ($X = 0$) is numerically equal to 0.13. It was also found that the tangent of the angle formed by the *o*-cresol + *m*-cresol line in Fig. I and a line drawn through the point representing 100 per cent *o*-cresol parallel to the axis ($X = 0$) is equal to 0.22. These angles are represented in Fig. I as " α *o.p.*" and " α *o.m.*," respectively. Calculated from this data the tangent of the angle formed by a line representing mixtures of *o*-cresol and a distillate composed of 50 per cent *m*- and 50 per cent *p*-cresol would be 0.175. The similar tangent calculated from the data obtained by Weiss and Downs for mixtures containing the same percentages of *o*-cresol and a coal-tar distillate containing 50 per cent *p*- and 50 per cent *m*-cresol using a line drawn through the maximum number of nearest points obtained by them was found to be 0.181, a very close agreement with the above, notwithstanding the fact that the constants themselves were very different.

With the other less pure samples various lines were obtained depending on the purity of the *o*-cresol, *p*-cresol or *m*-cresol used—the position of the line indicating the impurity present.

As may be seen by referring to Fig. I, lines drawn through the points represented by mixtures containing no phenol, 5 per cent phenol, 10 per cent phenol, etc., up to 30 per cent phenol, within the limits of the plot, are parallel in the case of *p*-cresol. This is also true of *m*-cresol and mixtures of *m*- and *p*-cresol in varying proportions. The general equation for the pure *o*-cresol + *p*-cresol lines, with or without phenol, as may be seen by inspection, is

$$1000 (G_o - G_p) - 0.126 (T_o - T_o) = 0.$$

That for the pure *o*-cresol + *m*-cresol lines, with or without phenol, is

$$1000 (G_o - G_m) - 0.218 (T_o - T_m) = 0,$$

where G_o = sp. gr. 25° C./25° C. of the *o*-cresol,

G_p = sp. gr. 25° C./25° C. of the *p*-cresol,

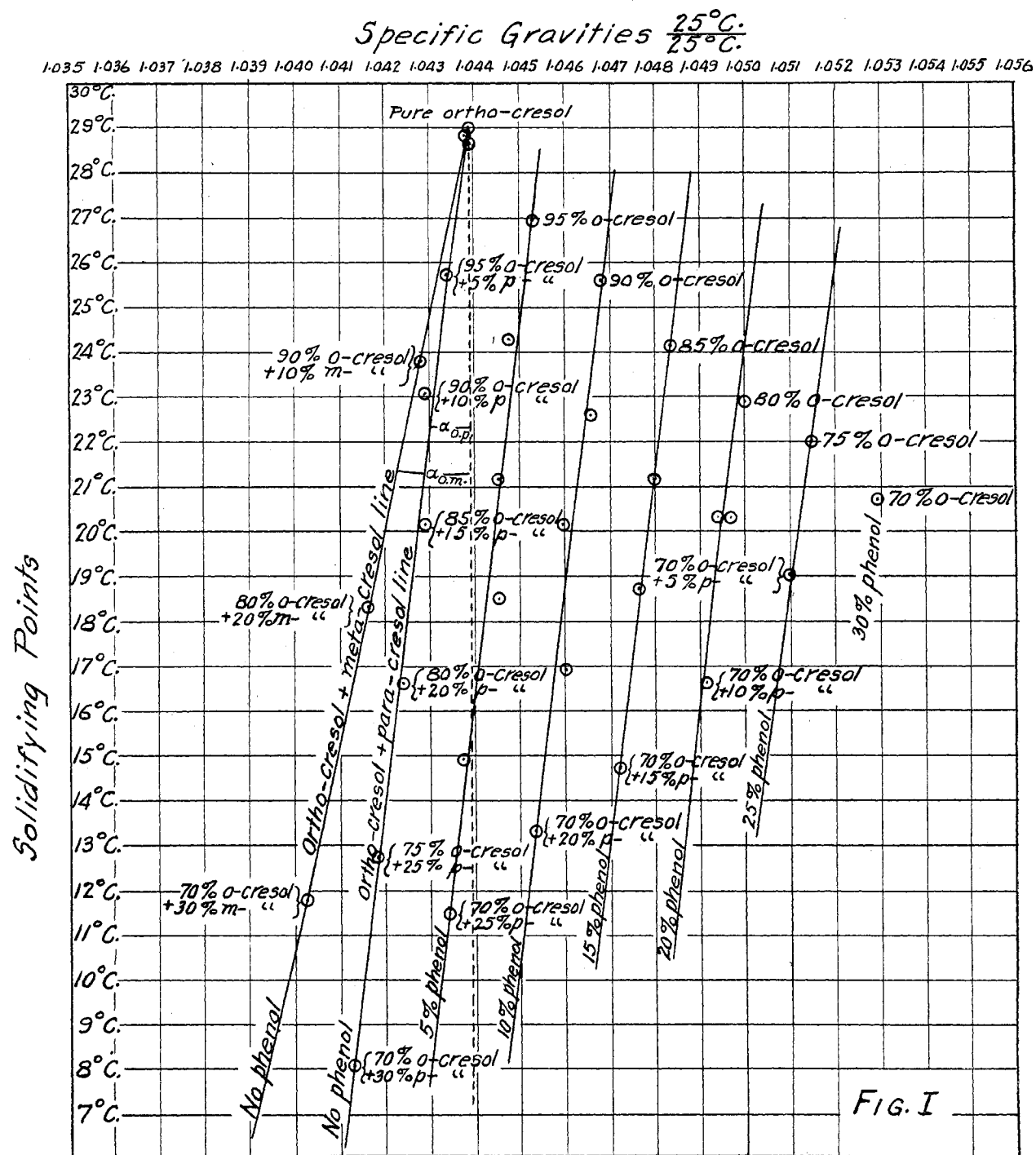
G_m = sp. gr. 25° C./25° C. of the *m*-cresol,

T_o = solidifying point of the *o*-cresol,

T_p = solidifying point of the *p*-cresol,

and T_m = solidifying point of the *m*-cresol.

These lines, in addition to being parallel, are also equi-distant for equal increments of phenol, both in the case of *p*-cresol mixtures and *m*-cresol mixtures, although for the same increments the distances between the lines are greater in the case of *m*-cresol than in the



case of *p*-cresol. In other words, with mixtures of *o*-cresol, *p*-cresol and phenol containing more than 70 per cent of *o*-cresol and less than 30 per cent phenol, and of the same solidifying point, the per cent of phenol varies directly with the specific gravity. The same rule holds true with mixtures of *o*-cresol, *m*-cresol and phenol and mixtures of *o*-cresol, phenol and varying proportions of *m*-cresol and *p*-cresol within the same limits. In the case of mixtures of *p*-cresol, *o*-cresol and phenol, the solidifying point remaining the same, it was found that each per cent of phenol increased

the specific gravity 0.0003367; in that of mixtures of *m*-cresol, *o*-cresol and phenol, 0.0003600; in that of mixtures of *p*-cresol, *m*-cresol, *o*-cresol and phenol proportionately intermediate values depending on the ratio of *p*-cresol to *m*-cresol.

Similarly it was found that, the specific gravity remaining constant, each per cent of phenol depressed the solidifying point 2.75° C. in case of the *p*-cresol mixtures, and 1.71° C. in that of the *m*-cresol mixtures.

These facts enable us to formulate an equation which will give the percentage of phenol without

having recourse to a plot in cases where (1) *o*-cresol, *p*-cresol and phenol, or (2) *o*-cresol, *m*-cresol and phenol are present in the mixtures, and 30 per cent of the mixture has been mixed with 70 per cent of pure *o*-cresol.

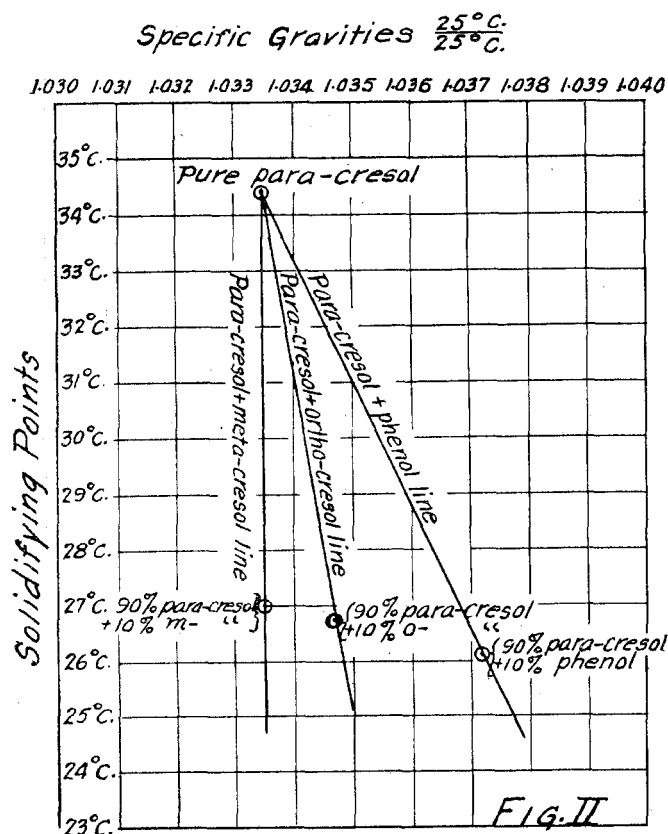
$$\text{Per cent phenol} = \frac{1.00}{2.73} (T_o - T_{so}) - \frac{1.00}{0.0003367} (G_o - G_{so}) \quad (\text{I})$$

or,
$$\text{Per cent phenol} = 0.366 (T_o - T_{so})$$

$$\text{Per cent phenol} = 0.585 \frac{(T_o - T_{so})}{2780(G_o - G_{so})} \quad (\text{II})$$

where T_o = solidifying point of the pure *o*-cresol used,
 T_{so} = solidifying point of mixture of 70 per cent of *o*-cresol + 30 per cent of substance,
 G_{so} = specific gravity 25° C./25° C. of mixture of 70 per cent of *o*-cresol + 30 per cent of substance,
 G_o = specific gravity 25° C./25° C. of the pure *o*-cresol used.

Since in the analysis of commercial products, as has been said before, the proportion of *m*- to *p*-cresol may vary over very wide limits, it is necessary to have some means of obtaining a measure of the amount of *m*- or *p*-cresol present in the portion of distillate used for determining the constants.



In the hope of finding such a means, mixtures of 90 per cent of pure *p*-cresol with 10 per cent of phenol and also with 10 per cent of *o*-cresol and 10 per cent of *m*-cresol, were made up separately, and the constants determined and plotted. The results are shown in

Fig. II. As a study of the plot failed to throw any light on the problem, this particular line of investigation was abandoned.

The effect of varying amounts of the different cresols on the constants of pure phenol was studied by making mixtures containing 90 to 70 per cent of the purest phenol and 10 to 30 per cent of the purest *o*-cresol and similar mixtures containing the same percentages of the purest *p*-cresol and the purest *m*-cresol separately in place of the *o*-cresol, determining the constants for each mixture and plotting the points representing them. The terminal points and the three lines drawn through the nearest points representing the three classes of mixtures are shown graphically in Fig. III as "Phenol + *m*-cresol line," "Phenol + *o*-cresol line" and "Phenol + *p*-cresol line."

The effect of using the slightly impure cresols was also studied to determine the effect of the small amounts of impurities present on the constants of the different mixtures. The results clearly indicated the impurities present in the same way as was the case with the mixtures of the different slightly impure substances with 70 per cent or more of the different *o*-cresols.

A study of the results obtained with the pure samples revealed the following facts:

The effect of the addition of each of the cresols on the solidifying point of phenol is widely different as may be seen by referring to Fig. III. Each per cent of *o*-cresol added, within the limits of the plot, depresses the solidifying point of the phenol about 0.65° C., each per cent of *m*-cresol depresses it about 0.55° C., and each per cent of *p*-cresol about 0.83° C. Obviously, under such circumstances it would be folly to attempt to determine the per cent of phenol in a mixture of the cresols by determining either the solidifying point alone or the solidifying point and specific gravity of a mixture of phenol and cresols containing 70 per cent or more of phenol unless the relative proportions of each cresol present in the mixture were known at least approximately. Meta-cresol can be determined by the Raschig method.¹ A number of distillates were analyzed by this method after first being purified and fractionally distilled. As the percentage of *m*-cresol found by this method varied over very wide limits and there seemed to be no connection between the distillation point and the amount of *m*-cresol found and as no way was devised for determining the relative proportions of *o*- and *p*-cresol present it was decided that this line of attack would be unproductive of results.

Further study of the results obtained on the mixtures of phenol and the separate cresols containing more than 70 per cent of phenol showed that the effect of the addition of the different cresols on the specific gravity of the phenol is also different in each case, as may be seen by referring to Fig. III. Each per cent of *o*-cresol added, within the limits of the plot, lowers the specific gravity (45° C./45° C.) of the phenol 0.00031, each per cent of *p*-cresol lowers it 0.00040, and each per cent of *m*-cresol, 0.00044.

¹ *Z. angew. Chem.*, 1900, 759.

Specific Gravities 45°C.
 45°C.

1.045 1.046 1.047 1.048 1.049 1.050 1.051 1.052 1.053 1.054 1.055 1.056 1.057 1.058 1.059 1.060 1.061 1.062 1.063 1.064 1.065 1.066

Solidifying Points

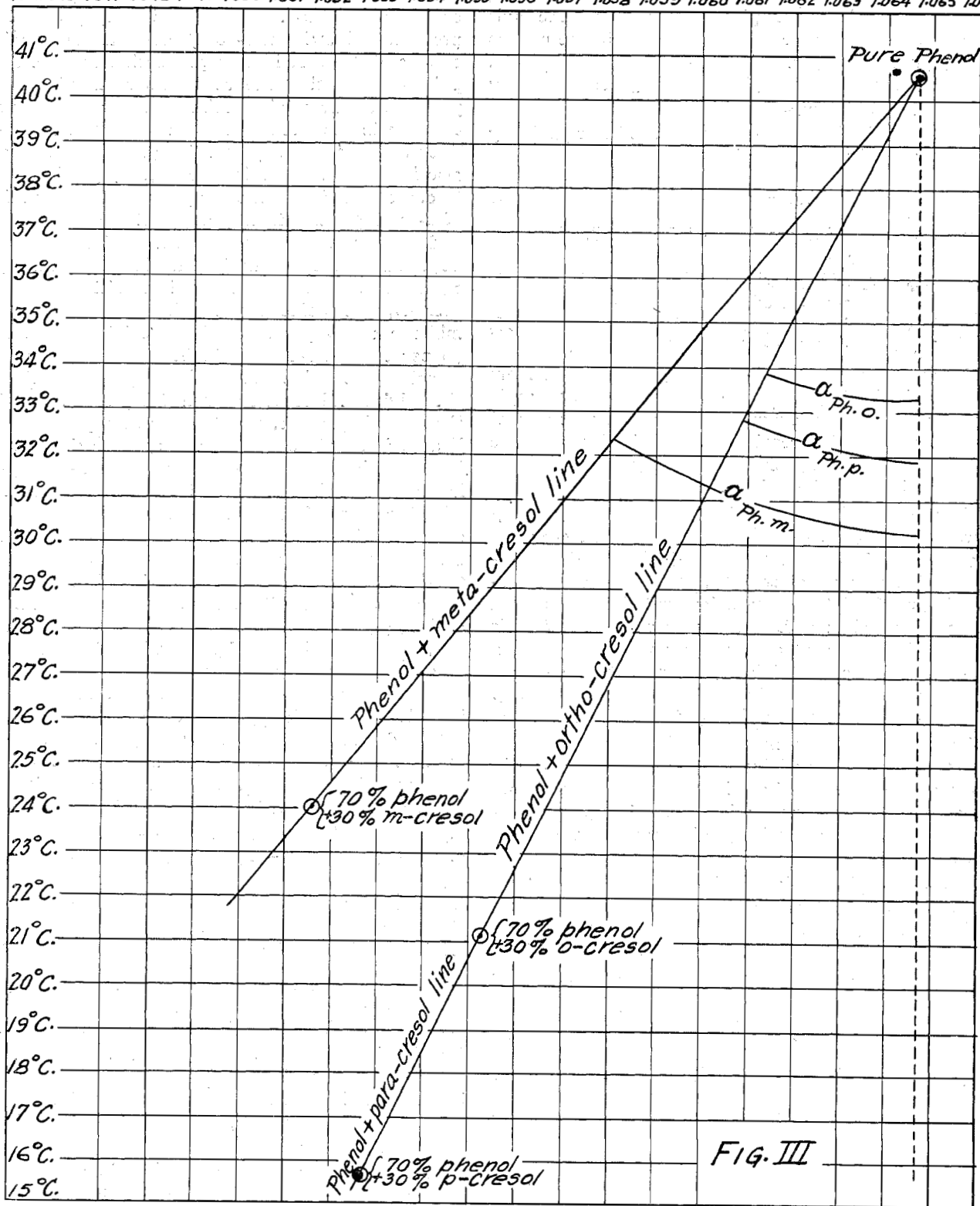


FIG. III

The combined effect of each cresol on the solidifying point and specific gravity of phenol is represented by the three lines shown in Fig. III and is measured in each case by the tangent of the angle formed by each line and a line drawn through the point representing the constants for pure phenol parallel to the axis ($X = 0$). These angles are represented in the plot as " $\alpha_{Ph.o.}$ " and " $\alpha_{Ph.m.}$ " and " $\alpha_{Ph.p.}$." Inspection of Fig. III will show that " $\alpha_{Ph.o.} = \alpha_{Ph.p.}$," consequently $\tan. \alpha_{Ph.o.} = \tan. \alpha_{Ph.p.}$.

The value of this tangent was found to be numerically equal to 0.482 by the formula

$$\tan. \alpha_{Ph.s.} = \frac{1000 (G_p - G_{sp})}{T_p - T_{sp}} \quad (III)$$

where G_p = specific gravity 45° C./45° C. of phenol used,

G_{sp} = specific gravity 45° C./45° C. of phenol + cresol used,

T_{sp} = solidifying point of phenol + cresol used,
 T_p = solidifying point of phenol used.

The same value was obtained by calculation from the data obtained by Weiss and Downs for their sample of pure phenol and their mixture of 70 per cent phenol and 30 per cent of *o*-cresol in spite of the fact that the constants obtained by them were very different from those obtained by the writers.

The tangent of the angle formed by the "phenol + *m*-cresol" line ($\tan. \alpha_{Ph.m.}$) was found to be equal to 0.794, while that of a "phenol + (50 *m* + 50 *p*)-cresol" line was equal to 0.65. The tangent corresponding to the latter case calculated from the data obtained by Weiss and Downs for their phenol and their mixture of 70 per cent of phenol plus 30 per cent of a coal-tar distillate containing 50 per cent of *m*-cresol and 50 per cent of *p*-cresol was found to be about 0.64.

Those results obtained by the writers for the tangents of the angles that are comparable with those calculated from the data obtained by Weiss and Downs, are in remarkable agreement, both in the case of the phenol mixtures and the *o*-cresol mixtures, although the constants themselves are widely different for the same mixtures.

By a series of experiments it was shown that if 30 per cent of a pure cresol or a mixture of cresols containing varying amounts of phenol were mixed with 70 per cent of pure phenol and the constants obtained on this mixture, the value of the $\tan. \alpha_{Ph.s.}$ calculated from the constants of the phenol and the mixture by Equation III would be the same, within the limit of error of the analytical work, regardless of the amount of phenol present, provided the same cresol or mixture of cresols were present and only the per cent of phenol varied. Consequently by calculating the $\tan. \alpha_{Ph.s.}$ for a given mixture of cresols containing any amount of phenol over 70 per cent the influence of any phenol originally present before the 70 per cent was added is eliminated and since $\tan. \alpha_{Ph.s.}$ for *o*-cresol and also for *p*-cresol is equal to 0.482, any increase in the value of $\tan. \alpha_{Ph.s.}$ over 0.482 gives a measure of the amount of *m*-cresol present.

Now the "phenol + *o*-cresol line" in Fig. III is

coincident with the "phenol + *p*-cresol line" and no matter how much phenol is present in the original mixture of cresol and phenol the point representing the constants after mixing with 70 per cent of phenol will lie somewhere on the line if *o*- or *p*-cresol alone or mixtures of *o*- and *p*-cresol in any proportion are present. Likewise if *o*- or *p*-cresol alone or mixtures of *o*- and *p*-cresol in any proportion are present, the point representing the constants of a mixture of 30 per cent of the original mixture and 70 per cent of *o*-cresol will lie somewhere on the "*o*-cresol-*p*-cresol line" shown in Fig. I, or a line parallel to it if phenol also is present. In this case $\tan. \alpha_{Ph.s.}$ will be equal to 0.482, showing that *o*- or *p*-cresol alone or mixtures of *o*- and *p*-cresol in any proportion are present only and the per cent of phenol in the original mixture may be calculated by Equation I. If the $\tan. \alpha_{Ph.s.}$ is equal to 0.794, only *m*-cresol in addition to phenol is present; the point representing the constants of a mixture of 30 per cent of the original mixture and 70 per cent of *o*-cresol will lie somewhere on the "*o*-cresol-*m*-cresol line" in Fig. I, if phenol is absent in the original mixture, or, on a line parallel to this line if phenol is present, and the per cent phenol present, if any, is obtained by the use of Equation II. Now if in addition to *o*- or *p*-cresol alone or *o*- and *p*-cresol in any proportion, *m*-cresol is also present, $\tan. \alpha_{Ph.s.}$ will be intermediate between 0.482 and 0.794; and the difference between the value found and 0.482 will give a measure of the *m*-cresol present in proportion to the other cresols present, which, if multiplied by the ratio of the difference between the $\tan. \alpha_{Ph.m.}$ and $\alpha_{Ph.o.}$ (Fig. III) to the difference between the $\tan. \alpha_{o.m.}$ and $\alpha_{o.p.}$ (Fig. I) will give the necessary factor for correcting Equation I for varying amounts of *m*-cresol present. The resulting equation is derived algebraically as follows:

The difference between $\tan. \alpha_{Ph.m.}$ and $\tan. \alpha_{Ph.o.}$, or $\tan. \alpha_{Ph.p.}$, = 0.794 - 0.482, or 0.312. The difference between $\tan. \alpha_{o.p.}$ and $\tan. \alpha_{o.m.}$ is equivalent to the difference between Equations I and II.

$$0.366 (T_o - T_{so}) - 2970 (G_o - G_{so}) = \% \text{ phenol}$$

$$0.585 (T_o - T_{so}) - 2780 (G_o - G_{so}) = \% \text{ phenol}$$

$$\text{or, } 0.219 (T_o - T_{so}) + 190 (G_o - G_{so}) = 0, \quad \text{for equal percentages of phenol.}$$

Dividing this equation by 0.312 gives

$$\frac{0.219}{0.312} (T_o - T_{so}) + \frac{190}{0.312} (G_o - G_{so}) = 0$$

$$\text{or, } 0.702 (T_o - T_{so}) + 609 (G_o - G_{so}) = 0.$$

Multiplying by ($\tan. \alpha_{Ph.s.} - \tan. \alpha_{Ph.o.}$) or ($\tan. \alpha_{Ph.s.} - 0.482$) which can be represented by the symbol L_s , meaning the tangential lowering of the constant of phenol caused by the substance compared with that caused by *o*- or *p*-cresol, gives

$$0.702 L_s (T_o - T_{so}) + 609 L_s (G_o - G_{so}) = 0.$$

Adding this equation to Equation I gives

$$(0.366 + 0.702 L_s) (T_o - T_{so}) + (609 L_s - 2970) (G_o - G_{so}) = \text{per cent phenol}$$

$$\text{or, } (0.366 + 0.702 L_s) (T_o - T_{so}) + (2970 - 609 L_s) (G_{so} - G_o) = \text{per cent phenol,} \quad (IV)$$

$$\text{where } L_s = \frac{1000 (G_p - G_{sp})}{T_p - T_{sp}} - 0.482$$

in which G_p = sp. gr. 45° C./45° C. of the phenol used,
 G_{sp} = sp. gr. 45° C./45° C. of the 70 per cent

phenol + 30 per cent cresol mixture,
 T_{sp} = solidifying point of the 70 per cent

phenol + 30 per cent cresol mixture
 and T_p = solidifying point of the 70 per cent,
 phenol used,

and where G_o = sp. gr. 25° C./25° C. of the *o*-cresol
 used,

G_{so} = sp. gr. 25° C./25° C. of the 70 per
 cent *o*-cresol + 30 per cent cresol
 mixture,

T_{so} = solidifying point of the 70 per cent
o-cresol + 30 per cent cresol mix-
 ture,

and T_o = solidifying point of the *o*-cresol used.

When the distillate analyzed is composed of *o*-cresol or *p*-cresol alone or a mixture of these two cresols in any proportion L_s becomes equal to 0.0 and Equation IV is transformed into Equation I. As the proportion of *m*-cresol to the other cresols present increases, L_s increases in value until 100 per cent of *m*-cresol is present, when L_s becomes equal to 0.312 and Equation IV is transformed into Equation II.

Although Equation IV does not give absolutely accurate results with all possible mixtures of the three isomeric cresols it does give them with any of the three cresols alone, with all possible mixtures of *o*- and *p*-cresol and all possible mixtures of *m*- and *p*-cresol. Where *o*-cresol and *m*-cresol are present in varying proportions and *p*-cresol is absent or present in very small quantities, results obtained are too low, the error increasing as *o*-cresol increases and *p*-cresol simultaneously decreases until the greatest is introduced where *p*-cresol is absent and less than 50 per cent of *m*-cresol and more than 50 per cent of *o*-cresol is present. Even in this case the error is compensated for, as the relative proportion of *o*- to *m*-cresol increases, by the factor $(T_o - T_{so})$ simultaneously decreasing proportionately, so the ultimate error is never very large in any case. Moreover, it is hard to conceive of a case in actual commercial practice where *o*- and *m*-cresol would occur together in the absence of, or in the presence of a small amount of *p*-cresol, since no evidence has ever been found that *p*-cresol was removed from a crude cresylic acid, as is the case with *m*-cresol, and, owing to the fact that *p*-cresol distills at a temperature between the boiling point of *o*-cresol and that of *m*-cresol, in the ordinary processes of distillation there is more likely to be a dearth of *o*- or *m*-cresol in a mixture of the three cresols in commercial products than of *p*-cresol. This fact is confirmed by Ihle¹ and by Tiemann and Schotten¹ who found "mostly *o*- and *p*-cresol with a little *m*-cresol" present, while Schulze² found "about 40 per cent *m*-, 35 per cent *o*- and 25 per cent *p*-cresol" in tar oils. In the latter case, as well as in practically all those cases ordinarily

¹ *Loc. cit.*

met with in commercial practice, where all three cresols are present in varying amounts, the probable error would amount to only a few tenths of a per cent in the final result, which is about the same as the probable error inherent to the determination of the constants of the different mixtures.

In the application of Equation IV to the determination of phenol in commercial products, such as crude cresylic acid, it is necessary to remove completely even small quantities of hydrocarbons, and to remove effectively xylenols, higher homologues and bases, inasmuch as it was found on practical application that the presence of even very small amounts of hydrocarbons would seriously affect the accuracy of the results while the presence of bases, xylenols and other higher homologues, though not affecting the ultimate result to so great a degree as the hydrocarbons, nevertheless introduced serious errors when present in very great amounts.

THE HYDROCARBONS were found to be more effectively removed by diluting the original sample with 2 volumes of benzol before extracting with caustic soda solution. In addition, this process in most cases renders unnecessary the preliminary distillation in the case of dark colored products.

THE BASES are effectively removed by the regular process of separating the tar acids, being left behind in the acid liquor on acidifying the carbolate solution.

The problem of separating effectively the XYLENOLS and HIGHER HOMOLOGUES from phenol and the cresols was investigated by comparing results obtained in actual analysis, using most of the still-heads enumerated and illustrated by Rittman and Dean¹ in their article on the analytical distillation of petroleum.

The results were far from satisfactory. Those still-heads that effectively removed the xylenols choked up and caused considerable annoyance and delay in the process of distillation, while those that distilled without choking up failed to remove the xylenols. To remedy these defects a special still-head was designed of the proper dimensions for this work. This still-head is described later on. It has been used for a long time now and has proved satisfactory.

Other details in the manipulation, the necessity for which will be obvious, were worked out and owing to the impracticability of obtaining thermometers and still-heads of exactly standard dimensions the distillation temperatures are given corrected for emergent steam, thus eliminating the necessity of having still-heads and thermometers of certain dimensions.

DESCRIPTION AND METHOD OF USE OF THE KNIGHT STILL-HEAD

This still-head is especially designed for use in separating xylenols and higher homologues from phenol and the cresols. It consists of three 2-in. bulbs joined by 2 glass tubes $\frac{3}{16}$ in. long and having a $\frac{9}{32}$ -in. aperture. The upper bulb is connected with a glass tube open at the top ($\frac{5}{8}$ in. inside diam. and 3 in. long) and having a side tube ($\frac{7}{32}$ in. inside diam.)

¹ THIS JOURNAL, 7 (1915), 755.

which is joined on about $1\frac{1}{4}$ in. above the upper bulb and is bent downward at any suitable angle and for any desired length. The lower bulb has a glass syphon tube ($\frac{1}{8}$ in. inside diam.) joined to the side of the bottom of the bulb and bent upward to slightly less than half way up the side of the lower bulb and then bent downward, following roughly the contour of the bulb, and passing through and down the center of another tube, $4\frac{1}{2}$ in. long and $\frac{3}{8}$ in. inside diam., along $3\frac{1}{2}$ in. of the lower part and $\frac{7}{32}$ in. inside diam.

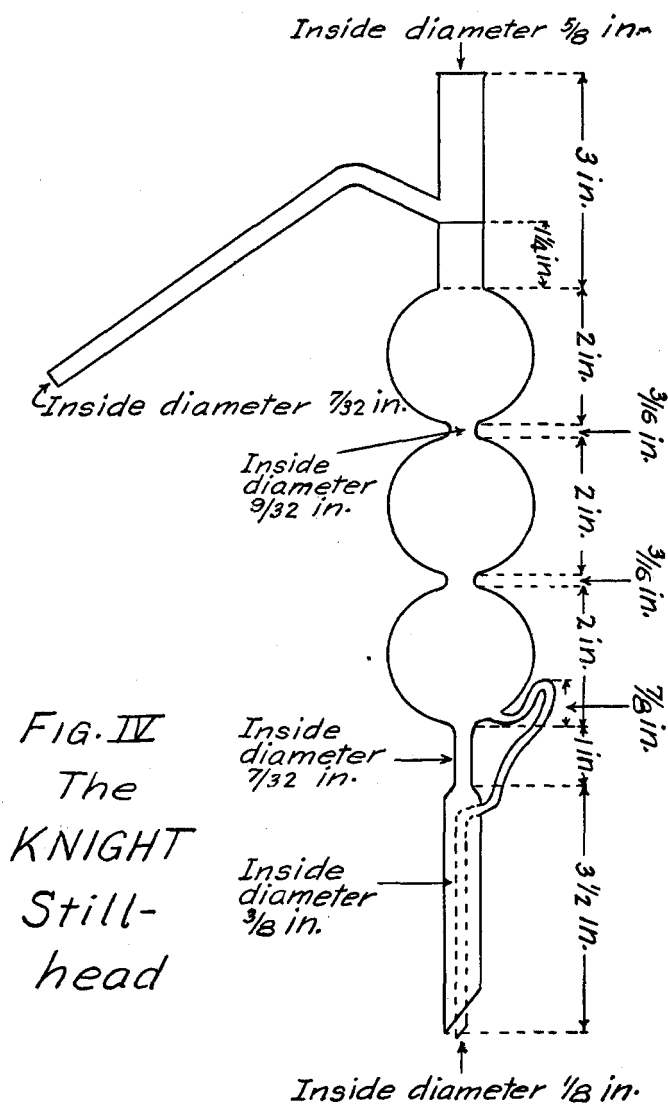


FIG. IV
The
KNIGHT
Still-
head

Scale $\frac{1}{2}$ in. = 1 in.

along 1 in. of the upper part where it is joined to the lowest bulb of the still-head. The syphon tube enters the $\frac{3}{8}$ in. diameter part of the lower tube about $1\frac{1}{2}$ in. from the bottom of the lower bulb and passes through the center of the tube to the bottom as shown in the accompanying diagram.

The dimension of the constriction in the lower tube is so calculated to the condensing area of the bulb of the still-head that when the distillation is carried

on at the specified rate more vapor will condense than can run back into the distilling flask through the constriction; thus a layer of liquid collects in the bottom of the lowest bulb and acts as a liquid condenser for all vapors passing through it having a higher boiling point than the temperature of the liquid layer. In this way the xylenols and higher homologues which tend to pass over with the phenol and cresols are retained in the liquid layer, and the temperature of the liquid layer is kept hot enough by the vapors to prevent phenol from being condensed. When the height of this layer reaches above the level of the top of the outside portion of the syphon tube, the syphon automatically empties the bulb of the liquid layer and delivers the condensed liquid back into the distilling flask again, provided the rate of distillation is not too fast. A Tirrell burner should be used as a source of heat on account of the ease with which the rate of distillation may be controlled by its use.

Towards the end of the redistillation of the 190-202° fraction, when all the phenol has been removed, occasionally such a small amount of liquid remains in the distilling flask that scorching is liable to occur. In this case, and in other cases where it seems necessary to carry a small amount of liquid layer in the lower bulb, this may be accomplished by tipping the top of the still-head away from the condenser so that the still-head instead of being vertical is inclined at an angle from top to bottom toward the condenser. By regulation of this angle the syphon may be made to empty as frequently as the operator desires.

METHOD

Weigh out 100 g. of the sample (W) in a tared beaker to centigrams. Pour the oil into a separatory funnel (500 cc. capacity); rinse the flask with 200 cc. of benzol, adding the rinsings to the sample contained in the separatory funnel. Mix the contents of the separatory funnel, add 100 cc. of a 20 per cent NaOH solution, shake thoroughly for two minutes, allow to settle, and draw off the lower layer¹ into another separatory funnel of 600-700 cc. capacity.

Repeat the extraction of the benzol layer with successive 100-cc. portions of 20 per cent NaOH solution, drawing off the lower layer as before until no more tar acids are extracted, as shown by acidifying the last portion (3 or 4 shake-outs are usually sufficient). Shake the combined NaOH extracts out with 30-cc. portions of benzol until any hydrocarbons that may have been carried through into the NaOH extracts by benzol and tar acids have been removed as shown by heating the NaOH solution in a beaker to a gentle boil until the odor of benzol disappears and the characteristic odor of coal-tar hydrocarbons can no longer be detected. Wash the combined benzol extracts a couple of times with 10 cc. of 20 per cent NaOH solution and add the washings to the NaOH solution.

¹ Occasionally a black tarry sample will be encountered with which it will be difficult to distinguish the line of separation of the layers. In this case it will be necessary, first to distil enough of 100 grams of the sample to be sure that all of the phenol has been removed, and then pour the distillate into the separatory funnel, add the 200 cc. of benzol and proceed as above.

Acidify the combined caustic soda extracts with dilute sulfuric acid (50 cc. of concentrated acid mixed with 150 cc. of water). The solution is conveniently held in a 1-liter Jena Erlenmeyer flask. The acid must be added in small portions at a time, and the solution cooled by immersing the flask in water or holding it under a tap of running water so that the temperature does not rise above 40° C. as measured by a thermometer placed in the flask.

As it approaches neutrality the solution becomes light in color, and should be tested occasionally with litmus paper. When neutral, add 4 to 5 cc. more of the dilute sulfuric acid, transfer to a 700-cc. separatory funnel rinsing flask and allow to stand till the two layers separate well (from 1 to 4 hours are necessary according to the character of the sample).

Draw off the lower layer into another separatory funnel. Shake the acid-water layer with 30 cc. of benzol; allow the two layers to separate well, draw off the lower layer into another separatory funnel and repeat the extraction with 20-cc. portions of benzol until no more tar acids are extracted, as shown by evaporating a test portion just to dryness on the water bath (usually 4 extractions are enough). Reject the exhausted water layer, add the second benzol shake-out to the first; add the third benzol shake-out to the separatory funnel which had contained the second benzol shake-out and then add it to the first two benzol shake-outs. Repeat this process with the fourth benzol extract, etc., rinsing out each successive funnel with the last benzol extract, and combine all the shake-outs with the first. Wash the combined benzol extracts with 10 cc. of saturated salt solution and draw off and reject the salt solution. Draw off the tar acids into a 300-cc. round bottom, short neck, distilling flask, made of Jena or other heat-resisting glass; rinse out the separatory funnel with the combined benzol shake-outs of the acid-water layer, and add to the tar acids in the distilling flask. Distil off the benzol and water into a separatory funnel, using a medium size Wurtz still-head having an inlet tube below the first bulb $\frac{9}{32}$ in. inside diameter (both will come off practically completely below 170° C., and there will be an abrupt rise beginning at about 100–120° C.). The distilling flask should rest on a $\frac{1}{4}$ in. asbestos board 6 in. square with an opening in the center $3\frac{1}{2}$ in. in diameter and be enclosed entirely in an asbestos shield; the thermometer should be a standard thermometer, calibrated by the Bureau of Standards and accurate to $\frac{1}{5}$ ° C., over the range 170 to 210° C.; the condenser should be long enough, and cooled with sufficient cold water, to prevent loss by lack of proper condensation; the top of the bulb of the thermometer should be on a level with the bottom of the outlet tube of the still-head, and the upper part of this still-head and the one used later should be protected with thick asbestos cloth held in place with copper wire hoops and extending from the top of the upper bulb to the top of the still-head. When water and benzol are out of the condenser, stop the distillation (it does not matter if some oil distils over with the water).

Allow the still to cool; rinse out the Wurtz still-head with a small amount of benzol and add the rinsing to the benzol and water distillate. Saturate the water layer with salt, shake, separate, reject the salt water layer, and extract the benzol layer with 5-cc. portions of 20 per cent NaOH solutions until any tar acids in the benzol layer are removed (as shown by acidifying a test portion of the last shake-out with dilute sulfuric acid.) (Usually 3 or 4 extractions are enough.) Acidify the combined NaOH extracts with dilute sulfuric acid as before, allow to stand, separate any tar acids that collect, and add to the tar acids in the distilling flask. Continue the distillation, using a Knight still-head in place of the Wurtz still-head, and collect the distillate, first in a 10-cc. burette, until the oil passes over clear, then change to a tared 100-cc. cylinder, weighed to centigrams, and collect up to 193° C. (corr.).¹ Meanwhile saturate with salt any water layer that may be mixed with the tar acids in the 10-cc. burette and allow to stand. At 193° C. (corr.) change the receiver, stop the distillation, allow the still to cool, separate the tar acids from the saturated salt water, if any, contained in the 10-cc. burette, rejecting the salt water and drawing off the tar acids into the distilling flask; continue the distillation and collect the distillate up to 206° C. (corr.), distilling, as nearly as possible, at the rate of 0.5 to 1.0 cc. per minute.

Transfer the distillate collected from 193 (corr.) to 206° C. (corr.) to another flask and redistil at the same rate as before, collecting the distillate up to 201° C. (corr.) in the same tared cylinder used for collecting up to 193° C. (corr.) in the initial distillation. Weigh the cylinder containing the distillate to centigrams and calculate the weight of the distillate (D). Pour the distillate into a suitable size Erlenmeyer flask and mix thoroughly by pouring back and forth, and then stopper the flask.

Weigh out as accurately as possible 4.5 g. of this distillate and 10.5 g. of *o*-cresol (solidifying point above 28° C.). Mix these two portions thoroughly; if necessary, heat cautiously in warm water to dissolve any crystals of *o*-cresol that may be undissolved, and keep in a stoppered flask.

Determine the SPECIFIC GRAVITY (G_{50}) of this mixture, at 25° C./25° C., in a carefully calibrated and tared 10-cc. Geissler pycnometer, having a thermometer carefully calibrated to within 0.1° C. at 25° C., being careful to make consecutive weighings and to wipe off the pycnometer thoroughly between weighings, until the weight is constant to a few tenths of a milligram.

Determine the solidifying point of the same mixture, using the apparatus and method described below.

The SOLIDIFYING POINT determination should be

¹ This temperature and all subsequent distillation temperatures are given corrected for stem exposure, using the formula: stem correction = $0.00016 N (T^\circ - t^\circ)$, where N = number of degrees exposed, T° = temperature of the thermometer bulb, and t° = average temperature of the exposed stem. This correction will make a difference of 3 to 40° C. at these temperatures, but the corrected temperatures will be consistent regardless of the thermometer used, provided it is a standard thermometer. A corrected temperature of 193° C. will usually give an observed reading of 190° C. although this will vary slightly with different thermometers.

made in an apparatus composed of a cylindrical glass vessel 6 in. in diameter by 7½ in. high filled with water or iced water at a temperature about 5° C. below the expected solidifying point and containing a cylindrical salt-mouthed bottle of about 3½ in. diameter and about 6¼ in. high, clamped in position so that the bottle is almost completely immersed. The bottle is closed with a cork stopper through which passes a short test tube 4 in. long by 7/8 in. diameter, fitted snugly into the stopper so that none of the tube extends above the top of the stopper. The test-tube is closed with a rubber stopper through which pass the standard thermometer and a looped platinum stirrer. The thermometer used should be a standard thermometer reading to tenths and calibrated by the Bureau of Standards to hundredths of a degree over the range between 6 and 41° C. The determination should be conducted as follows:

Pour enough of the mixture into the test-tube to give a layer more than sufficient to cover the bulb of the thermometer. Insert the thermometer and the platinum stirrer passing through the rubber stopper into the mixture; press the stopper tightly into the test-tube and stir the mixture continuously with the platinum stirrer till the temperature is near the expected solidifying point. Then introduce a few fine crystals of *o*-cresol into the mixture and continue the stirring until the mass crystallizes, and the temperature rises to a maximum point and remains constant. This temperature is the solidifying point (T_{so}).

Repeat the determination of the specific gravity and solidifying point (T_{sp}) of the distillate, using phenol of 40° C. or higher solidifying point, instead of *o*-cresol, and determining the specific gravity at 45° C./45° C. (G_{sp}), instead of 25° C./25° C.

The following procedure should be followed in determining the specific gravities:

In the case of phenol and phenol mixtures, where the specific gravity is determined at 45° C., the pycnometer with the cap and thermometer removed is filled with the phenol or phenol mixture which has previously been heated very cautiously in warm water at a temperature of about 50° C. until the phenol crystals have dissolved and the phenol reached a temperature of about 45° C. The thermometer is then placed in the pycnometer and the pycnometer immersed in water at a temperature slightly higher than 45° C. The water in the bath is then repeatedly adjusted until it is at 45° C. at the same time that the pycnometer thermometer registers 45° C. (The pycnometer is immersed in the warm water almost up to the point where the thermometer enters the pycnometer.) The pycnometer is then removed from the water, the cap put on, the whole pycnometer carefully wiped dry, weighed to tenths of a milligram, removed from the scale pan, wiped again and weighed again until two successive weighings check to within a few tenths of a milligram.

In the case where the specific gravity is determined at 25° C. and the room temperature is above 25° C., the mixture to be tested, after first being heated, if

necessary, in water at about 30–35° C. to melt any *o*-cresol crystals, should be first cooled in cold water to a few degrees below 25° C. and then the pycnometer filled, immersed up to the neck in water slightly above 25° C., etc., the same procedure being followed as described above. The cap in this case should have a slight perforation at the top to relieve any pressure that might raise the cap and cause loss.

The per cent of phenol in the original substance is calculated in the following manner:

First calculate the relative tangential lowering of the specific gravity of the phenol-distillate mixture (L_s) by the equation

$$L_s = \frac{1000 (G_p - G_{sp})}{T_p - T_{sp}} - 0.482.$$

Then calculate the per cent phenol in the sample by the following equation:

$$\text{Per cent phenol} = 100 D [(T_s - T_{so}) (0.366 + 0.702 L_s) + (G_{so} - G_o) (2970 - 609 L_s)] / 30W,$$

where G_p = sp. gr. 45°/45° C. of the phenol used,
 G_{sp} = sp. gr. 45°/45° C. phenol + distillate mixture,

T_p = solidifying point of the phenol used,

T_{sp} = solidifying point of the phenol + distillate mixture,

D = weight of total distillate below 197° C.,

G_o = sp. gr. 25°/25° C. of the *o*-cresol used,

G_{so} = sp. gr. 25°/25° C. of the *o*-cresol + distillate mixture,

T_o = solidifying point of the *o*-cresol used,

T_{so} = solidifying point of the *o*-cresol + distillate mixture,

and W = weight of the sample used,

SUMMARY

For the determination of phenol in the presence of the three cresols, a feasible method is developed which not only obviates the necessity of referring to a plot in calculating results, but gives concordant and reliable results with all the different combinations and percentages of the different cresols and phenol likely to be met with in commercial practice; in addition, the method is not dependent for its accuracy on the purity of the particular *o*-cresol used by the investigators for the derivation of their formula for calculating the per cent of phenol. In applying the principle involved to the practical determination of phenol in crude commercial tar acids, suitable provision is made for the complete separation of the small amounts of hydrocarbons that are usually present in crude cresylic acids, especially those made from blast furnace tar, which would otherwise introduce serious error. A new still-head, especially designed for this kind of work, is used for the more complete and satisfactory removal of the xylenols and higher homologues.