

I must also note a regrettable error in my own recalculation² of Wood's value, which should read 3.07 at 25° instead of 3.67. This calculation is based on the temperature coefficients determined in this Laboratory.³

³ Hall and Sprinkle, *THIS JOURNAL*, **54**, 3469 (1932).

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ANALYSIS OF SMALL QUANTITIES OF VOLATILE MATERIAL BY DETERMINATION OF THE VAPOR PRESSURE AND MOLECULAR WEIGHT DURING DISTILLATION

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The distillation analysis of liquid petroleum products is of importance as a criterion of their technical properties. Conclusions as to the adaptability of a motor to changes of load, the determination of the necessary preheating of the main air, of the cooling water temperature, etc., may be drawn from the behavior of a benzene during distillation.¹

The A. S. T. M. method² specifies the use of 100 cc. of liquid in accordance with the original method of Engler-Ubbelohde.³ In the course of our catalytic work on a laboratory scale, however, it often became necessary to analyze such reaction products, available in very small quantity. Yields of liquid products of 12–14 cc. usually result from 100 liters of water gas in a gasoline synthesis with cobalt catalysts by the Fischer-Tropsch method.⁴ Small amounts of hydrocarbons are often produced in high pressure hydrogenations, and their behavior during distillation is of interest.

The distillation analysis of small quantities of material has been the subject of numerous researches, so a survey of the subject is unnecessary. The procedures of Gawalowski,⁵ Gross and Wright,⁶ and those of Pregl⁷ are microdistillation methods. In all of them the apparatus has been designed for the handling of small amounts of material. Berl and Althoff⁸ have designed such an apparatus, using a packed tower and a dephlegmator at a definite temperature; this apparatus works satisfactorily with 8–10 cc.

¹ Wa. Ostwald, *Glückauf*, **61**, 550 (1925).

² A. S. T. M. Ser. design, D. 86-27; Bureau of Mines, *Tech. Papers* 323, b. p. 49.

³ Ubbelohde, *Mitt. a. d. Materialprüf.-Amt. Berlin*, **25**, 261 (1907).

⁴ F. Fischer and H. Tropsch, *Ber.*, **59**, 830 (1926); literature by Fischer, *Brennstoff-Chemie*, **11**, 489 (1930).

⁵ Gawalowski, *Z. anal. Chem.*, **49**, 744 (1910).

⁶ P. Gross and A. H. Wright, *J. Ind. Eng. Chem.*, **13**, 701 (1921).

⁷ F. Pregl, "Die quantitative organische Mikroanalyse," Julius Springer, Berlin, 1930, p. 220.

⁸ E. Berl and F. W. Althoff, *Die Chem. Fabrik*, **3**, 220 (1930).

of liquid. Stock and his collaborators⁹ have worked with a closed system under high vacuum, distilling fractions of a volatile liquid or condensed gas into a cooled buret, and ascertaining the weight and homogeneity from the volume and the vapor pressure. Stock¹⁰ has also carried out determinations of vapor density by means of adjustments in the vacuum apparatus. The distillation analysis of gaseous hydrocarbon mixtures by Tropsch and Dittrich¹¹ is a further improvement of Stock's principle. In this process the hydrocarbon condensate is again evaporated and the gases are led through a series of vessels at successively lower temperatures. In the Podbielniak¹² process of fractional vacuum distillation, the temperature of the distillation flask and the dephlegmation column are regulated so that a higher pressure (usually 1 atm.) is maintained in these than in the receiver, where the vapor pressure of the condensate is measured. Wawrziniok and Lindner¹³ have devised a method for determining the saturation pressure of fuels, which depends on the temperature, and pointed out the relationship between saturation pressure and the behavior of the fuel in the engine, particularly as related to the preheating temperature. C. Conrad¹⁴ has carried out distillation analyses of liquid fuels on the basis of weight, with greater precision than in the process of Engler for gasolines or that of Krämer-Spilker for benzols.

We have tried to devise a simple method for ascertaining the behavior during distillation of liquid mixtures which are available only in small amounts. With this in mind we have chosen a method involving the determination of the vapor pressure, in which the behavior of the material during an Engler distillation may be calculated from the isobarometric temperature-distillate mass diagram. The mean molecular weight of various fractions may also be determined by this procedure. It is thus possible not only to observe the behavior during distillation, but also to determine the mean molecular weight of individual fractions.

Apparatus and Procedure

We have made use of Hüttig's tension eudiometer,¹⁵ an apparatus much used in inorganic chemistry, and will describe it briefly.

The apparatus is shown in Fig. 1. The sample to be analyzed is weighed into the bulb A, which is connected to the rest of the apparatus through the

⁹ A. Stock, *Ber.*, **47**, 154 (1914); **50**, 989 (1917); **51**, 983 (1918); **53**, 751 (1920); **54**, 142 (1921).

¹⁰ Stock and Massenez, *ibid.*, **45**, 3561 (1912); Stock, *ibid.*, **50**, 1003 (1917); Stock and Zeidler, *ibid.*, **54**, 534 (1921).

¹¹ H. Tropsch and E. Dittrich, *Brennstoff-Chemie*, **6**, 169 (1925).

¹² W. J. Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **3**, 177 (1931).

¹³ Wawrziniok and Lindner, *Automobiltech. Z.*, **34**, 653, 724 (1931).

¹⁴ Conrad, Lecture at the 44th General Meeting of the V. D. Ch., Vienna, 1931.

¹⁵ G. F. Hüttig, *Z. anorg. allgem. Chem.*, **114**, 162 (1920).

stopcock F and a ground joint. The large bulb B has a volume of about 1.5 liters and is carefully calibrated before it is sealed into the system; by means of it, the volume of all the apparatus may be ascertained. The large volume of vapor which it contains even at a pressure of 20 mm. also serves to render negligible the usual errors of weighing and operation. C is a mercury manometer while the stopcocks D and E serve to admit air and connect the system to the vacuum pump. Mercury cut-offs have been avoided, for simplification. Contamination from stopcock grease has been

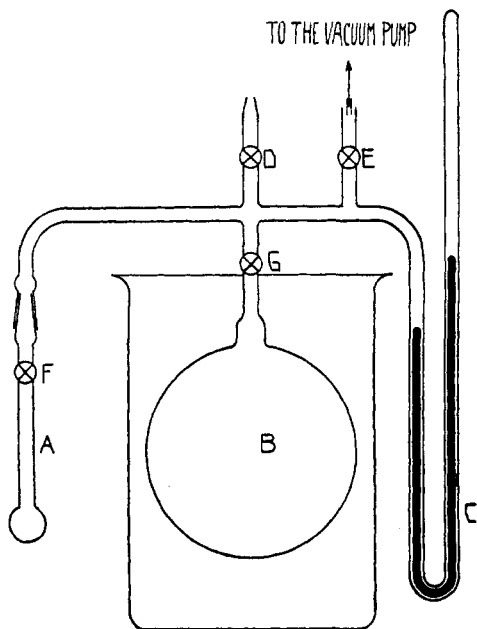


Fig. 1.

minimized by applying it only to the outer one-third of grindings.¹⁶ Sirupy phosphoric acid also has been used as a lubricant.

In carrying out an experiment, F is closed, the sample in A is cooled with liquid air and the rest of the apparatus is evacuated. Stopcock E is now closed, F is opened and closed and the system pumped out. This step is repeated, resulting finally in complete evacuation of the system with little or no loss of material from A. The part A is now weighed.

The vapor pressure determinations were carried out at a constant pressure of 20 mm., so the temperature varied from -22 to 18° . Constant temperatures were produced by the

use of liquid air in an aluminum block provided with a drilled hole for the bulb A of the apparatus. The block is placed in a Dewar vessel. As soon as the constant pressure, 20 mm., has been established (five to ten minutes), F is closed and A is detached and weighed. A is then again connected and the temperature raised until a pressure of 20 mm. is again established. The test portion of material usually amounted to 0.8 g. in the case of benzines, corresponding to 6–7 points on the temperature–distillate mass diagram. The method can be applied to small quantities of any substance by choosing a suitable constant pressure or adjusting the size of the flask B. In case the boiling point of the substance requires a temperature above that of the room, a lower pressure should be chosen.

¹⁶ Stähler, "Handbuch der Arbeitsmethoden i. d. anorg. Chem.," 1925, Vol. II, p. 887.

The determination of the mean molecular weight follows from the gas law, $pv = nRT$, in which n is the weight of gas divided by its molecular weight; the other quantities are all known by observation.

The work of Rogers and Brown¹⁷ indicates that hydrocarbon mixtures such as gasoline do not follow Raoult's law strictly, but deviate from it by 5–15%, depending on the composition. Our molecular weights, therefore, are not truly exact; they are, however, quite satisfactory as applied technically to hydrocarbon mixtures.

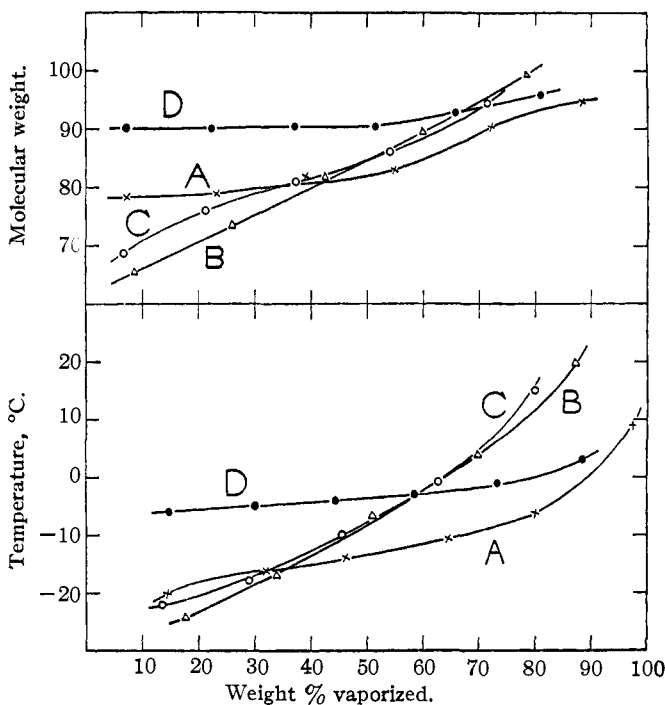


Fig. 2.

Experiments

In order to test the apparatus we made an experiment with chemically pure benzene and found a value, 77.73, which compares favorably with the theoretical value, 78. This result indicates that the apparatus and procedure are satisfactory for practical purposes.

Vapor pressure measurements have been carried out on four gasolines: a surgical gasoline (A), a light motor gasoline (B), a synthetic material (C) and normal gasoline (Kahlbaum) (D). The results are shown in Fig. 2, in which the percentage by weight is plotted on the abscissa and the temperature and mean molecular weight on the ordinate. It should be noted

¹⁷ M. C. Rogers and G. G. Brown, *Ind. Eng. Chem.*, **22**, 258 (1930).

that in the graphical presentation of the molecular weight, the middle points of the distances representing the separate fractions have been joined by a curve which agrees with the mean values of the molecular weights.

Measurements also have been carried out on three kinds of benzene: Motor benzol (E), a commercial benzol (F) and so-called pure benzene (G). The results are given in Fig. 3.

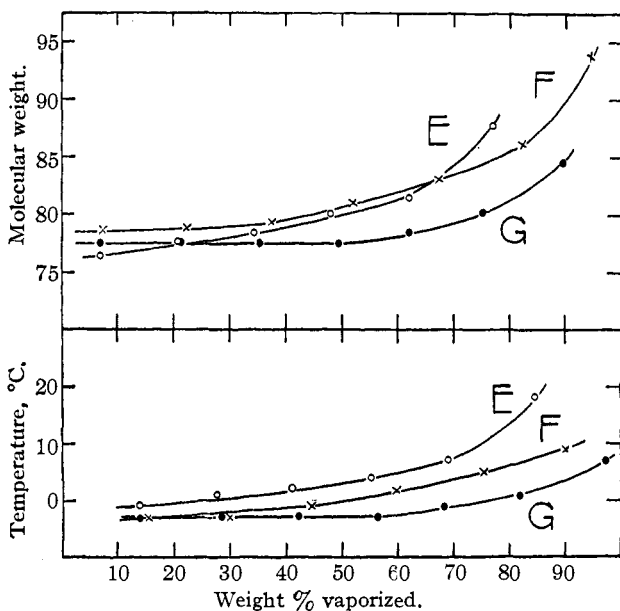


Fig. 3.

In addition, Dynalcol (H), a motor fuel used in Czechoslovakia, consisting of 30% gasoline, 20% benzene and 50% ethyl alcohol, as well as a mixture of 80% of acetone and 20% methyl alcohol (I) have been investigated, the results being shown in Fig. 4. This last mixture was chosen to demonstrate that our method is practicable for characterizing mixtures the components of which have no great difference in boiling point or specific gravity but a great difference in molecular weight.

On the assumption that there are no excessive differences between the specific gravity of the mixture being examined and of its components, we may calculate in a simple manner from the vapor pressure measurements the behavior of the material in a regular Engler distillation, and it will be shown subsequently that this behavior of various kinds of gasoline and benzene may be calculated accurately enough for technical purposes.

On the basis of the relationships formulated by Young and Krafft, Gary¹⁸ has prepared a nomogram for use in ascertaining the normal boiling

¹⁸ W. W. Gary, *Petroleum World Oil Age*, **26**, 115-152 (1929).

point from vacuum distillation. In our work the calculations were based on the following relationships. Using the approximation formula of Nernst for a pressure of 20 mm. corresponding to our isobarometric process,

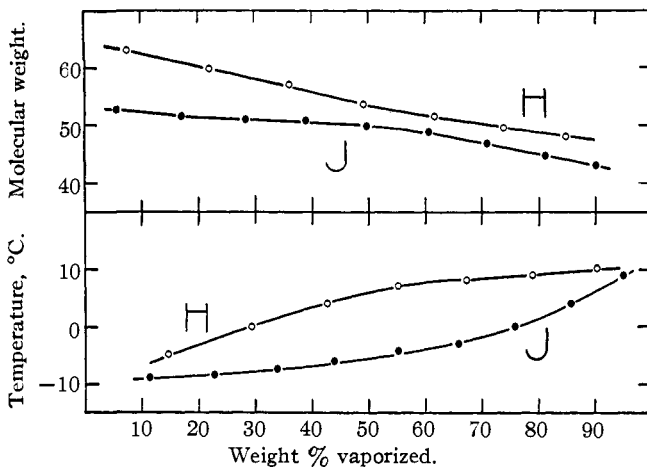


Fig. 4.

and for one atmosphere, according to the A. S. T. M. method, there are available the equations

$$\log \frac{20}{760} = -\frac{\lambda_0}{4.571T_1} + 1.75 \log T_1 + j'$$

$$\log 1 = -\frac{\lambda_0}{4.571T_2} + 1.75 \log T_2 + j'$$

in which λ_0 is the heat of evaporation, T_1 is the absolute temperature for the measurements at 20 mm., T_2 is the absolute temperature for the same numerical values of the mass of distillate in the A. S. T. M. method at 760 mm. (assuming that the specific gravities differ only by amounts comparable to the other experimental errors) and j' is the appropriate chemical constant.

By subtracting one equation from the other we obtain

$$\log \frac{760}{20} = 1.58 = \frac{\lambda_0}{4.571} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) + 1.75 \log \frac{T_2}{T_1}$$

The value of $1.75 \log (T_2/T_1)$ is 0.20 for gasolines and benzenes, which may be confirmed by comparing the vapor pressure measurements with the results of the A. S. T. M. method.¹⁹ We may therefore take this expression as a constant in the calculation and thus obtain the relation as obtained

$$1.38 = \frac{\lambda_0}{4.571} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\lambda_0 = 4.571T_1(1.75 \log T_1 + j' + 1.58)$$

from the Nernst formula. Substituting the numerical value of the chemi-

¹⁹ The deviations from this value amount at most to ≈ 0.01 .

cal constant j' , which amounts to 3 for benzene, and the mean value of $1.75 \log T_1$, which is 4.25, we obtain a simple relation for λ_0 , namely

$$\lambda_0 = 4.571T_1(4.25 + 3 + 1.58) = 4.571 \times 8.83 \times T_1$$

We have taken $1.75 \log T_1$ as equal to 4.25 for the reason that the measurements are made in the temperature range -22 to $+18^\circ$, so that $1.75 \log T_1$ lies between 4.20 and 4.31, the mean of which is 4.25.

$$1.38 = 8.83T_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right), \text{ and}$$

$$T_2 = 1.18T_1$$

We have not used this formula as a basis for our calculations; it shows clearly, however, that there is a direct proportionality between T_1 and T_2 . By comparing the results of our experiments, we derived the empirical formula $T_2 = 1.306T_1$, which we have used in our calculations.

TABLE I
CALCULATED AND OBSERVED VALUES

Vol., % of distillate	Temperature, °C.		Vol., % of distillate	Temperature, °C.	
	Calcd.	Found		Calcd.	Found
Surgical Gasoline (A)			Motor Benzol (E)		
25	60	60	25	83.1	84.3
50	65.9	66	50	87.4	87.2
75	73.7	75	75	97	95.5
Motor Gasoline (B)			85	107	106
25	56.7	59.5	Commercial Benzol (F)		
50	73.7	75	25	80.3	83
75	94	95	50	83.5	84.5
Synthetic Gasoline (C)			75	90	88
25	57.4	55.5	90	95.3	98
50	72.1	68			
75	95.3	91			
85	110.3	108			

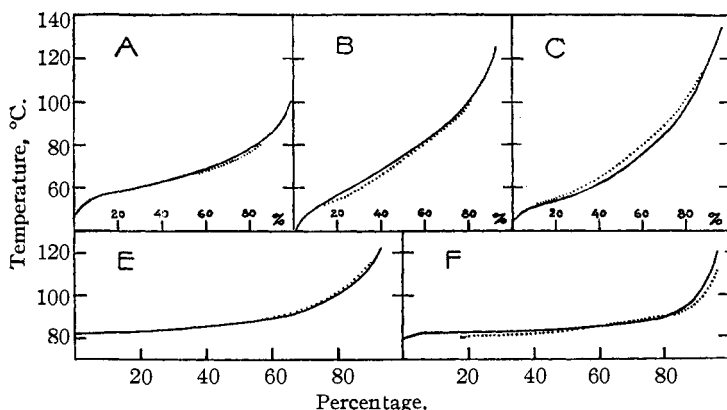


Fig. 5.——— Experimental, Calculated.

The values calculated in this way from the vapor pressure measurements, as well as those found in the normal distillation of gasoline according to the A. S. T. M. method and for benzenes by the method of Krämer-Spilker, are given in Table I and are shown in Fig. 5.

Comparison shows that the differences in specific gravity of the components of a mixture make possible a direct calculation from the vapor pressure measurements of the temperature in the A. S. T. M. method corresponding to the numerical volume percentages of the distillate, with an accuracy sufficient for technical purposes.

Summary

A method has been described for ascertaining the behavior of small quantities of material during distillation. In this method temperatures are measured in a tension eudiometer at 20 mm. From these measurements it is possible to calculate the behavior of a substance in a regular A. S. T. M. distillation or in one carried out by the Krämer-Spilker method. The mean molecular weight of the distillate fractions may be determined simultaneously in the tension eudiometer, which is a further valuable attribute in the characterization of liquid mixtures.

PRAGUE, CZECHOSLOVAKIA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF WASHINGTON]

PREPARATION OF CERTAIN REDUCTION PRODUCTS OF BENZOIN

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Theoretically benzoin can yield thirteen reduction products; all of these except the optically active phenylbenzylcarbinols are known. Isostilbene has not been prepared by the reduction of benzoin; we have prepared didesyl and isodidesyl by reduction of benzoin. All of the other compounds have been prepared from benzoin; however, most of them have usually been prepared either from one another or from other compounds.

Since benzoin is easily and cheaply prepared,¹ it seemed desirable to prepare from it certain of these reduction products. Superior yields and simple methods of preparation of stilbene, desoxybenzoin and β -desoxybenzoinpinacone were developed.

Stilbene.²—In a one-liter beaker or large evaporating dish are placed in order, 50 g. of mercuric chloride, 500 cc. of water and 200 g. of zinc dust, the last having been freed

¹ "Organic Syntheses," John Wiley and Sons, Inc., New York, 1921, Vol. I, p. 33.

² Hitherto stilbene has best been prepared by the Grignard reaction, involving the intermediate formation of benzylmagnesium bromide, phenylbenzylcarbinol and the acetate of the carbinol [Hell, *Ber.*, **37**, 453 (1904)]. The above-described method gives 50% yields in two to three hours by one operation. Variations of conditions and materials gave no larger yields, because, perhaps, only the *d*- or the *l*-form of benzoin is reduced.