tion of +1.3° C. This would be added to −42° C., making −40.7° C. the corrected 90 per cent point. This value would then be plotted against the 10 per cent point, using the graph shown in Figure 6.

Isobutane, in concentration up to 50 per cent of the butane fraction, was found to have no appreciable effect on the 90 per cent point over the range covered by Figure 6.

Applying the above correction for the propylene content, several typical analyses of stabilizer gases and stabilizer reflux are presented in Table II for comparison with the results by the fractionation method.

Since the results of this investigation have been satisfactory for the range covered, it is planned to extend the work with the view of developing graphs which will cover many types of refinery gases.

**Table II—Comparison of Short-Cut Method with Fractionation in Podbielniak Column**

| CONSTITUENT | RUN 1 | | RUN 2 | | RUN 3 | |
|---|---|---|---|---|---|---|
| | Pod. | Short cut | Pod. | Short cut | Pod. | Short cut |
| | % | % | % | % | % | % |
| Fixed gas and methane | 9.4 | 9.1 | 13.6 | 12.8 | 1.6 | 0.1 |
| Ethane | 23.8 | 23.8 | 21.1 | 21.6 | 13.5 | 13.2 |
| Propane | 63.5 | 64.1 | 62.0 | 62.5 | 84.2 | 85.7 |
| Butane | 3.3 | 3.0 | 3.3 | 3.1 | 0.7 | 1.0 |

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# Apparatus for Experimental Pyrolytic Production of Diphenyl[1]

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**An apparatus is described for the pyrolytic production of diphenyl from benzene, using a bath of molten lead. Trends of conversion efficiency, chemical efficiency, and rate of production are given for various sets of operating conditions with this apparatus. Pressures above atmospheric favor the conversion to diphenyl. The optimum temperature for the reaction is around 740° C.**

IT HAS been known for some time that diphenyl could be produced by the pyrolytic decomposition of benzene. Among the early workers in this field were Berthelot (*1*), Schmidt (*7*), and others (*4, 5, 6, 9*) who discovered that diphenyl could be prepared by passing benzene through a red-hot tube. There has been at Columbia University a continuing interest in this pyrolytic action since the first work here by Zanetti and Egloff (*10*). This background, and the recent commercial production of diphenyl, led the authors to seek an apparatus in which diphenyl could be produced continuously without the impedance to flow and the excessively high furnace temperatures which result when tar is deposited. The advantages of a constantly clean surface and of uniform heating possessed by a molten bath seemed desirable here (*2, 3, 8*). In the experiments reported in this paper, lead was used exclusively as the molten bath. The experiments were restricted to benzene, but the apparatus showed possibilities for use in the pyrolysis of other organic substances—for example, toluene, xylene, cymene—and also for the simultaneous interaction of these materials with gases such as chlorine, ammonia, sulfur dioxide, and hydrogen, using suitable baths.

### Description and Operation of Apparatus

The apparatus used by the authors is shown in Figures 1 and 2. Referring to Figure 1, *A* is the benzene reservoir; *B*, the preheating vaporizer; *C*, the reactor; *D*, the condensing system; and *E*, the gas meter. The liquid benzene contained in the reservoir *A*, which consists of a standard 3-inch pipe (7.6-cm.) fitted with caps and a graduated sight glass, is passed under pressure maintained by carbon dioxide from a cylinder, through the line *L* to the preheating vaporizer, *B*. The vaporizer is heated by a 12 × 1¹/₄ inch (30.48 × 4.17 cm.) electric resistance furnace. The hot benzene vapors continue up the line *L* and down the central downtake pipe which is surrounded by molten lead to a depth of 17 inches (43.18 cm.) contained in the reactor, *C*. The reactor consists of a ³/₄-inch (2.5-cm.) extra-heavy seamless steel tube fitted with heavy ammonia flanges and heated by a standard three-section electric resistance furnace. A helical baffle of iron wire wound around the central downtake pipe serves to break up the bubbles of benzene vapor issuing from the serrated orifice at the bottom of the downtake pipe. Preliminary experiments disclosed that the operation of such a helical baffle produced satisfactory subdivision of gas bubbles during their passage through the liquid heating medium. The mixed diphenyl and benzene vapors leave the reactor at the top through the offtake. The vapors are then conveyed through the lagged pipe to the condensing system, *D*, and the fixed gases then pass to the gas meter, *E*.

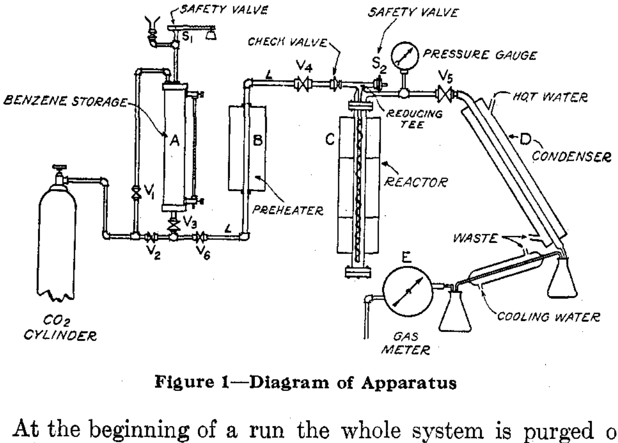

Figure 1—Diagram of Apparatus

At the beginning of a run the whole system is purged of air by means of a stream of carbon dioxide. By manipulating the valves $V_1$ and $V_2$, the carbon dioxide pressure is applied to the surface of the benzene in the reservoir. The rate of flow of the liquid benzene into the preheating vaporizer is

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[1] Received March 25, 1931.

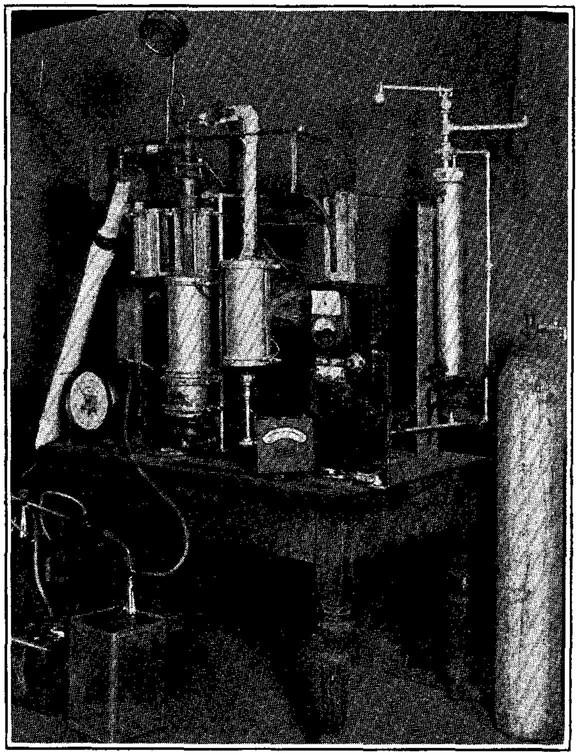

Figure 2—Apparatus Ready for Use

controlled by the valves $V_3$ and $V_6$. The temperature of the vaporizer is maintained at about 500° C. The safety valve $S_1$ relieves excess pressure in the reservoir. The rate of flow of benzene vapor is controlled by the valve $V_4$. The pyrometer junction for measuring the temperature of the reactor is shielded from the heating elements by asbestos. The safety valve $S_2$ relieves excess pressure in the reactor, and the outlet valve $V_5$ maintains the desired pressure in the reactor.

### Effect of Variables on Efficiency of Method

The apparatus was employed for making characteristic test runs for producing diphenyl by this pyrolytic method, and the curves reveal the behavior under five typical sets of operating conditions, and demonstrate the influence of temperature, pressure, and rate of flow. The effects of these variables on the conversion efficiency, the chemical efficiency, and the rate of production were studied with respect to the given conditions.

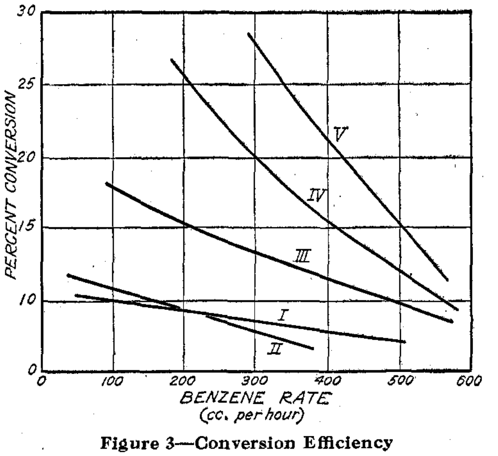

Figure 3—Conversion Efficiency

I—700° C., 1 atm. pressure
II—800° C., 1 atm. pressure
III—710° C., 100 lb./sq. in. gage pressure
IV—800° C., 50 lb./sq. in. gage pressure
V—740° C., 125 lb./sq. in. gage pressure

The conversion efficiency is the weight ratio of diphenyl to total benzene passed through the apparatus. The unconverted benzene is distilled off from the condensate for subsequent re-use. This conversion efficiency has been plotted against rates of flow for the several conditions in Figure 3. These curves indicate that the conversion of benzene into diphenyl decreases with increase in rate of flow, but that it does so less rapidly under atmospheric pressure than at elevated pressures. The conversion is increased at all rates of flow by increasing the pressure. The optimum temperature for the production of diphenyl appears to be about 740° C.

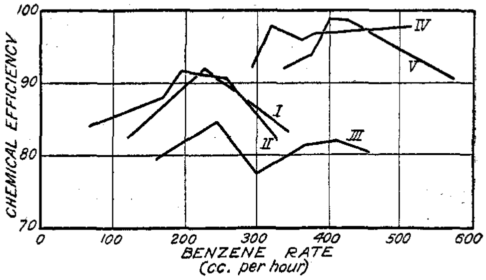

Figure 4—Chemical Efficiency

I—700° C., 1 atm. pressure
II—800° C., 1 atm. pressure
III—800° C., 50 lb./sq. in gage pressure
IV—710° C., 100 lb./sq. in. gage pressure
V—750° C., 125 lb./sq. in. gage pressure

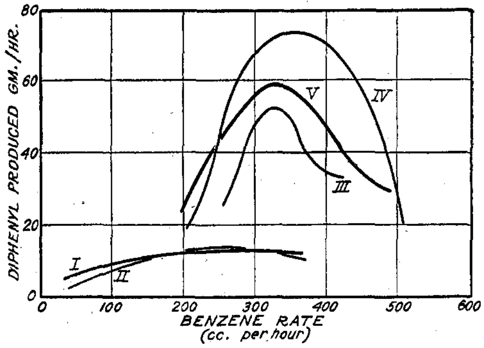

Figure 5—Rate of Production

I—700° C., 1 atm. pressure
II—800° C., 1 atm. pressure
III—710° C., 100 lb./sq. in. gage pressure
IV—800° C., 50 lb./sq. in. gage pressure
V—740° C., 125 lb./sq. in. gage pressure

The chemical efficiency is the weight ratio of diphenyl to unrecovered benzene. This figure is an index of the production of diphenyl rather than of other products. The actual values are dependent not alone upon the variables studied but upon the design of the apparatus. The chemical efficiency has been plotted against various rates of flow in Figure 4. These curves indicate that under atmospheric pressure, with moderate rates of benzene flow, chemical efficiencies in this apparatus reach maxima of 92 per cent, while with higher pressures and greater flow of liquid benzene, the maxima appear at about 98 per cent.

The rate of production is expressed in grams of diphenyl produced per hour, and is significant in determining the capacity of the apparatus. This has been plotted against various rates in Figure 5. These curves show that under atmospheric pressure and moderate rates of benzene flow, production rates of about 14 grams of diphenyl were obtained, whereas under higher pressures and somewhat greater rates of flow of liquid benzene, the production of diphenyl was about 50 to 75 grams of diphenyl per hour. It is to be noted in this connection that the volume of available space for reaction was 10 cubic inches (164 cc.) and the depth of lead 17 inches (43.2 cm.).

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# Irregularities in Sodium Determination by Sodium Sulfate Method[1]

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Over twenty years ago, Puckner and Hilpert (*1*) of this laboratory obtained reliable results for the sodium content of sodium diethyl barbiturate (barbital soluble U. S. P. X, known then under proprietary names of Veronal-Sodium and Medinal) by the well-known method of treatment with sulfuric acid—namely, a weighed quantity of the substance sodium diethyl barbiturate was moistened with sulfuric acid, evaporated cautiously to dryness, the charred residue ignited, and finally converted to sodium sulfate. These workers reported comparable results with two other similar methods: (1) precipitation of the barbituric acid derivative by means of diluted sulfuric acid, extraction with ether, subsequent evaporation of the acid aqueous fraction, igniting the residue, and weighing as sodium sulfate; (2) charring the substance, leaching the residue with diluted hydrochloric acid, filtering the mixture, evaporating the filtrate to dryness, and weighing as sodium chloride. In all methods examined, closely comparable results were obtained. Since then there has been occasion to reëxamine barbital soluble, and also to investigate several others of the proprietary barbital derivatives. In these investigations, whenever the product existed as a sodium salt and the sodium content was desired, the method of digestion with sulfuric acid, followed by careful evaporation and ignition, gave excellent results.

Recently, however, some irregularities have been noticed in the elaboration of standards for the identity, purity, and assay of the sodium salts of two of the isomeric amylethyl barbituric acid derivatives—namely, sodium ethylisoamyl barbiturate and two brands of sodium ethyl (*l*-methylbutyl) barbiturate, that have been introduced in medicine under various trade names. The names of the products were Sodium Amytal-Lilly, and Pentobarbital Sodium-Abbott (introduced as Nembutal) and Pentobarbital Sodium-Lilly (introduced as Sodium isoamytal). When determinations were made by the foregoing method on the preparation mentioned, the sodium content appeared to be low. These findings were communicated to the Abbott Laboratories and to Eli Lilly & Company. Both firms replied that when other methods were used, the sodium determinations were close to theoretical values. However, they did confirm the results obtained by the present investigator when using the direct "sulfate" method. Both firms, as well as this laboratory, did coöperative work on various methods. The author's results were as indicated in Table I.

The procedure for the method by extraction and sulfation shown in Table I is as follows: An accurately weighed quantity of the specimen was transferred to a suitable Erlenmeyer flask, dissolved in 50 cc. of water followed by the addition of 10 cc. of diluted hydrochloric acid, and extracted with nine successive portions of ether. The acidulated aqueous portion from the immiscible solvent extraction was transferred to a suitable tared platinum dish, carefully evaporated to dryness on the steam bath; subsequently the residue was moistened with an excess of sulfuric acid, heated cautiously on an electric heater while the fumes of sulfur trioxide were evolved, finally ignited, and weighed as sodium sulfate.

The direct sulfation method was carried out as follows: To a quantity of the specimen, accurately weighed, in a tared platinum dish are added 5 cc. of sulfuric acid, the mixture is evaporated cautiously to dryness, and the charred residue ignited. The foregoing procedure is repeated twice using 1 cc. of sulfuric acid, finally igniting, and weighing as sodium sulfate.

The procedure for the direct titration method is as follows: An accurately weighed quantity of the specimen in a 250-cc. glass-stoppered Erlenmeyer flask was dissolved in 50 cc. of previously boiled water (to remove any carbon dioxide present) and titrated with 0.1 *N* hydrochloric acid, using methyl red as an indicator.

**Table I—Determination of Sodium in Sodium Salts of Isomeric Amylethyl Barbituric Acid Derivatives by Various Methods[a]**

| Method | Sodium Amytal-Lilly | Pentobarbital-Sodium | |
|---|---|---|---|
| | | Nembutal | Sodium isoamytal |
| | % | % | % |
| Theory | 9.27 | 9.27 | 9.27 |
| Extraction and sulfation | 9.13 | 9.14 | 9.06 |
| | 9.08 | 9.08 | 9.08 |
| Direct sulfation | 8.46 | 8.74 | 8.66 |
| | 8.73 | 8.39 | 8.75 |
| | 8.38 | 8.44 | 8.38 |
| | 8.37 | 8.51 | |
| Direct titration | 9.14 | 9.06 | 9.03 |
| | 9.08 | 9.07 | 8.96 |
| | | 9.13 | 9.06 |
| | | 9.17 | |

[a] All figures calculated to dried basis.

The purpose of this paper is to point out the anomaly found in the three laboratories—namely, that the direct sulfate method gives low results in the presence of the five carbon side-chain derivatives of malonyl urea. The author is not prepared to state the exact explanation of this apparent irregularity, though there is a possibility that a portion of a sodium salt is carried over in the vapors containing isoamyl or methylbutyl compounds. It is interesting to note that after removal of the freed barbituric acid derivatives (acidification followed by an ether extraction), the sulfate method applied to the solution of the sodium salts gives accurate results, as do also titration methods.

*Note*—Since this article was submitted for publication, the author has noted that irregularities occur in the determination of sodium by the direct sulfate method on certain 3 and 4 carbon side-chain barbituric acid derivatives—namely, sodium ethylisopropyl barbiturate (Ipral sodium) and sodium *sec*-butylbromallyl barbiturate (Pernoston-sodium).

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[1] Received April 6, 1931.