Ferko [a] furnished some valuable information, particularly with regard to the direction of reactions. He passed the vapors of several hydrocarbons, either pure or mixed with ethylene gas, through an iron tube heated over a 40-cm. length in a gas furnace. The products were condensed and their composition studied. The more important of the results obtained by Ferko are summarized in Table 29 following.

TABLE 29.—*Summary of results obtained by Ferko in his experiments on the transformation obtained by passing various original hydrocarbons through a tube heated to "red heat."*

Original material.		Reaction products.								
Hydrocarbon.	Quantity.	Benzene.	Toluene.	Styrolene.	Ethylbenzene.	Dinaphthalene.	Diphenyl.	Naphthalene.	Phenanthrene.	Anthracene.
	Grams.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
Benzene and ethylene	1,320	6.0	0.0	1.3	0.0	0.0	22.7	0.0	0.8	1.1
Toluene	1,300	11.5	13.8	.5	.0	.0	2.1	3.0	1.1	1.0
Toluene and ethylene	1,300	15.4	12.3	.8	.0	.0	.0	.0	.0	1.5
Naphthalene and ethylene	900	.0	.0	.0	.0	13.3	.0	44.5	.1	.0
Ethyl-benzene	500	15.0	1.0	2.0	4.0	.0	.6	2.2	2.6	.4

The table shows that no reaction products were obtained that were not in the order of decrease of saturation or of molecular weight if the saturation remained unchanged. Thus benzene yielded no toluene nor any other compound of equal saturation and of greater molecular weight. Naphthalene yielded neither benzene nor toluene. From ethyl-benzene, however, it was possible to obtain toluene, benzene, and compounds of lower saturation. The work of Ferko seems to have been the most valuable of all hitherto done in this field, but it gives little attention to the influence of temperature and none to that of pressure.

Haber [b] studied the pyrogenic reactions of various substances, among them benzene, at temperatures ranging between 600° and 800° C. and 900° and 1,000° C. One of his observations is contrary to the results of the authors' experiments. He states that although benzene goes readily to diphenyl it does not form naphthalene.

McKee,[c] as a result of some qualitative experiments, has concluded that the order of hydrocarbon decomposition is as follows: Higher paraffins → lower paraffins → olefins → acetylenes → benzene and homologues → diphenyl → naphthalene, etc., → tarry matter → carbon and gas. In McKee's experiments benzene was passed through

[a] Ferko, Paul, Über einige pyrogéné Reactions: Ber. Deut. chem. Gesell., Jahrg. 20, Bd. 1, 1887, pp. 660–664.

[b] Haber, F., Theorie der pyrogen reactionen aliphatischer Kohlenwasserstoffe: Ber. Deut. chem. Gesell., Jahrg. 29, Bd. 3, 1896, pp. 2691–2700.

[c] McKee, G. W., On the decomposition of benzene at high temperatures: Jour. Soc. Chem. Ind., vol. 23, Apr. 30, 1904, pp. 403–404.

a hot copper tube and the degree of decomposition determined by the change in the specific gravity of the product. No analysis or separation of the product seems to have been attempted.

Smith and Lewcock [a] passed benzene through an iron tube, and at 800° C. obtained a 25 per cent yield of diphenyl. They were not, however, able to reverse the reaction, a condition that they attributed to experimental difficulties. They observed that the quantity of diphenyl produced increased with the rate of feed, indicating that diphenyl is not an equilibrium product, but simply an intermediate one.

EXPERIMENTS WITH PURE AROMATIC HYDROCARBONS AS STARTING MATERIAL.

In the experiments described in this report, cracking was produced in a system having a single (gaseous) phase. The characteristics and advantages of this method of procedure have already been discussed in detail.

Equilibrium relations for some of the reactions involved may be found in Table 4, which contains values figured according to the Nernst approximation formula.

The scheme of procedure followed in the experiments under consideration was, with slight exceptions, identical with that described for the other series. One modification in the making of the "run" is worthy of mention. In the earlier series of experiments pressures were built up in the cracking furnace by the decomposition of some of the oil used in the run. This method introduced a source of error, which, in the more recent experiments, it has been possible to eliminate. Before the beginning of each pressure run the system was connected with a compressor and with natural gas, which was pumped in until the gage gave the proper reading. The compressor was then shut off by closing a valve and the run started. Natural gas was used because it is largely methane, which is one of the end products of all cracking reactions.

For all the liquid hydrocarbons the original material was allowed to flow into the furnace at the rate of about 6 c.c. per minute. When the solid hydrocarbons naphthalene and anthracene were used as initial material it was, of course, necessary to keep them in a molten condition during the run by applying heat to the feed cup. Even then considerable experimental difficulty was involved and no attempt was made to obtain results of more than qualitative accuracy.

The supplementary determinations were made with quantities of recovered oil too small to permit separation of pure products. A single analytical distillation was made through an 8-inch Hempel

[a] Smith, Clarence, and Lewcock, William, Pyrogenic decomposition—Benzene: Jour. Chem. Soc., vol. 101, pt. 2, 1912, pp. 1453–1459.