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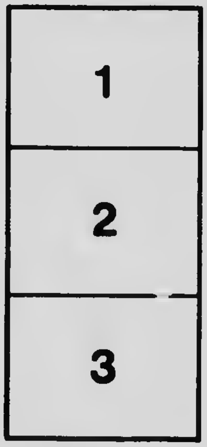
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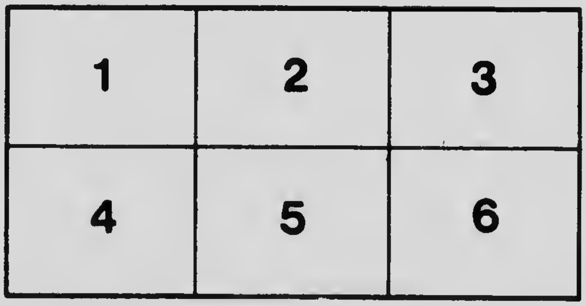
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UNIVERSITY OF TORONTO STUDIES

PAPERS FROM THE CHEMICAL LABORATORIES

No. 45: ON THE DECOMPOSITION OF BENZENE AT HIGH TEMPERATURES

BY G. W. McKEE

(REPRINTED FROM THE JOURNAL OF THE SOCIETY OF CHEMICAL INDUSTRY, VOL. XXIII.)

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ON THE DECOMPOSITION OF BENZENE AT HIGH TEMPERATURES.

BY G. W. McKEE.

In the manufacture of both coal gas and carburetted water-gas it is a matter of great practical importance that we should have a knowledge of the temperatures at which the various hydrocarbons decompose (especially those used for enriching purposes), and the extent to which the decomposition increases with increasing temperature. The most important among these reactions is the decomposition of benzene (C_6H_6). Suppose, for instance, we start with the gas oils which are higher normal paraffins, the pyrogenetic reactions are such as are indicated by the following:—Higher paraffins → lower paraffins → olefines → acetylenes → benzenes → diphenyl, &c. → naphthalene, &c. → tarry matter → carbon and hydrogen. The great value of benzene in increasing the illuminating value of gas is well known; and the nuisance that arises from the formation of solid substances like diphenyl and naphthalene, which stop up both pipes and machinery, is one of the greatest obstacles in the manufacture of coal gas.

The precise nature of the above reactions becomes then of practical importance, and the experiments carried out were undertaken to throw some light, if possible, on the transition temperatures of these substances. The apparatus used is shown in Fig. 1.

To heat the furnace F, the rheostat R and the furnace F were joined in parallel and connected with the street circuit. The switch S was also inserted to permit of complete control of the current from the working table. The furnace was heated by means of hot platinum resistance wires embedded in its fire-brick walls It was found con-

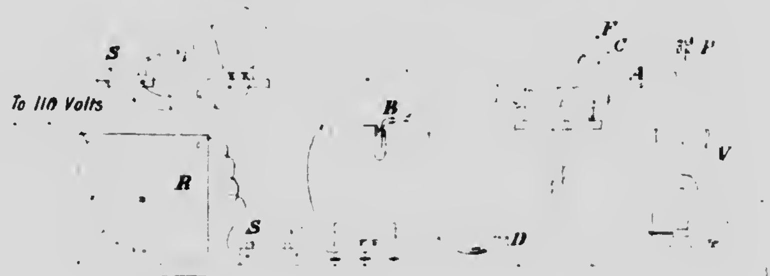

Fig. 1.

venient to surround it with $\frac{3}{4}$ in. asbestos millboard, pieces of which were readily cut without disturbing the edges, by placing it between pine boards and using a saw. In assembling these into a box the edges were preserved for nailing by securing the pieces in a vice. In front of the furnace was placed a piece of asbestos with three holes, which were punched by means of a sharpened brass tube against a hardwood block. Two of these were for the inlet and outlet of the copper tube which was to carry the benzol vapour, while the third was for the introduction of a thermo couple

The pyrometer used was a Le Chatelier made by Keiser and Schmidt, Berlin. A thermo-couple, of 50 cm. length, of platinum and platinum with 10 per cent. rhodium, was introduced into the furnace by means of a porcelain tube about $\frac{1}{2}$ in. in diameter and perforated by two holes, each about 1 mm. in diameter. To the thermo-couple were joined the copper wires in the porcelain dish D, which was kept at zero by means of melting ice. The copper wires were joined, as shown, to the pyrometer, which was provided with an auxiliary switch. The calibrations of the thermo-couple were plotted on section paper for interpolation purposes.

For vaporising the benzene the device shown at V in the right of the figure was used. An electric lamp was mounted on a block. On the same block was secured a piece of tin pipe about 4 ins. in diameter. A piece of $\frac{1}{4}$ in. asbestos was cut and rolled to fit the inside of the tin and thus prevent loss of heat by radiation. The benzene to be decomposed was placed in the pear-shaped funnel P. The stem of this funnel was so drawn out that the drops issuing from it would be very small; the supply was further capable of control by the tap on the stem of the funnel. In this way small drops of benzene were allowed to fall on the heated bottom of the flask, where they were at once vaporised and subsequently passed through the furnace, the rate being easily regulated by counting the drops.

About 6 ft. of seamless copper tubing, thin-walled, and about $\frac{1}{4}$ in. external diameter, the temper drawn by passing it slowly through a blow-pipe flame, were coiled around a prepared spool, so that a coil of about $1\frac{1}{2}$ ft. of it fitted nicely in the furnace, leaving an aperture between the coils sufficiently large to allow the tube which insulated the thermo-couple being passed through to the middle of the furnace. The ends of the copper tube passed through the holes shown in the asbestos pad which formed the door of the furnace, and were bent at right angles so as to terminate at A and B (see Fig. 1).

The distilling flask was selected so that its delivery tube fitted accurately into the copper tube at A, and the joint was further secured by means of suitable packing. The other end B, of the copper tube was provided with a short glass condenser 6 ins. in length, while an adapter of glass tubing was slipped over the end of the copper tube, and secured by means of a section of rubber tubing. The adapter passed through a stopper into a small glass vessel in which were caught the products of decomposition.

To determine whether the benzene had been decomposed or not, specific gravity determinations were made by means of a pyknometer. In all cases these were taken at 18° C., the variation of the specific gravity of benzene for a difference of one degree centigrade being very considerable.

	Per Cent.
Specific gravity of the benzol employed	0·88181
" of products after heating to 448° C.	0·88175
" " " 550° C.	0·88202
" " " 664° C.	0·88362
" " " 720° C.	0·88963
" " " 765° C.	0·90276

These results may be expressed graphically by the following curve :—

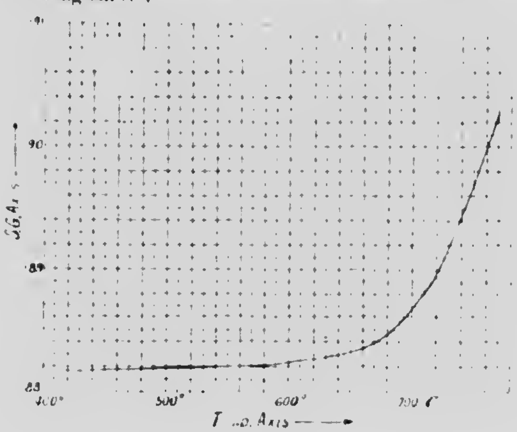

Fig. 2.

A second method of determining if decomposition had taken place was to slowly evaporate a portion of the product to dryness, and to examine the residue, if any, by the polarising microscope. The accompanying table shows the results obtained. The tube was further washed thoroughly with pure benzol, and a number of fractions taken from 514° to 550°, but it could not be said that the action became decidedly perceptible until after 550° had been passed. From that point onwards reference to the curve (Fig. 2) shows the extent to which the benzene vapours become decomposed as the temperature rises.

Quantity evaporated.	Temperature to which it had been subjected in passing through Tube.	Appearance when examined by Polarising Microscope.
c.c.	° C.	
20	Not heated	No crystalline structure.
10	494	" "
10	528	" "
5	550	Polarisation colours scarcely visible in residue.
5	562	Crystalline residue prominent. small crystals easily distinguished.

It would thus seem advisable, in adding enriching material to, say, a water-gas, to prevent the added material from being subjected to a temperature much greater than 700° C.

The author wishes to express his thanks to Prof. W R. Lang, of the University of Toronto, for the interest shown and the assistance rendered in this investigation.