KINETIC CONSIDERATIONS.

The cracking or decomposition of organic compounds by heat is generally explained on the basis of the occurrence of intermolecular collisions of such violence that the bonds holding together the various atoms or groups are ruptured. This kinetic theory seems to take account of all the phenomena of the reaction. The degree of cracking varies in the same direction as the temperature to which the substance is heated; that is, the higher the temperature the greater is the cracking. This is as would be expected when it is remembered that the velocity of molecular vibration, and consequently the violence of impact, increases with temperature.

Likewise it is known that, other factors being equal, cracking is more easily produced in compounds of large than of small molecular weight. If velocities of vibration are equal, then the large molecule has a larger momentum than the smaller, and at the instant of collision is subjected to a greater strain.

Molecular structure is another factor having an influence that can be largely predicted on the basis of kinetic considerations. Cyclic compounds are more stable than those of the straight-chain type, as would be expected in view of their greater compactness of structure. Likewise if a compound consists of a cyclic nucleus with an attached side chain, or of two cyclic nuclei united through a straight chain, the weak point is undoubtedly the chain. As indicated later, there is a general tendency for decomposition of petroleum up to a certain stage to result in the production of benzene, which is the simplest and most stable of the monocyclic hydrocarbons.

With the preceding considerations in view it is easy to understand the character of the cracking process as indicated by the information already at hand. It may be stated also that the indications obtained from the equilibrium constants, figured according to the Nernst equation (see Table 4), are entirely in accord with those just mentioned.

Some important indications may be obtained regarding relative degrees of formation of various aromatic hydrocarbons without considering the absolute conditions of cracking. Experience has indicated that large paraffin molecules are less stable than small ones, that paraffins are less stable than olefins, and that stability increases with decrease in saturation. It appears, therefore, that benzene formation requires a more strenuous reaction in the cracking process than does toluene formation, as toluene is in part aliphatic, owing to the presence of the methyl group that makes up the side chain. Likewise it appears that xylene, having two methyl groups, should show the same variation in stability as toluene but that it should always occur in about half the quantity of toluene. The probability

of its formation is half that of the formation of toluene and the probability of its decomposition twice as great.

The formation of naphthalene and anthracene seems to necessitate the decomposition of benzene nuclei. The formation of these polycyclic hydrocarbons should, therefore, be coincident with a decrease in the number of monocyclic molecules.

EXPERIMENTS WITH INTERAROMATIC REACTIONS.

Both scientifically and commercially the differences among the various aromatic hydrocarbons are of almost, if not quite, as great importance as the differences among classes. Two series of experiments were, therefore, conducted for the purpose of establishing facts concerning the influence of varying conditions of temperature and pressure on interaromatic reactions. In the first series four typical monocyclic hydrocarbons, cymene, xylene, toluene, and benzene, were subjected to cracking, each at three different temperatures, and at each temperature under four pressures. The solid polycyclic hydrocarbons, naphthalene and anthracene, were also cracked, but on account of experimental difficulties the results obtained were only qualitative. In the second series petroleum was employed as the original material. A radically different scheme of procedure was used, but the results agreed entirely with those of the first series.

A study of reaction products has furnished indications that may be generally summarized as follows:

The course of the reaction is in the direction of decrease in size of molecule when the degree of saturation is unchanged.

Reactions may occur in the direction of dehydrogenation either with increase or with decrease in size of molecule.

Practically no reverse reactions occur.

WORK OF OTHER INVESTIGATORS.

More or less work has been done by several previous investigators on the problem of thermal reactions of aromatic compounds, but no one has made a systematic study of such reactions. The information desired at present concerns the influence of conditions of temperature and pressure on quantitative and qualitative relations among end products and this is not adequately supplied by the literature. The following brief abstracts deal with experiments that seem most important in the present connection.

The classic researches of Bertholet [a] have furnished a foundation for the knowledge in this general field. His series of pyrogenic reactions is comprehensive and the results obtained are valuable, though not such as to meet the needs under consideration.

[a] Bertholet, M., Action de la chaleur sur quelques carburés d'hydrogène, Théorie des corps pyrogénés; Ann. chim. phys., ser. 4, t. 9, 1866, pp. 445–483; Des carburés pyrogénés, Ann. chim. phys., ser. 4, t. 12, 1867, pp. 5–96, t. 16, 1869, pp. 143–187.