EFFECT ON CRACKING REACTION OF HIGH CONCENTRATION OF END PRODUCTS.

The tendency mentioned above is promoted by a high concentration or increase in the density of the permanent gases that are retained in the sphere of reaction. Concentration of a given gas is a function of pressure, but the character of the concentration products exerts a material influence on the reaction products.

The relation between pressure and concentration can best be understood from the well-known thermodynamic relationship for any temperature in which—

$$\text{Pressure} \times \text{volume} = \text{constant}$$
$$\text{volume} = 1 \text{ divided by concentration.}$$

The thermodynamic relationship can be expressed by the equation

$$\text{Pressure} = \text{concentration} \times \text{constant},$$

from which it becomes evident that the concentration of end-product hydrogen and other permanent gases is directly proportional to the pressure exerted by such gases.

In the ordinary cracking processes some decomposition of the hydrocarbon material is necessary to produce hydrogen and other gases required to establish an equilibrium at the temperature of operation. The degree of this extreme decomposition might, of course, be limited by the addition of the necessary hydrogen and the other gases from extraneous sources. However, as free hydrogen is costly, such a procedure is commercially impracticable. Some investigators have sought to attain the same end by the decomposition of steam.

In the experiments resulting in the discovery of the process for the manufacture of gasoline, it was found that if oil is cracked in the presence of an excess of the hydrogen and other permanent gases produced by the process itself and retained in the zone of reaction, little of the hydrogen contained in the oil splits off in a free condition. In fact, when ethylene is sought, a considerable part of the added hydrogen enters into combination and produces more hydrocarbons than would otherwise be obtainable. The value of this feature lies in the fact that there is no necessity of generating new gaseous products at the expense of the more valuable substances. With more hydrogen present than is required by equilibrium conditions the natural tendency is for the hydrogen to combine. This feature constitutes one of the essentials of both processes. The general effect of changed concentration of one of the constituents in an equilbrium has been discussed by one of the authors.[a] The important bearing of the atmosphere in which the decomposition

[a] Rittman, W. F., Application of physical chemistry to industrial processes: Jour. Ind. and Eng Chem., vol. 6, August, 1914, p. 684.

of oil occurs has been noted by other experimenters. Hempel,[a] for example, found that when oil is cracked in an atmosphere of hydrogen none of the hydrogen is split off from the hydrocarbons, and a part of the admixed hydrogen actually combines for the formation and preservation of hydrocarbons. The result of experiments conducted by one of the authors[b] fully confirms this; furthermore the same principles have been successfully applied in gas manufacturing by the Joneses on the Pacific coast. Hempel also found that the greater part of the hydrogen admixed enters into combination to form saturated hydrocarbons when cracking is done under pressure. This fact likewise has been confirmed by one of the authors.

TEMPERATURE.

As organic substances generally decompose on application of heat, it is obvious that increase in temperature favors a high degree of decomposition. Heavy molecules are less stable than light ones of similar structure. For example, methane is stable at 400° C., whereas at that temperature a higher member of the same series, such as paraffin wax, undergoes considerable decomposition. Thus the selection of temperature in the processes under discussion depends on the character of the hydrocarbon materials to be treated, as decomposition of each group of hydrocarbons is most favored by a specific temperature. In this respect these processes have a material advantage, because there are no mechanical limitations regarding the character of hydrocarbons that may be employed as original material. Any petroleum product, from gasoline to the heaviest residuum, can be utilized for the production of low-boiling aromatic hydrocarbons or gasoline. Of course, in the production of gasoline, higher-boiling hydrocarbons than those commercially known as gasoline would be utilized, as there would be no object in cracking a natural gasoline, although such cracking would be possible.

RELATION OF TEMPERATURE TO PRESSURE.

Indications of the effect of temperature on cracking processes may be obtained from thermodynamics. According to a proposition put forward by Bertholet and Thomsen, "every chemical change gives rise to those substances that occasion the greatest development of heat." If this were true, the problem of obtaining temperature indications would be as simple as that of obtaining pressure indications for reactions proceeding to equilibrium.

To-day it is recognized that this statement is only a first approximation, because in all reactions one deals with the additional molecular

[a] Hempel, H., Über Gasöle und Ölgas: Jour. Gasbel, Jahrg. 53, Jan. 15, 1910, pp. 53-58.
[b] Whitaker, M. C., and Rittman, W. F., Thermal reactions in carbureting water gas: Jour. Ind. and Eng. Chem., vol. 6, 1914, pp. 383-392; Jour. Soc. Chem. Ind., vol. 33, July 15, 1914, p. 682.