Second. Much higher temperatures and pressures can be used than in liquid or liquid-vapor processes.

Third. The speed of reaction incident to high temperatures can be readily attained.

Fourth. Control conditions can be varied at will.

CHEMICAL FACTORS IN GASEOUS REACTIONS.

The chemical factors that influence equilibrium in any gaseous chemical reaction are as follows:

1. Temperature.
2. Pressure.
3. Concentration (mass action).
4. Duration.
5. Contact surface (catalysis).

EQUILIBRIUM.

True equilibrium is considered to be that state in which reactions proceed equally in each direction. Under constant pressure there is a definite proportion of the individual constituents for each temperature. Likewise for each pressure, under constant temperature, there is a definite proportion between the reacting hydrocarbons. This in spite of the fact that the numerical value of the equilibrium constant is a function only of temperature. Although the action of heat can impart the energy necessary to disturb an existing state of chemical inertia and induce reaction between the various molecular formations, too high temperatures for a period of time will defeat the end sought by permitting the hydrocarbon to decompose into coke and permanent gases.

It is well known that the tendency of substances to react depends on the nature of the substances and the distance of the system from stable equilibrium. This tendency is offset by chemical inertia, which decreases with increasing temperature. Also to be considered is the fact that increasing the temperature may bring the system farther from or nearer to the desired equilibrium point.

BEARING OF THEORETICAL EQUILIBRIUM RELATIONS ON INDUSTRIAL OPERATIONS.

Equilibrium values, therefore, are of high importance in industrial operations as they indicate the direction and magnitude of reactions. Knowledge that a given reaction will be attended by evolution, or absorption of heat, is of aid in determining operating conditions. No single equilibrium, however, can be considered by itself, as not only must a particular equilibrium relationship be satisfied, but all the constituents must also be in equilibrium. In other words, there

must be a symphony of equilibria between all the components of the system. The moment there is an unbalanced system of gases there is a tendency for an equilibrium to be established between all the components of that system. All the reactions that occur in a hydrocarbon process are interrelated and must all be taken into consideration, although a single reaction or set of reactions may be extremely important as indicating a prevailing tendency.

RESULTS OF CRACKING IN AN ATMOSPHERE OF ADMIXED GASES.

If petroleum is cracked in an atmosphere containing all the hydrocarbon gases with the exception of ethylene, one may expect that the only fixed gas produced in any quantity will be ethylene, at least until there is ethylene enough to satisfy equilibrium conditions between all the constituents present in the reaction chamber at the given temperature of operation. Advantage is taken of this fact in the processes described herein, as the fixed gases are retained in the reaction zone so that equilibrium conditions with respect to these gases are continuously satisfied without further decomposition for their formation.

In general, in the operation of the processes two classes of gases are formed—first, those that are readily condensable at temperatures above, say, 30° C., and second, those that remain uncondensed below 30° C., such as hydrogen, ethane, methane, and like hydrocarbon gases, which are herein termed fixed or permanent gases. If the condensable gases, so called, be continually withdrawn, and if oil, which is gasified, be constantly supplied, and if the permanent gases, or a considerable part thereof, be held in the sphere of reaction, there is a tendency for the equilibrium to be restored and for condensable hydrocarbons rather than noncondensable or permanent gases to be formed.

Thus it is not necessary to generate new gaseous end products at the expense of more valuable condensable hydrocarbons. The continuous removal of the condensable products from the cracking zone aids the establishing of equilibrium by the continual formation of these products. What is attempted is to have the reaction products approach a state of equilibrium with a constant removal of the liquid end products, so that the reaction will proceed continuously in the desired direction. Stated in another way, the addition of any of the end products in any decomposition process checks decomposition in that direction and causes it to proceed in another direction until equilibrium has been established. Continuous removal of the products of reaction from the reaction chamber is merely in obedience to the indications of the law of mass action and permits the reaction to proceed to approximate completion.