As previously stated, each equilibrium constant has a definite value for definite temperature, but the reaction that proceeds at one temperature may be reversed at another temperature. Although pressure does not change the value of the equilibrium constant at a given temperature, it does have a material effect on the yields obtainable and the character of the product. The relation of temperature to pressure in the processes herein outlined, however, is essentially different from their relationship in any two-phase system. As regards processes carried out entirely in the gaseous state, the temperature can be chosen that is most favorable for the maximum of conversion and the minimum of decomposition into undesirable end products, whereas that pressure is employed which experiment has determined to be most favorable in increasing yields and improving the character of the product. This judicious selection of a combination of most favorable temperature and pressure is possible only in a single-phase system, for the reason fully outlined in the discussion of the limitations of two-phase systems.

TEMPERATURES EMPLOYED IN BUREAU OF MINES PROCESSES.

Gaseous-phase processes have been operated by the authors at temperatures higher than 950° C. and lower than 400° C. At the high temperatures, as was to be expected, the products went entirely to carbon and hydrogen and other fixed gases. The lower temperatures gave such slight conversion that their use was demonstrated to be commercially impracticable on account of the time element.

Gasoline formation seems to begin at a temperature higher than 400° C., and to approach a maximum between 500° and 550° C.

As regards aromatic hydrocarbons, it appears that a maximum content is discovered in oils cracked at a temperature of 650° to 700° C. It appears, however, that greater yields, on the basis of original oil, may be obtained at lower temperatures, as the lower temperatures permit a larger recovery of cracked oil. For practical operation, a temperature of 625° to 675° C. has been found most desirable. The particular temperature chosen will depend largely on the aromatic hydrocarbon desired in greatest quantity, as the yield of any given aromatic compound can be increased or diminished by approaching or departing from the temperature most favorable for its formation. For example, the proportionate yields of benzene and toluene can be varied at will up to the maximum percentage for each.

The temperatures indicated are relative only, as it has been found that each oil has its own optimum conditions. The suitability of a given temperature is dependent also on the size of the reaction chamber and the rate of feed of oil into the chamber.

PRESSURE.

According to an application of the principle of Le Chatelier, pressure favors any reaction resulting in decrease of volume and opposes any reaction that is accompanied by an increase in volume. It appears possible, therefore, to obtain indications of the effect of pressure by the simple process of writing an equation and summing up the volume changes.

The effect of varying the pressure when a hydrocarbon mixture is to be cracked may be illustrated by considering the general reaction $A = 2B$, in which a condition of equilibrium exists when $K = \frac{(P_B)^2}{P_A}$ and $KP_A = (P_B)^2$. This equilibrium constant is identical with the one mentioned under the discussion of temperature, but deals with the partial pressures at equilibrium under different conditions of pressure. If the value of K be assumed as equal to 1, then, for partial pressures, when A equals 100, B equals 10, or when A equals 0.01, B equals 0.1. In the first instance the partial pressure A is 10 times as great as that of B. In the second instance the partial pressure of A is only one-tenth the partial pressure of B. In other words, simply by changing the total pressure on the system and keeping all other pressures constant the ratio of A to B for the pressure chosen has been divided by 100. It follows that, as previously indicated, diminished pressure increases decomposition, whereas increase of pressure decreases decomposition. As illustrative of the practical bearing of these facts, it has been demonstrated that diminished pressure favors the manufacture of gas, whereas the manufacture of gasoline from heavy hydrocarbons is favored by increased pressure.

On first thought this statement with respect to gasoline formation may appear to be an anomaly. One would expect to use vacuum in order to help pull the larger molecules apart; but in gasoline formation it is important to produce all the saturated molecules possible, and this involves a building up or saturating (hydrogenation) process. Temperature accomplishes the dissociating of the big molecules and pressure causes saturation (hydrogenation) of the lower boiling and more stable gasoline molecules. The possibility of using high pressures, irrespective of the temperature, constitutes one of the most important advantages of the processes under discussion.

LIMITATIONS AS TO USE OF PRESSURE.

The velocity with which the reaction occurs is an important factor in determining the yield of any product when the time is fixed. According to the law of mass action, reaction velocity is proportional to concentration,[a] and, in gaseous-phase reactions, concentration is

[a] The concentration of any substance in a gas mixture is proportional to its partial pressure and these terms are used interchangeably with suitable constants.