

and CO or CO<sub>2</sub>. Except at low pressures and high temperatures, the experimental evidence is that CO<sub>2</sub> is not present.

Thermodynamic data indicate that at moderate pressures paraffinic hydrocarbons can form below 350°C and olefins below 250°C by reactions between carbon dioxide and hydrogen; although the free energy changes of such reactions are much less negative than carbon monoxide-hydrogen reactions. The water-gas reaction ( $H_2 + CO_2 = CO + H_2O$ ) also is pertinent. Equilibrium constants for the water-gas reaction show that at temperatures below 800°C, equilibrium very much favors the formation of carbon dioxide and hydrogen.<sup>1</sup> The point is that CO<sub>2</sub> is thermodynamically stable with regard to both the water-gas reaction and, at the temperatures of the experiments, in regard to hydrogenation, but it is not found in the gas analyses except under the stated restricted conditions of low pressure and high temperature. For the experimental conditions investigated, therefore, a direct methanation of the calcite appears to be the plausible reaction.

The position that CO is not generally an intermediate product in the dissociation of calcite is not as defensible as the argument against CO<sub>2</sub>. The reaction of CO with H<sub>2</sub> forms the basis of the Fischer-Tropsch hydrocarbon synthesis. In this synthesis the best yields of hydrocarbons occur if the CO and H<sub>2</sub> are introduced in the ratio of 1:2 by volume at about 100 psi total pressure. The hydrocarbon yield rapidly decreases with increasing hydrogen content and increasing total pressure. Figure 2 shows that under most of our experimental conditions, the formation of the lighter hydrocarbons (C<sub>1</sub> to C<sub>4</sub>) by reaction between CO and H<sub>2</sub> is thermodynamically favorable. The initial reaction:  $H_2 + CaCO_3 = CO + Ca(OH)_2$  under standard conditions results in a substantial increase (+22.64 kcal/mole) in free energy. The subsequent reaction:  $CO + 3H_2 = CH_4 + H_2O$  yields a large decrease (-34.01 kcal/mole) in free energy. The sum of these two reactions, of course, equals the overall free energy change for the reaction:  $CaCO_3 + 4H_2 = CH_4 + Ca(OH)_2 + H_2O$  which yields methane directly.

Again, however, the best evidence that CO is not a general reaction product is found in the gas analyses. Under conditions of some of our experiments CO does occur in the presence of excess hydrogen. This is shown by the gas analyses of experiments 75 and 42 (Tables 1 and 3). However, CO is absent from all other gas analyses and it is reasonable to assume that it never was present in detectable quantities. These observa-

<sup>1</sup> The persistence of H<sub>2</sub>O and CO in some of the reaction gases below 800°C is another indication of disequilibrium, and is due to the slowness of the subsequent water-gas reaction.

tions, therefore, also appear to support the view that the reaction is a direct methanation rather than hydrogenation.

The kinetics of the thermal dissociation of calcite and dolomite, has received considerable attention. It has been proposed that the diffusion of H<sub>2</sub> through the sample is the rate-determining step (Zadwadowski and Bretsznajer, 1932; Britton, *et al.*, 1958). The heat to and within the sample has been shown to be the rate-determining step. More recently a rate expression for the dissociation of CO<sub>2</sub> pressures and a temperature dependence has been proposed (*et al.*, 1958).

Although the calcite-hydrogenation reaction appears to be a direct methanation at temperatures well below the dissociation temperature, the reaction kinetics describing the calcite dissociation are not in agreement with the kinetics for the thermal dissociation of calcite. The calcite dissociation appears to simulate a vacuum dissociation.

The determination of any reaction order from a plot of concentration versus time does not accurately reflect the kinetics of the reaction:  $CH_4 = C + 2H_2$ . The weight of the solid is an appropriate concentration measure. Because equal amounts of calcite were used for each run, the weight percent of the solid converted into conventional units is a constant. It is sufficient to use the weight percent of the solid in the experimental conditions weight percent concentration in the solid.

An unusual form of the concentration versus time reaction is first order because the reaction is independent of the initial concentration. The concentration is initially very large and the change in the hydrogen concentration is small. During the experiments, the hydrogen concentration is nearly constant, and because the reaction is first order, it is pseudo-first order<sup>1</sup> and successive half-lives are constant.

A plot of the rate constants versus

<sup>1</sup> A second-order reaction in terms of concentration of a reactant in a given time interval with initial concentrations. If  $b$  represents the initial concentration of hydrogen reaction at 605°C and 2000 psi, the relation between 2 and 16 hours is 0.998 to 0.999. The relation of a first order reaction is  $\ln(a-x) = kt$ .