

and CO or CO₂. Except at low pressures and high temperatures, the experimental evidence is that CO₂ 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.¹ The point is that CO₂ 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 CO₂. The reaction of CO with H₂ forms the basis of the Fischer-Tropsch hydrocarbon synthesis. In this synthesis the best yields of hydrocarbons occur if the CO and H₂ 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 (C₁ to C₄) by reaction between CO and H₂ 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-

¹ The persistence of H₂O 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 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 H₂ through the sample is the rate-determining step (Zadwadowski and Bretsznajer, 1932; Britton, *et al.*, 1958). The heat to and within the sample has also been considered as a rate-determining step. More recently a rate expression for the dissociation of calcite at low CO₂ pressures and a temperature range of 400-600°C has been proposed (*et al.*, 1958).

Although the calcite-hydrogen reaction has been studied at temperatures well below 400°C, the reaction kinetics describing the calcite dissociation in the presence of hydrogen appears to simulate a vacuum dissociation.

The determination of any rate law for the dissociation of calcite as a function of concentration as a function of time does not accurately reflect the reaction: $CH_4 = C + 2H_2$. The weight of calcite in the solid is an appropriate concentration. Because equal amounts of calcite were used for each run, the weight of calcite converted into conventional units is a constant. It is sufficient to use the initial concentration in the solid.

An unusual form of the concentration-time relation is first order because the rate of reaction is independent of the initial concentration. The initial concentration is initially very large and the change in the hydrogen concentration is small. During the experiments, therefore, the concentration is nearly constant, and because the reaction is pseudo-first order¹ and successive runs are made at the same temperature.

A plot of the rate constants

¹ A second-order reaction in terms of the concentration of a reactant in a given time interval. If b represents the initial concentration of a reactant in a given time interval, the rate of a hydrogen reaction at 605°C and 200 psi between 2 and 16 hours is 0.998 to 1.000. If a represents the initial concentration of a reactant in a given time interval, the relation of a first order reaction is $k(a-x)$.