



FIG. 5. In the calcite-hydrogen system, plot of mole % CH<sub>4</sub> generated and residual CO<sub>2</sub> remaining as calcite in experiments run for 2 hours; 2000 psi (H<sub>2</sub>); at 535, 605, 735, 790, and 870°C.

Analysis of the reaction gases shows that the reaction compounds are restricted in number even though a large population of compounds are possible in the C-H-O system. The gases present are the following: CH<sub>4</sub>; C<sub>2</sub>H<sub>6</sub>; H<sub>2</sub>O; CO; and CO<sub>2</sub>. The latter two appeared in only one experiment (no. 75). This experiment was unique in that the original hydrogen pressure was only 200 psi.<sup>1</sup> The appearance of CO and CO<sub>2</sub> at low pressures may be explained, at least in part, through thermodynamic calculations for a simplified C-H-O gaseous system (French, 1966). These calculations show that decreasing pressure favors the formation of CO<sub>2</sub> and water relative to methane and are in agreement with our experimental findings.

It appears that methane and, if within the stability field, homologues of methane, form directly rather than from reactions between hydrogen

<sup>1</sup> Fugacities vary with pressure, consequently the proportion of each substance present in the equilibrium will also vary with pressure.

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 ( $\text{H}_2 + \text{CO}_2 = \text{CO} + \text{H}_2\text{O}$ ) 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:  $\text{H}_2 + \text{CaCO}_3 = \text{CO} + \text{Ca(OH)}_2$  under standard conditions results in a substantial increase (+22.64 kcal/mole) in free energy. The subsequent reaction:  $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$  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:  $\text{CaCO}_3 + 4\text{H}_2 = \text{CH}_4 + \text{Ca(OH)}_2 + \text{H}_2\text{O}$  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.