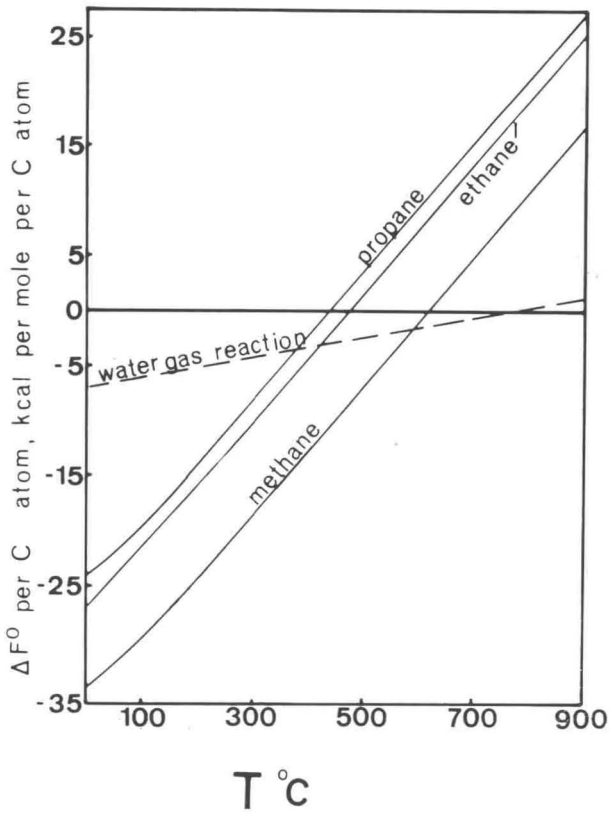

FIG. 2. Standard-state free energies of formation of methane, ethane, and propane by reactions of the type: $(2n+1)H_2+nCO=C_nH_{2n+2}+nH_2O$; and the free-energy variation of the water-gas reaction (data after Rossini *et al.*, 1947).

experiment was run to investigate the effect of high pressures. A calcite cleavage rhomb showed no discernible alteration after being held at 228°C under 80,000 psi hydrogen pressure for 23 hours.

The mass spectrographic analyses were done by Drs. Richard and Patricia Crawford, Chemistry Department, University of California, Lawrence Radiation Laboratory, on a Consolidated Electrodynamics Corporation model 21-103C analytical mass spectrometer. The analytical sensitivity is 0.01% by volume. Samples with simple compositions were compared with known patterns using a step-wise regression program, and more complex compositions were interpreted using the computer step-wise regression program of D. D. Tunnicliff and P. A. Wadsworth at Shell Development Co.

All of the starting carbonates were minerals. The calcite was optical grade obtained from Ward's. The dolomite was also from Ward's. The siderite was donated by Dr. Dennis Radcliffe. All starting minerals were examined optically, hand picked for impurities, crushed, and heated in 30 percent hydrogen peroxide.

Calcite-Hydrogen

In the calcite-hydrogen system using calcite fragments of 40 to 60 mesh, between 535–870°C, and 200–8000 psi of initial hydrogen, the following compounds were observed: solid CaO; Ca $(OH)_2$; graphite; and carbon "soot." Gaseous CH_4; C_2H_6; CO; CO_2; and H_2O also formed.

The experimental results are summarized in Table 1 and plotted in Figures 3, 4, and 5. The weight percent CO_2 in the remaining solid and the mole percent CH_4 formed are plotted against the duration of the run in hours at 2000 psi (P_{H_2}).

Below its dissociation temperature $Ca(OH)_2$ is the stable solid reaction phase. In runs allowed to cool to room temperature under the reaction gases, $Ca(OH)_2$ is always present. In experiments run above the dissociation temperature of $Ca(OH)_2$, CaO is present if the reaction gases are replaced with helium at the operating temperature. Analyses of the reaction gases indicate that water is the oxygenated product. Simplified equations for the reactions are the following:

$$\text{(A)} \quad CaCO_3 + 4H_2 = CaO + CH_4 + 2H_2O$$

$$\text{(B)} \quad CaCO_3 + 4H_2 = Ca(OH)_2 + CH_4 + H_2O$$

The change in free energy for reaction B is negative below approximately 325°C; whereas for reaction A it is positive. However, the free en-

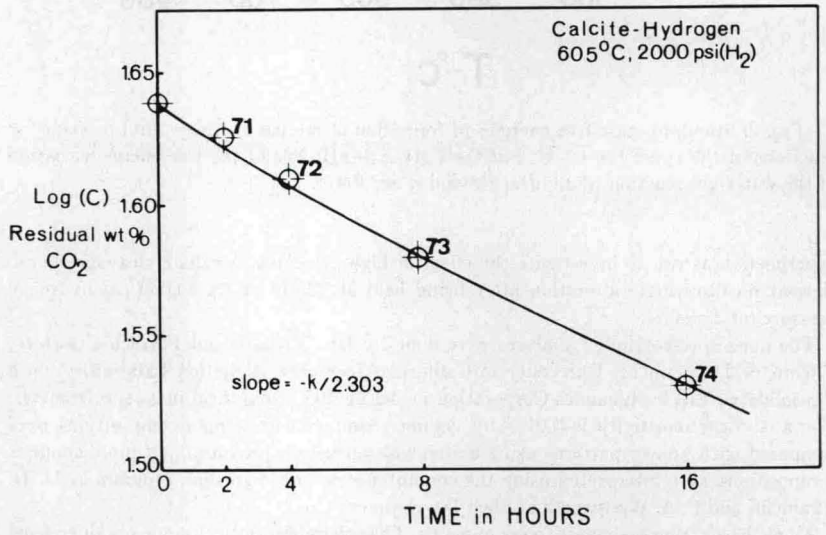

FIG. 3. Linear plot of log C against time for calcite-hydrogen data from experiments 71, 72, 73, and 74; run at 605°C, 2000 psi (H_2) illustrating the pseudo-first-order nature of the reaction.