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-

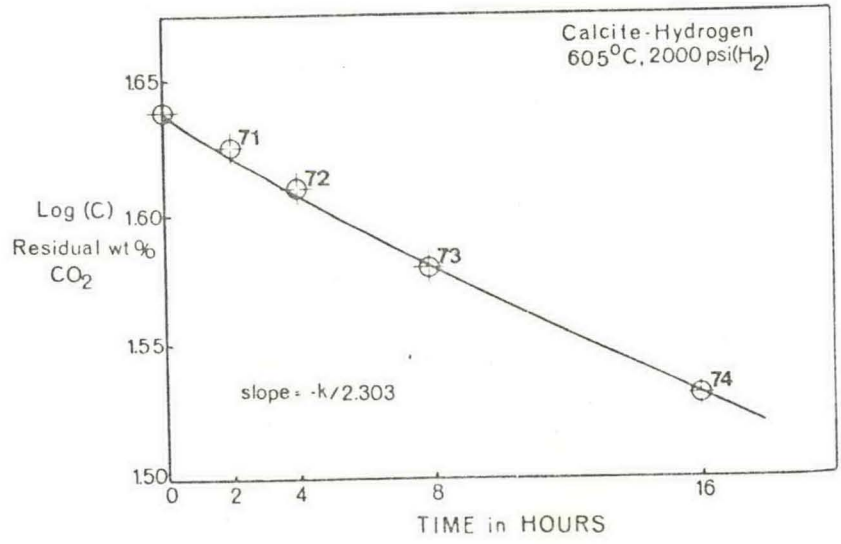

FIG. 3. Linear plot of log C against time for calcite-hydrogen data from experiments 71, 72, 73, and 74; run at 605°C, 2000 psi (H_2) illustrating the pseudo-first-order nature of the reaction.

TABLE 1. MASS SPECTROGRAPHIC ANALYSES OF REACTION GASES[a,b,c] AND WET-CHEMICAL ANALYSES OF RESIDUAL CO_2 IN UNREACTED CALCITE: CALCITE-HYDROGEN SYSTEM

Experiment No.	70	71	72	73	74	75	77	78	79	80	81	82	90	91	92	93
Temperature (°C)	535	605	605	605	605	700	700	700	700	700	870	650	610	735	713	700
Pressure (psi)	2000	2000	2000	2000	2000	200	2000	8000	2000	2000	2000	2000	2000	2000	400	4000