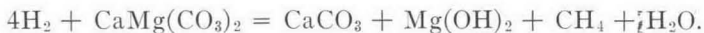


FIG. 9. Plot of mole % CH<sub>4</sub> generated and residual wt % CO<sub>2</sub> in the solid for the dolomite-hydrogen system at 5000 psi (H<sub>2</sub>); 4 hour experiments; at temperatures of 525, 550, 620, and 735°C.



At 5000 psi (H<sub>2</sub>) reaction initiates as low as 520°C (Table 4). Calcite formed from dolomite persists at higher temperatures than does calcite alone in the calcite-hydrogen system. Similarities exist between the thermal dissociation of carbonates and the reaction of carbonates with hydrogen. In the dolomite-hydrogen system CH<sub>4</sub> may influence the reaction in a manner similar to CO<sub>2</sub> in the thermal decomposition of calcite. This possibility will be explored in future studies.

Mg(OH)<sub>2</sub> or MgO formed in the first stage is non-crystalline to X-rays. Chemical analyses by atomic absorption indicates 17% MgO in the solid reaction products.

A very minor amount of black lustrous material is present in the reaction products. It is similar in all appearances to the graphite formed in the calcite experiments. "Soot-like" material also was present in the bomb, and again was particularly noticeable at higher temperatures.

The reaction gases were those also present in the calcite experiments. (Table 4). Carbon dioxide appears in two experiments (nos. 83, 84) but

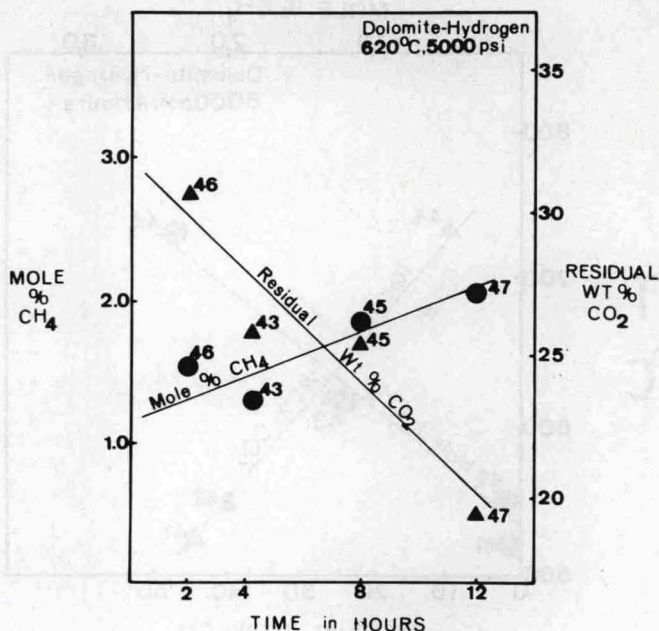


FIG. 10. Plot of mole % CH<sub>4</sub> generated and the residual wt % CH<sub>2</sub> in the solid for the dolomite-hydrogen system at 620°C; 5000 psi (H<sub>2</sub>); for 2, 4, 8, and 12 hour experiments.

only in very small amounts. Both of these experiments were run at a lower pressure of 2000 psi. The discussion on the reaction gases for the calcite-hydrogen experiments applies also to the dolomite-hydrogen system.

The kinetics of the dolomite-hydrogen system are considerably more complex than in the calcite-hydrogen system. An evaluation of the rate constant for each successive concentration-reaction time pair at 620°C assuming the reaction is first, second or third order, shows wide scatter, and no trend for the rate constant. The wide divergence from linearity is illustrated by a plot of the Arrhenius equation for a plot of the six temperature-concentration pairs. An interpretation of kinetic data into physical terms for this system is not realistic with the limited data available.

#### SIDERITE AND H<sub>2</sub>

The reaction between one-half gram of 40 to 60 mesh siderite fragments and hydrogen is more complex than the preceding calcite-hydrogen and dolomite hydrogen reactions. It is also the least studied with only four experiments. These four runs were between 400 to 605°C and 2000 to 5000 psi (H<sub>2</sub>), all for 4 hours. A "thermal soak" under helium was used in