

that the six sides of a cleavage rhombohedron of calcite always showed the same figures and solubility rates, whereas dolomite showed unlike solubility of the rhombohedral cleavage faces. The crystallographic orientation of the unequal reaction rims, as determined optically on the remaining calcite core of our specimens, shows that the  $c$  axis does not pass through the intersection of the three similarly reacted faces. The crystallographic anisotropy of the reaction implies more than a loss of the symmetry center.

#### DOLOMITE AND HYDROGEN

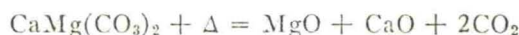
Dolomite and hydrogen were reacted under the following conditions: (1) fragment size 40–60 mesh; (2) 520°C to 835°C; (3) 2000 to 5000 psi initial hydrogen pressure; and (4) experiments lasting between 2 and 12 hours. Solid reactants observed include:  $\text{CaCO}_3$  (calcite);  $\text{Ca}(\text{OH})_2$ ;  $\text{CaO}$ ; non-crystalline  $\text{Mg}(\text{OH})_2$ ; elemental carbon or graphite, and "soot". Gas analyses show:  $\text{CH}_4$ ;  $\text{C}_2\text{H}_6$ ;  $\text{CO}$ ; and  $\text{CO}_2$ . Water is the oxygenated product from all of the experiments.

The experimental results are summarized in Table 4 and plotted in Figures 9 and 10. The weight percent  $\text{CO}_2$  remaining in the solid and the mole percent  $\text{CH}_4$  formed are again plotted against time at 5000 psi for 620°C, and against temperature at 5000 psi for 4-hour runs.

In the thermal dissociation of dolomite under the vapor pressure of the system, the reaction occurs in two stages. The first dissociation, stoichiometrically simplified, is given as follows:



With increasing temperature, the remaining calcite decomposes to lime and carbon dioxide with the exact dissociation temperature determined by the carbon dioxide pressure. If the  $P_{\text{CO}_2}$  never exceeds 100 mm, dolomite decomposes in a single stage dissociation as follows:



In the dolomite-hydrogen reaction  $\text{CO}_2$  is not a reaction product under most of the experimental conditions and appears only as a minor component of the reaction gases at lower hydrogen pressures (Table 4). It likely is incidental to the main reaction of direct methanation. The basis for this statement is found in the dolomite-hydrogen gas analyses and the reasoning previously used in discussing the calcite-hydrogen system.

The dolomite-hydrogen reaction occurs in two steps. The first stage is represented by the following equation:

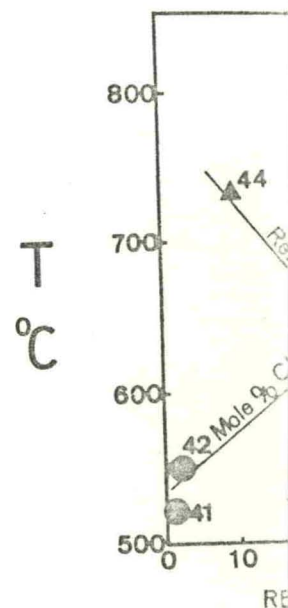


Fig. 9. Plot of mole %  $\text{CH}_4$  generated versus reaction time for a dolomite-hydrogen system at 5000 psi (11.6 MPa) for 4-hour runs at 620, and 735°C.



At 5000 psi ( $\text{H}_2$ ) reaction initiated from dolomite persists alone in the calcite-hydrogen thermal dissociation of carbon dioxide and hydrogen. In the dolomite-hydrogen reaction in a manner similar to calcite. This possibility will be discussed later.

$\text{Mg}(\text{OH})_2$  or  $\text{MgO}$  formed in the reaction products. Chemical analyses by atomic absorption spectroscopy of the reaction products.

A very minor amount of carbon dioxide was observed in the reaction products. It is similar to the calcite experiments. "Soot" was observed in the bomb, and again was part of the reaction products.

The reaction gases were analyzed (Table 4). Carbon dioxide was