

FIG. 4. Plot of mole % CH₄ generated in the calcite-hydrogen system and residual CO₂ remaining as calcite in experiments run at 605°C; 2000 psi (H₂); for 2, 4, 8, and 16 hours.

ergy change for reaction A is less sensitive to increasing temperature and at about 540°C reaction A is thermodynamically favored over reaction B.

Graphite is present mainly along calcium hydroxide surfaces, with lesser amounts occurring within the calcium hydroxide. At runs at higher temperatures (>700°C) a "soot-like" material formed in the bomb. It was readily wiped clean from the sides of the bomb. Only rarely was this "soot-like" material ever associated with the solids within the platinum cassette. Examination of the analytical data (Table I) reveals that at higher temperatures (experiment 81) there is a much larger weight loss of carbon as CO₂ in the solid than can be accounted for as carbon in the generated CH₄. This discrepancy is beyond analytical error. The "soot-like" material appears to be amorphous carbon formed through the thermal dissociation of methane, and higher hydrocarbons if they formed. Any higher hydrocarbons formed by pyrolysis of the methane would be unstable and none were found in the gas analysis. Carbon and hydrogen are the end products of methane pyrolysis, but equilibrium is difficult to attain. Catalysis can hasten equilibrium. The dissociation of methane is catalytically promoted by platinum, iron, nickel, all of which are present in these experiments.

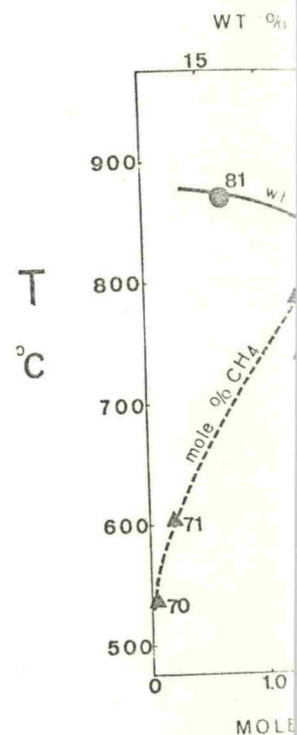


FIG. 5. In the calcite-hydrogen system CO₂ remaining as calcite in experiments run at 790 and 870°C.

Analysis of the reaction gases is restricted in number even though possible in the C-H-O system. The products are CH₄, H₂, H₂O, CO, and CO₂. The last experiment (no. 75). This experiment was run at a pressure of only 200 psi.¹ The results may be explained, at least in part, by calculations for a simplified C-H-O gas system. Calculations show that decreasing pressure favors the formation of water relative to methane and other products.

It appears that methane and hydrogen, rather than carbon and hydrogen, form directly rather than through the dissociation of methane.

¹ Fugacities vary with pressure, composition, and temperature. In the equilibrium will also vary with pressure.