

TABLE 1. MASS SPECTROGRAPHIC ANALYSES OF REACTION GASES^{a,b,c} AND WET-CHEMICAL ANALYSES OF RESIDUAL CO₂ 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	790	870	650	610	735	713	700
Pressure (psi)	2000	2000	2000	2000	2000	200	2000	8000	2000	2000	2000	2000	2600	2000	400	4000
Wt. % CO remaining in solid	43.0	42.0	41.0	39.3	34.2	41.2	26.8	36.0	33.4	34.5	16.3	36.9	N.A. ^d	37.8	N.A. ^d	N.A. ^d
Duration of run (hours)	2	2	4	8	16	2	8	2	4	2	2	4	12.5	2	2	2
Mole % CH ₄ in gas	0.02	0.17	0.28	0.53	1.38	1.83	2.67	0.37	1.34	1.43	1.95	0.89	1.64	1.39	2.37	0.99
Mole % C ₂ H ₆ in gas	—	—	—	—	—	—	—	—	—	—	—	—	0.01	—	—	—
Mole % CO in gas	—	—	—	—	—	1.10	—	—	—	—	—	—	—	—	0.31	—
Mole % CO ₂ in gas	—	—	—	—	—	0.11	—	—	—	—	—	—	—	—	0.04	—
Mole % H ₂ in gas	99.6	99.8	99.7	99.4	99.5	96.2	97.2	99.6	98.6	98.3	98.0	99.0	98.1	98.6	97.2	99.0
Mole % He in gas	0.40	0.08	0.04	0.07	0.09	0.75	0.11	0.02	0.07	0.23	0.06	0.10	0.24	—	0.11	20.01

^a Analysis calculated on water free basis.

^b Starting hydrogen impurities given as follows: less than 5 ppm N₂, less than 1 ppm O₂, less than 1/2 ppm CO₂, less than 1/2 ppm CO₂, Dew Point—100°F.

^c Detection limit 0.01%.

^d Not analyzed.

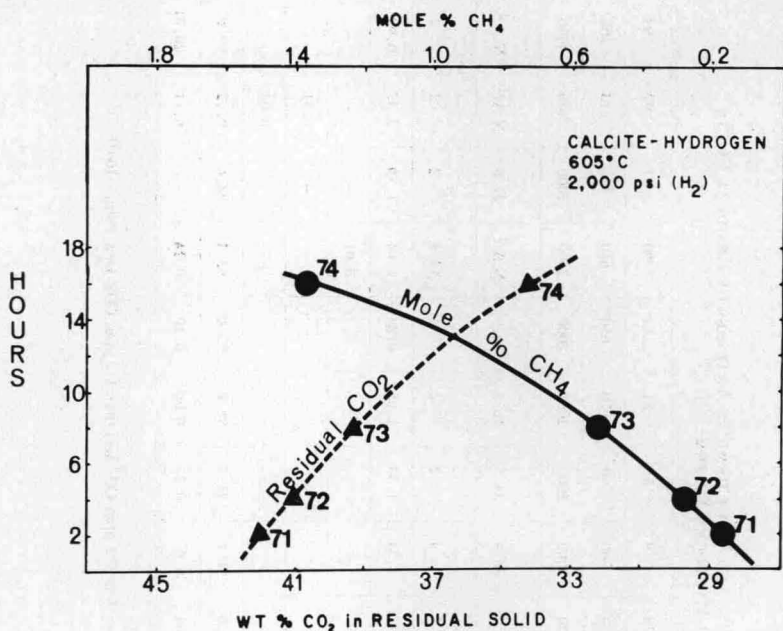


FIG. 4. Plot of mole % CH₄ generated in the calcite-hydrogen system and residual CO₂ remaining as calcite in experiments run at 605°C; 2000 psi (H₂); for 2, 4, 8, and 16 hours.

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.