

tions, therefore, also appear to support a reaction involving direct methanation rather than hydrogenation of CO or CO₂.

The kinetics of the thermal dissociation of carbonates, especially calcite and dolomite, has received considerable attention over the years. It has been proposed that the diffusion of released CO₂ is the rate controlling step (Zadwadski and Bretsznajer, 1933a, 1933b, 1938a, 1938b; Maskill and Turner, 1932; Britton, *et al.*, 1952a, 1952b, 1952c). The conduction of heat to and within the sample has also been held to be the determining step. More recently a rate expression involving actual and equilibrium CO₂ pressures and a temperature constant has been proposed (Hyatt *et al.*, 1958).

Although the calcite-hydrogen reaction is bimolecular and reaction begins at temperatures well below the "in air" calcination of calcite, the reaction kinetics describing the calcite-hydrogen system possess similarities to the kinetics for the thermal dissociation of calcite in vacuum. Hydrogen appears to simulate a vacuum environment.

The determination of any reaction rate inevitable reduces to the determination of concentration as a function of time. The methane concentration does not accurately reflect the reaction because of the subsequent reaction: $\text{CH}_4 = \text{C} + 2\text{H}_2$. The weight percent carbon dioxide remaining in the solid is an appropriate concentration measure of the reaction rate. Because equal amounts of calcite, sieved to a common grain size, were used for each run, the weight percent CO₂ remaining in the solid can be converted into conventional units, i.e. moles/cc, by introducing the necessary constant. It is sufficient here to recognize that under the experimental conditions weight percent CO₂ is a measure of the calcite concentration in the solid.

An unusual form of the concentration unit is no inconvenience if the reaction is first order because the value of the rate constant for a first order reaction is independent of the concentration unit. The hydrogen concentration is initially very large relative to calcite, and the percentage change in the hydrogen concentration is small even in runs of 16 hours. During the experiments, therefore, the hydrogen concentration factor is nearly constant, and because of this the reaction can be considered pseudo-first order¹ and successfully treated as such.

A plot of the rate constants calculated from experiments 71, 72, 73, 74,

¹ A second-order reaction in terms of the variable x representing the decrease in concentration of a reactant in a given time is: $dx/dt = k(a-x)(b-x)$ where a and b represent the initial concentrations. If b represents the initial hydrogen concentration in the calcite-hydrogen reaction at 605°C and 2000 psi $p(\text{H}_2)$ then the value of $(b-x)$ for the interval between 2 and 16 hours is 0.998 to 0.985. The term $(b-x)$ can be neglected leaving $dx/dt = k(a-x)$, the relation of a first order reaction.

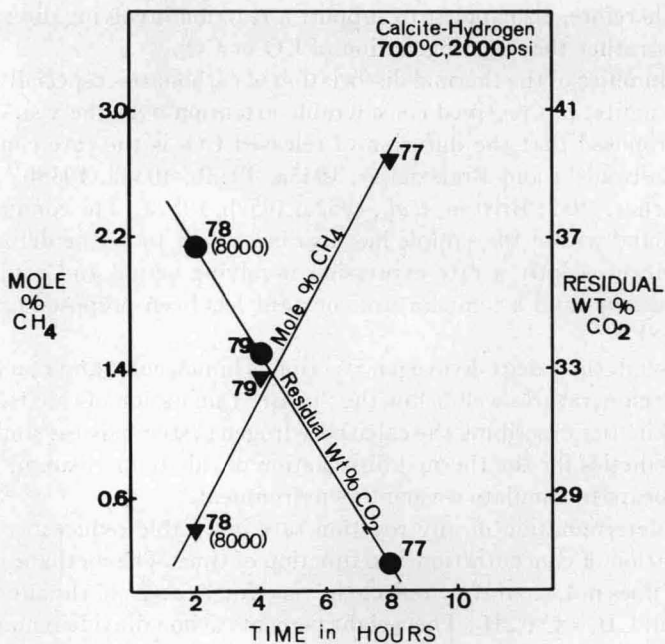


FIG. 6. Plot of calcite-hydrogen system showing mole % CH_4 generated and residual CO_2 remaining as calcite in experiments run at 700°C ; 2000 psi (H_2) exp. no. 77, 79 and 8000 psi (H_2) exp. no. 78; for 8, 4, and 2 hours respectively.

run at 605°C and 2000 psi $P(\text{H}_2)$ for 2, 4, 8, 16 hours respectively is shown in Figure 3. The deviation from linearity is not excessive, and the agreement of the calculated rate constants for the same experiments is within the experimental error (Table 2). Both evaluations support the assumption of a pseudo-first-order reaction.

TABLE 2. CALCITE-HYDROGEN AT 605°C , 2000 PSI $P(\text{H}_2)$

t (hours)	Wt % CO_2^a remaining in solid	k (hour^{-1})
2	42.0	0.019
4	41.0	0.016
8	37.8	0.018
16	34.2	0.015
		mean = 0.017

^a Initial CO_2 Wt % is 43.7.