

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 (Zadwadowski and Bretsznajer, 1933a, 1933b, 1038a, 1938b; Maskill and Turner, 1932; Britton, *et al.*, 1952a, 1952b, 1952c). The determination of heat to and within the sample has also been held to be the determining factor for the formation of CO₂ (Hyllberg, 1958). 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 depends on 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: CH₄ = C + 2H₂. 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, and 75 (Tables 1 and 3) and it is reasonable to expect that the rate constants for the calcite-hydrogen reaction at 605°C and 2000 psi p(H₂) 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.

temperatures, the ex-
 re pressures parallel
 low 250°C by reactions
 the free energy changes
 on monoxide-hydrogen
 (H₂O) also is perti-
 tion show that at tem-
 favors the formation of
 CO₂ is thermodynamically
 tion and, at the temper-
 ation, but it is not
 restricted conditions in-
 experimental conditions in-
 calcite appears to be
 mediate product in the
 argument against (CO)
 Fischer-Tropsch hy-
 ds of hydrocarbons oc-
 2 by volume at about
 dly decreases with in-
 Figure 2 shows
 the formation of the
 CO and H₂ is ther-
 m: H₂ + CaCO₃ = (CO)
 a substantial increase
 in reaction: CO + 3H₂
 (e) in free energy. The
 overall free energy
 Ca(OH)₂ + H₂O which
 of a general reaction
 ons of some of our ex-
 ss hydrogen. This is
 42 (Tables 1 and 3).
 and it is reasonable to
 titles. These observa-
 es below 800°C is another
 subsequent water-gas reac-