

temperatures, the ex-

te pressures paraffin
low 250°C by reactions
he free energy changes
on monoxide-hydrogen
($\text{CO} + \text{H}_2\text{O}$) also is parti-
tion show that at tem-
persors the formation of
 CO_2 is thermodynamically
tion and, at the temper-
eration, but it is not
restricted conditions of
perimental conditions in-
calcite appears to be

mediate product in the
rgument against CO_2 .
e Fischer-Tropsch hy-
ds of hydrocarbons oc-
:2 by volume at about
dly decreases with in-
essure. Figure 2 shows
the formation of the
en CO and H_2 is ther-
n: $\text{H}_2 + \text{CaCO}_3 = \text{CO}$
a substantial increase
at reaction: $\text{CO} + 3\text{H}_2$
le) in free energy. The
e overall free energy
 $\text{Ca}(\text{OH})_2 + \text{H}_2\text{O}$ which

ot a general reaction
ons of some of our ex-
ss hydrogen. This is
42 (Tables 1 and 3).
and it is reasonable to
tities. These observa-

es below 800°C is another
subsequent water-gas reac-

tions, therefore, also appear to support a reaction involving direct meth-
anation rather than hydrogenation of CO or CO_2 .

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 CO_2 is the rate controlling
step (Zadwinski and Bretznajer, 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
 CO_2 pressures and a temperature constant has been proposed (Hyatt *et al.*,
1958).

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

The determination of any reaction rate inevitably reduces to the de-
termination of concentration as a function of time. The methane concen-
tration 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 CO_2 remaining in the solid can be
converted into conventional units, i.e. moles/cc, by introducing the neces-
sary constant. It is sufficient here to recognize that under the experi-
mental conditions weight percent CO_2 is a measure of the calcite concen-
tration 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 or-
der reaction is independent of the concentration unit. The hydrogen concen-
tration 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 con-
centration 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.