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KINETICS AND RELATIONS IN THE CALCITE-HYDROGEN REACTION AND RELATIONS IN THE DOLOMITE-HYDROGEN AND SIDERITE-HYDROGEN SYSTEMS

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ABSTRACT

Reactions of calcite, dolomite, and siderite with hydrogen at elevated temperatures and pressures result in the formation of inorganic hydrocarbons up to and including butane. The carbonate-hydrogen experiments were run in a "cold-seal" type vessel. The analyses of the reaction products were done by mass spectrometry for the gases, and by wet chemical, atomic absorption spectroscopy, and X-ray methods for the solids.

Hydrocarbons appear to form directly from a carbonate surface-gas reaction rather than from a reaction between generated gas and hydrogen. An inverse relation holds between the complexity of the hydrocarbon formed and the temperature of formation.

An evaluation of the kinetic data for calcite-hydrogen shows the reaction to be pseudo-first-order. For the experimental system the Arrhenius apparent activation energy is 18,000 cal/mole.

INTRODUCTION

Recent evidence (Ikorskii, 1964; Ikorskii and Romanikhim, 1964; Petersilie, 1958; Petersilie, 1963; Petersilie, 1964; Zakrshevskaya, 1964) indicates that reducing gases were present during the crystallization of some igneous rocks. Thermodynamic calculations (French, 1966) suggest that in graphite-bearing rocks the equilibrium gases should be reducing in composition. The predominant emphasis in experimental petrology to date has been the study of systems in air; under their own vapor pressures, carbonate and sulfide systems for example; or under an imposed pressure, usually H_2O or CO_2. The writers believe that the study of natural and synthetic systems under reducing atmospheres will yield information that is pertinent to a number of petrologic problems. This manuscript reports some of our findings in the systems calcite-hydrogen, dolomite-hydrogen, and siderite-hydrogen.

Calcite, dolomite, and siderite under the appropriate conditions react with hydrogen to produce hydrocarbons. These reactions have been studied under various *P-T* conditions.

EXPERIMENTAL PROCEDURES

The following materials were investigated in the hope that they would have a catalytic effect upon the reactions: metallic nickel, platinum, copper, titanium, magnesium, and iron; commercial mixtures of 0.5 percent palladium, platinum, and rhodium on alumina; and dried silica gel, activated alumina, hematite, magnetite, chromic oxide, chromium trioxide, and various "Kieselguhr" mixtures. The possible autocatalytic effects of product hydrous and anhydrous oxides and pyrolitic carbon also were investigated. None of the

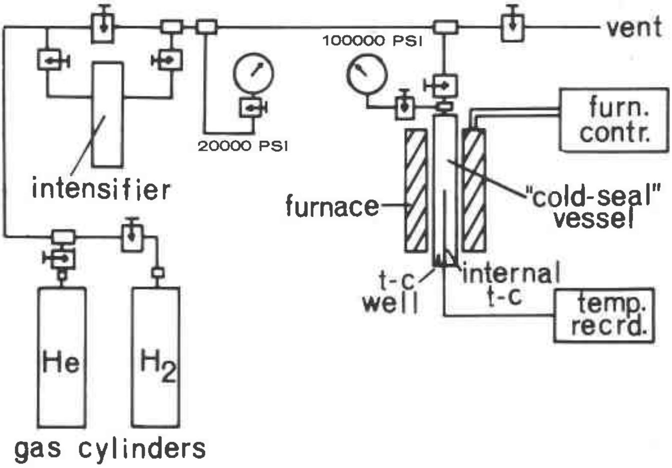

FIG. 1. Schematic drawing of the apparatus used for studies in the calcite-hydrogen, dolomite-hydrogen, and siderite-hydrogen systems.

above mentioned materials had any discernible effect upon the reaction rate. Several of the metals, particularly iron, increased the rate of pyrolitic dissociation of the generated methane.

The experimental system is shown schematically in Figure 1. The bulk of the experiments were carried out in a "cold seal" vessel made from Kelsay-Hayes Co. Udimet 500 stainless steel. A 20,000 psi Heise gauge measured the gas pressures. A platinum-wound muffle furnace was used to heat the lower section of the reaction vessel. A stainless steel sheathed Cr-Al thermocouple was inserted into the reaction vessel through the cold seal by means of a pressure fitting to measure the internal temperature. External bottom well thermocouples also were used. A Leeds and Northrup model 60 control unit with a Fincor saturable reactor and later an API digital setpoint SCR proportioning controller maintained the temperature automatically. Equilibrium, although approached, was not established in these experiments.

The procedure used for most of the experiments was as follows:

1. The carbonate mineral was weighed and loosely housed in platinum foil;
2. The sample was placed in the vessel, connected to the pressure system, flushed 2 times with pure helium, at about 1000 psi, then charged with helium to about 1000 psi;
3. Upon reaching the operating temperature, the helium was vented and the system given 3 hydrogen flushes and then pressurized to the desired hydrogen pressure;
4. After the experimental interval the excess hydrogen plus reaction gases were vented (in some experiments a fraction was collected for mass spectrographic analysis) and the vessel flushed and pressurized with helium;
5. The furnance was drawn from the vessel and the latter air-quenched under the internal helium pressure;
6. After cooling, most of the samples were opened in air and placed in argon-filled containers. Some experiments were opened in an argon-filled dry glove box (Na dessicant) and samples sealed in glass capillary tubes.

Most of the experiments were conducted at pressures below 10,000 psi. However, one

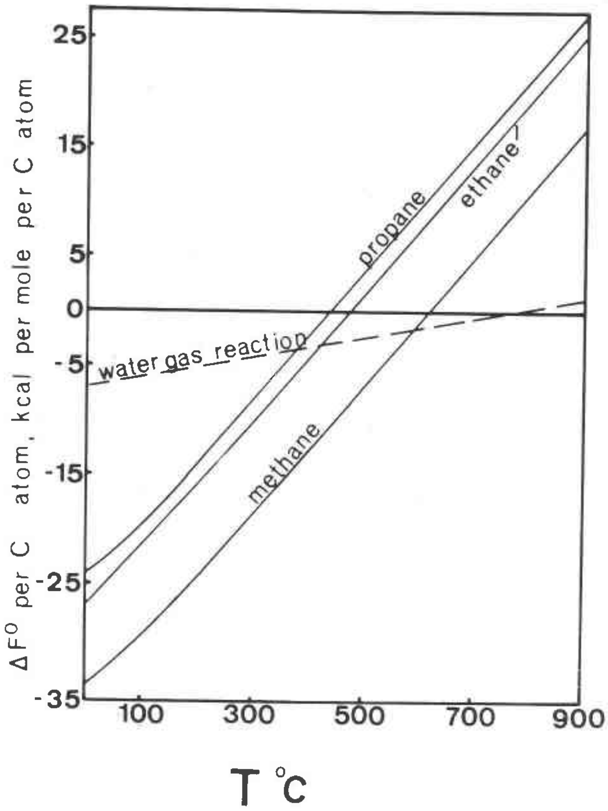

FIG. 2. Standard-state free energies of formation of methane, ethane, and propane by reactions of the type: $(2n+1)H_2+nCO=C_nH_{2n+2}+nH_2O$; and the free-energy variation of the water-gas reaction (data after Rossini *et al.*, 1947).

experiment was run to investigate the effect of high pressures. A calcite cleavage rhomb showed no discernible alteration after being held at 228°C under 80,000 psi hydrogen pressure for 23 hours.

The mass spectrographic analyses were done by Drs. Richard and Patricia Crawford, Chemistry Department, University of California, Lawrence Radiation Laboratory, on a Consolidated Electrodynamics Corporation model 21-103C analytical mass spectrometer. The analytical sensitivity is 0.01% by volume. Samples with simple compositions were compared with known patterns using a step-wise regression program, and more complex compositions were interpreted using the computer step-wise regression program of D. D. Tunnicliff and P. A. Wadsworth at Shell Development Co.

All of the starting carbonates were minerals. The calcite was optical grade obtained from Ward's. The dolomite was also from Ward's. The siderite was donated by Dr. Dennis Radcliffe. All starting minerals were examined optically, hand picked for impurities, crushed, and heated in 30 percent hydrogen peroxide.

CALCITE-HYDROGEN

In the calcite-hydrogen system using calcite fragments of 40 to 60 mesh, between 535–870°C, and 200–8000 psi of initial hydrogen, the following compounds were observed: solid CaO; Ca $(OH)_2$; graphite; and carbon "soot." Gaseous CH_4; C_2H_6; CO; CO_2; and H_2O also formed.

The experimental results are summarized in Table 1 and plotted in Figures 3, 4, and 5. The weight percent CO_2 in the remaining solid and the mole percent CH_4 formed are plotted against the duration of the run in hours at 2000 psi (P_{H_2}).

Below its dissociation temperature $Ca(OH)_2$ is the stable solid reaction phase. In runs allowed to cool to room temperature under the reaction gases, $Ca(OH)_2$ is always present. In experiments run above the dissociation temperature of $Ca(OH)_2$, CaO is present if the reaction gases are replaced with helium at the operating temperature. Analyses of the reaction gases indicate that water is the oxygenated product. Simplified equations for the reactions are the following:

$$\text{(A)} \quad CaCO_3 + 4H_2 = CaO + CH_4 + 2H_2O$$

$$\text{(B)} \quad CaCO_3 + 4H_2 = Ca(OH)_2 + CH_4 + H_2O$$

The change in free energy for reaction B is negative below approximately 325°C; whereas for reaction A it is positive. However, the free en-

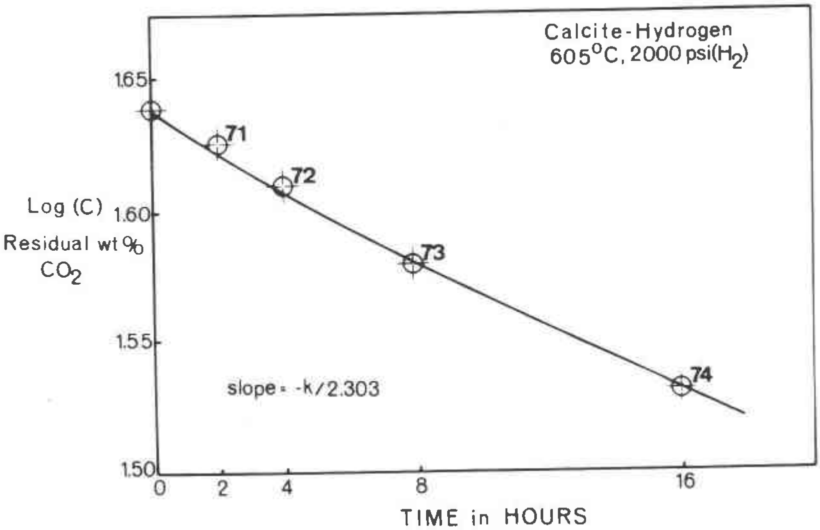

FIG. 3. Linear plot of log C against time for calcite-hydrogen data from experiments 71, 72, 73, and 74; run at 605°C, 2000 psi (H_2) illustrating the pseudo-first-order nature of the reaction.

TABLE 1. MASS SPECTROGRAPHIC ANALYSES OF REACTION GASES[a,b,c] AND WET-CHEMICAL ANALYSES OF RESIDUAL CO_2 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_2H_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 N_2, less than 1 ppm O_2, less than 1/2 ppm CO_2, less than 1/2 ppm CO_2, Dew Point—100°F.

[c] Detection limit 0.01%.

[d] Not analyzed.

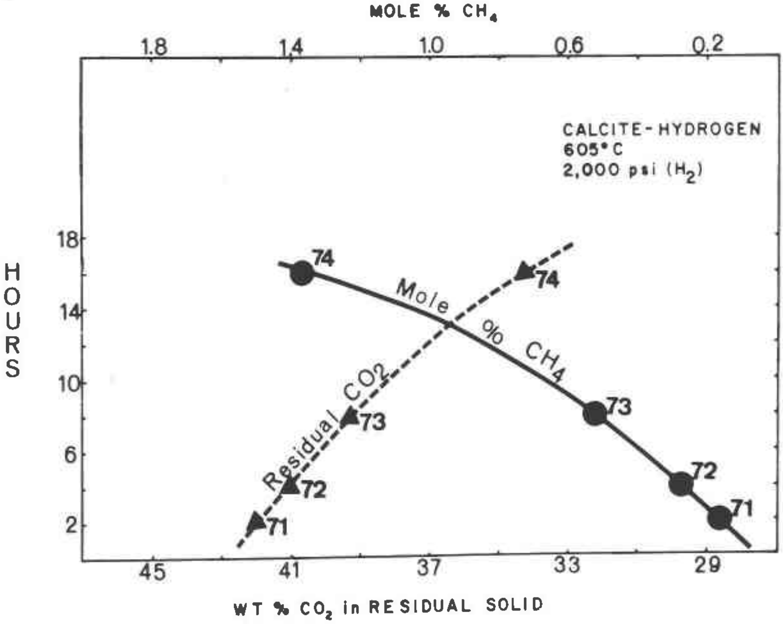

FIG. 4. Plot of mole % CH_4 generated in the calcite-hydrogen system and residual CO_2 remaining as calcite in experiments run at 605°C; 2000 psi (H_2); for 2, 4, 8, and 16 hours.

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 CO_2 in the solid than can be accounted for as carbon in the generated CH_4. 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.

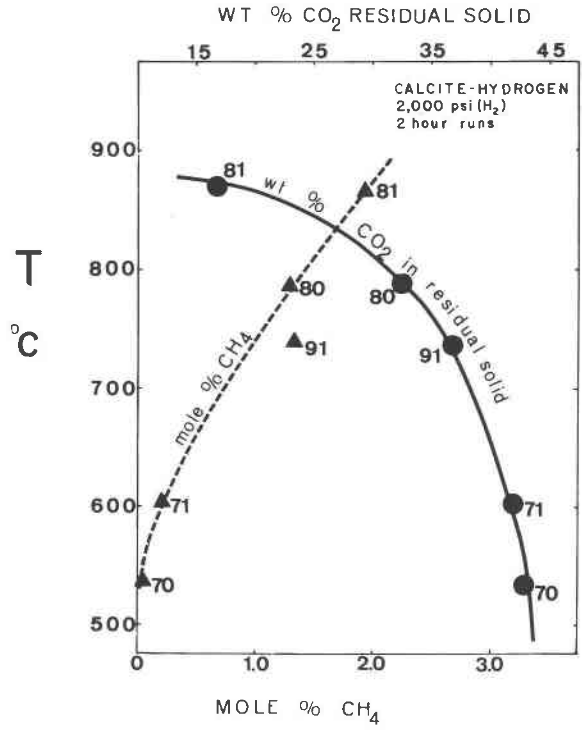

FIG. 5. In the calcite-hydrogen system, plot of mole % CH_4 generated and residual CO_2 remaining as calcite in experiments run for 2 hours; 2000 psi (H_2); at 535, 605, 735, 790, and 870°C.

Analysis of the reaction gases shows that the reaction compounds are restricted in number even though a large population of compounds are possible in the C-H-O system. The gases present are the following: CH_4; C_2H_6; H_2O; CO; and CO_2. The latter two appeared in only one experiment (no. 75). This experiment was unique in that the original hydrogen pressure was only 200 psi.[1] The appearance of CO and CO_2 at low pressures may be explained, at least in part, through thermodynamic calculations for a simplified C-H-O gaseous system (French, 1966). These calculations show that decreasing pressure favors the formation of CO_2 and water relative to methane and are in agreement with our experimental findings.

It appears that methane and, if within the stability field, homologues of methane, form directly rather than from reactions between hydrogen

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[1] Fugacities vary with pressure, consequently the proportion of each substance present in the equilibrium will also vary with pressure.

and CO or CO_2. Except at low pressures and high temperatures, the experimental evidence is that CO_2 is not present.

Thermodynamic data indicate that at moderate pressures paraffinic hydrocarbons can form below 350°C and olefins below 250°C by reactions between carbon dioxide and hydrogen; although the free energy changes of such reactions are much less negative than carbon monoxide-hydrogen reactions. The water-gas reaction ($H_2+CO_2=CO+H_2O$) also is pertinent. Equilibrium constants for the water-gas reaction show that at temperatures below 800°C, equilibrium very much favors the formation of carbon dioxide and hydrogen.[1] The point is that CO_2 is thermodynamically stable with regard to both the water-gas reaction and, at the temperatures of the experiments, in regard to hydrogenation, but it is not found in the gas analyses except under the stated restricted conditions of low pressure and high temperature. For the experimental conditions investigated, therefore, a direct methanation of the calcite appears to be the plausible reaction.

The position that CO is not generally an intermediate product in the dissociation of calcite is not as defensible as the argument against CO_2. The reaction of CO with H_2 forms the basis of the Fischer-Tropsch hydrocarbon synthesis. In this synthesis the best yields of hydrocarbons occur if the CO and H_2 are introduced in the ratio of 1:2 by volume at about 100 psi total pressure. The hydrocarbon yield rapidly decreases with increasing hydrogen content and increasing total pressure. Figure 2 shows that under most of our experimental conditions, the formation of the lighter hydrocarbons (C_1 to C_4) by reaction between CO and H_2 is thermodynamically favorable. The initial reaction: $H_2+CaCO_3=CO+Ca(OH)_2$ under standard conditions results in a substantial increase (+22.64 kcal/mole) in free energy. The subsequent reaction: $CO+3H_2$ CH_4+H_2O yields a large decrease (−34.01 kcal/mole) in free energy. The sum of these two reactions, of course, equals the overall free energy change for the reaction: $CaCO_3+4H_2=CH_4+Ca(OH)_2+H_2O$ which yields methane directly.

Again, however, the best evidence that CO is not a general reaction product is found in the gas analyses. Under conditions of some of our experiments CO does occur in the presence of excess hydrogen. This is shown by the gas analyses of experiments 75 and 42 (Tables 1 and 3). However, CO is absent from all other gas analyses and it is reasonable to assume that it never was present in detectable quantities. These observa-

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[1] The peristance of H_2O and CO in some of the reaction gases below 800°C is another indication of disequilibrium, and is due to the slowness of the subsequent water-gas reaction.

tions, therefore, also appear to support a reaction involving direct methanation 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 (Zadwadski and Bretsznajer, 1933a, 1933b, 1038a, 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 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: $CH_4 = C + 2H_2$. 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 necessary constant. It is sufficient here to recognize that under the experimental conditions weight percent CO_2 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 order[1] and successfully treated as such.

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

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[1] A second-order reaction in terms of the variable x representing the decrease in concentration of a reactant in a given time is: $dx/dt = k(a\text{-}x)\ (b\text{-}x)$ 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 $p(H_2)$ then the value of $(b\text{-}x)$ for the interval between 2 and 16 hours is 0.998 to 0.985. The term $(b\text{-}x)$ can be neglected leaving $dx/dt = k\ (a\text{-}x)$, the relation of a first order reaction.

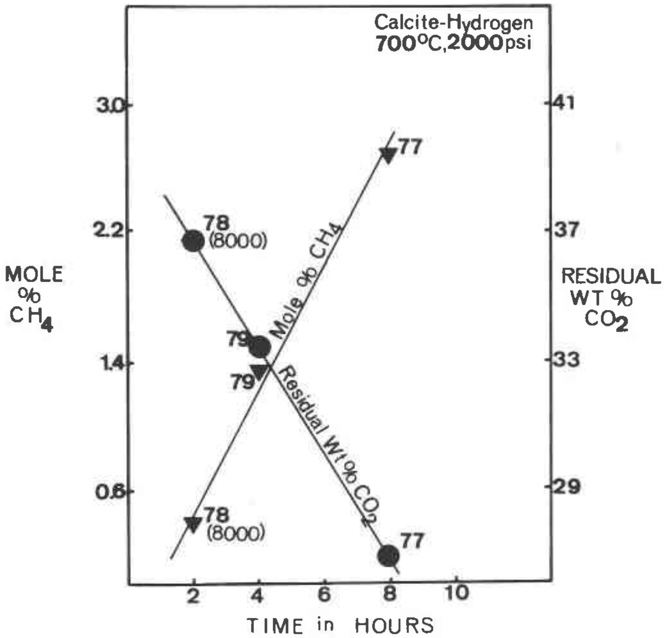

FIG. 6. Plot of calcite-hydrogen system showing mole % CH_4 generated and residual CO_2 remaining as calcite in experiments run at 700°C; 2000 psi (H_2) exp. no. 77, 79 and 8000 psi (H_2) exp. no. 78; for 8, 4, and 2 hours respectively.

run at 605°C and 2000 psi $P(H_2)$ 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 $P(H_2)$

t (hours)	Wt % CO[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.

The Arrhenius equation:

$$\frac{d \ln k}{d\ T} = \frac{E_a}{RT^2}$$

can be used with the data from experiments 71, 91 and 80 to evaluate the variation of the rate constants with temperature, and to calculate the Arrhenius apparent energy of activation (E_a).

Figure 7 is a plot of the Arrhenius equation using data from experiments nos. 70, 71, 91, 80, and 81. The pressure (2000 psi) and the time (2 hours) were common to all experiments. The temperatures are 535°C, 605°C, 735°C, 790°C, and 870°C respectively. The apparent activation energy is calculated from the linear portion of the plot.

The Arrhenius equation: $d \ln k/dT = E_a/RT^2$, because E_a is constant,

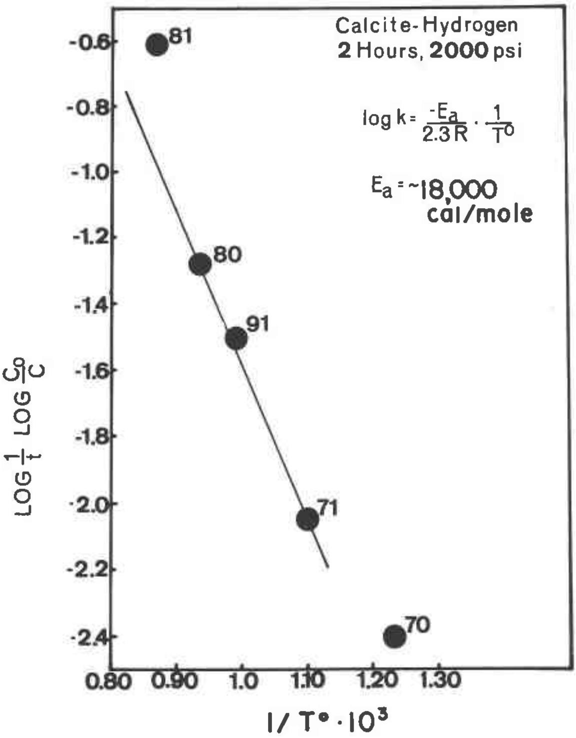

FIG. 7. Plot of $\log(1/t \log C_0/C)$ or $\log k$ against the reciprocal of the absolute temperature for experiments numbered 70, 71, 92, 80, and 81. These experiments were run at 2000 psi (H_2); 2 hours; at 535, 605, 735, 790, and 870° respectively. The Arrhenius activation energy calculated from the slope of experiments 71, 91, and 80 is 23,000 cal/mole.

can be integrated with respect to T to give $\ln k = -E_a/RT + C$. This latter form was used with the data from experiments 71, 91, and 80 to calculate the Arrhenius apparent activation energy (E_a). This activation energy is 18,000 cal/mole.

TABLE 3. DATA USED IN THE EVALUATION OF THE ACTIVATION ENERGY IN FIG. 7

Exp. No.	°C	$1/T°$	C_0	C	C_0/C	$\log C_0/C$	$\frac{1}{t}\log C_0/C$	$\log\left(\frac{1}{t}\log\frac{C_0}{C}\right)$
70	535	1.23×10^{-3}	43.7	43.0	1.02	0.0086	0.004	−2.40
71	605	1.14×10^{-3}		43.0	1.04	.0170	.008	−2.05
91	735	0.99×10^{-3}		37.8	1.16	.0645	.032	−1.50
80	790	$.94\times10^{-3}$		34.5	1.27	.1038	.052	−1.28
81	870	$.87\times10^{-3}$		16.3	2.68	.4281	.214	−0.61

The relation between the rate constant and the initial and final concentration of a reactant in a first-order reaction is as follows:

$$k = \frac{1}{t} \ln \frac{C_0}{C};$$

and the activation energy can be evaluated from Figure 7.

The slope was determined by using only the information from experiments 71, 91, and 80. Experiment 70 was excluded because of the analytical uncertainty in determining so small a change in the amount of reacted calcite. Experiment 81 was excluded because of the likelihood of a change in the behavior of the system at higher temperatures.

The digression from linearity of the sample at 870°C may result from the interaction of a competing reaction. The competing reaction may be either or both the thermal dissociation of calcite and the pyrolysis of methane.

Usually a homogeneous reaction has a higher activation energy and so is favored at high temperatures, whereas the heterogeneous reaction predominates at lower temperatures. The pyrolysis methane decomposition may also effect the calcite-hydrogen reaction rate. Britton, Gregg and Winsor (1952a) and Britton Gregg, Winsor and Willing (1952) on the basis of a study of the thermal decomposition of calcite in vacuum, concluded that the rate of dissociation was proportional to the area of the interface. Our studies support the conclusion that the calcite-hydrogen reaction is surface dependent.

In earlier work where a single cleavage rhombohedron was used for the calcite charge, it was common to recover a core of unreacted calcite enveloped by a cohesive rim of calcium hydroxide. Many of these samples

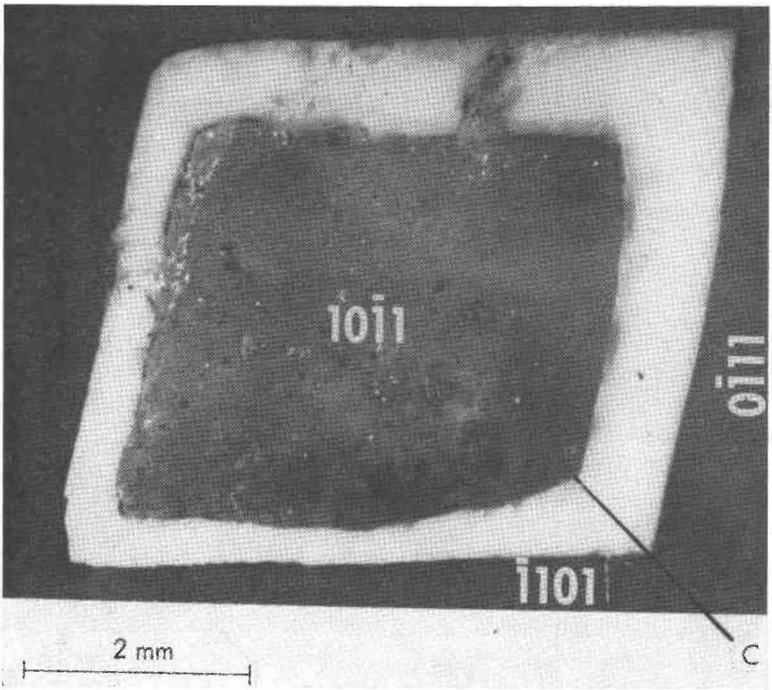

FIG. 8. Unequal depth of reaction envelope of $Ca(OH)_2$ developed on cleavage rhombohedron of optical calcite. Experimental conditions: 665°C; 10,000 psi (H_2); 4 hours. The unreacted calcite core was cleanly plucked from the $Ca(OH)_2$ rim during grinding and for illustrative purposes the calcite void was filled with plastic.

were immediately imbedded in quick-setting plastic, and flats were carefully ground normal to the side cleavage surfaces. If the samples were not potted, spontaneous spalling of the reaction film and shattering of the core generally occurred on standing. In addition to normal cleavage, conchoidal fracture was sometimes observed on the shattered calcite. The depth of alteration was measured optically and found to be very anisotropic and crystallographically similar for all crystals. The average ratio of maximum to minimum depth of the anisotropic reaction rim (for 29 samples) is 2.1.

The crystallographic orientation of several specimens was determined by using thin sections, a petrographic microscope, and a universal stage. The reaction rims and crystallographic orientation are shown in Figure 5. In a sense, the reaction rims may be compared to etch figures. Under normal conditions, the calcite I crystal system and class are given as: trigonal, $\bar{3}2/m$. Honess and Jones (1937) in their investigation of etch figures in carbonate minerals by optically active solvents, noted that the six sides of a cleavage rhombohedron of calcite always showed the same figures and solubility rates, whereas dolomite showed unlike solubility of the rhombohedral cleavage faces. The crystallographic orientation of the unequal reaction rims, as determined optically on the remaining calcite core of our specimens, shows that the *c* axis does not pass through the intersection of the three similarly reacted faces. The crystallographic anisotropy of the reaction implies more than a loss of the symmetry center.

DOLOMITE AND HYDROGEN

Dolomite and hydrogen were reacted under the following conditions: (1) fragment size 40–60 mesh; (2) 520°C to 835°C; (3) 2000 to 5000 psi initial hydrogen pressure; and (4) experiments lasting between 2 and 12 hours. Solid reactants observed include: $CaCO_3$(calcite); $Ca(OH)_2$; CaO; non-crystalline $Mg(OH)_2$; elemental carbon or graphite, and "soot". Gas analyses show: CH_4; C_2H_6; CO; and CO_2. Water is the oxygenated product from all of the experiments.

The experimental results are summarized in Table 4 and plotted in Figures 9 and 10. The weight percent CO_2 remaining in the solid and the mole percent CH_4 formed are again plotted against time at 5000 psi for 620°C, and against temperature at 5000 psi for 4-hour runs.

In the thermal dissociation of dolomite under the vapor pressure of the system, the reaction occurs in two stages. The first dissociation, stoichiometrically simplified, is given as follows:

$$CaMg(CO_3)_2 + \Delta = MgO + CaCO_3 + CO_2$$

With increasing temperature, the remaining calcite decomposes to lime and carbon dioxide with the exact dissociation temperature determined by the carbon dioxide pressure. If the P_{CO_2} never exceeds 100 mm, dolomite decomposes in a single stage dissociation as follows:

$$CaMg(CO_3)_2 + \Delta = MgO + CaO + 2CO_2$$

In the dolomite-hydrogen reaction CO_2 is not a reaction product under most of the experimental conditions and appears only as a minor component of the reaction gases at lower hydrogen pressures (Table 4). It likely is incidental to the main reaction of direct methanation. The basis for this statement is found in the dolomite-hydrogen gas analyses and the reasoning previously used in discussing the calcite-hydrogen system.

The dolomite-hydrogen reaction occurs in two steps. The first stage is represented by the following equation:

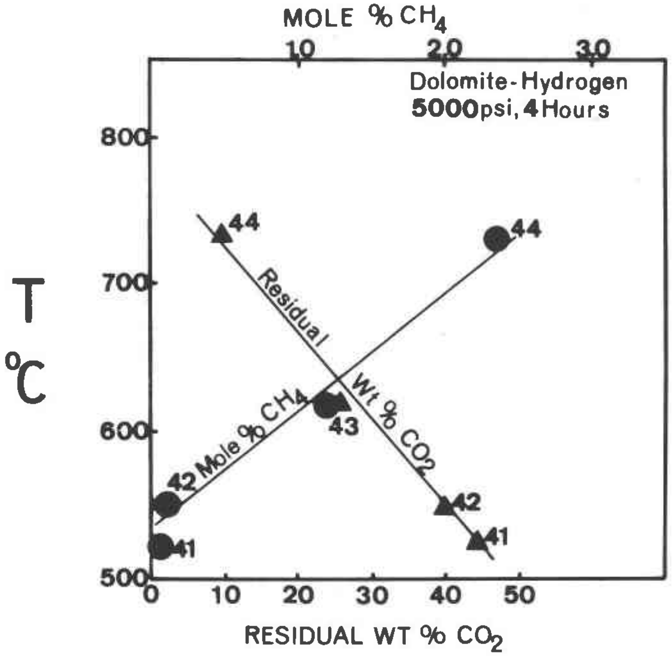

FIG. 9. Plot of mole % CH_4 generated and residual wt % CO_2 in the solid for the dolomite-hydrogen system at 5000 psi (H_2); 4 hour experiments; at temperatures of 525, 550, 620, and 735°C.

$$4H_2 + CaMg(CO_3)_2 = CaCO_3 + Mg(OH)_2 + CH_4 + H_2O.$$

At 5000 psi (H_2) reaction initiates as low as 520°C (Table 4). Calcite formed from dolomite persists at higher temperatures than does calcite alone in the calcite-hydrogen system. Similarities exist between the thermal dissociation of carbonates and the reaction of carbonates with hydrogen. In the dolomite-hydrogen system CH_4 may influence the reaction in a manner similar to CO_2 in the thermal decomposition of calcite. This possibility will be explored in future studies.

$Mg(OH)_2$ or MgO formed in the first stage is non-crystalline to X-rays. Chemical analyses by atomic absorption indicates 17% MgO in the solid reaction products.

A very minor amount of black lustrous material is present in the reaction products. It is similar in all appearances to the graphite formed in the calcite experiments. "Soot-like" material also was present in the bomb, and again was particularly noticeable at higher temperatures.

The reaction gases were those also present in the calcite experiments. (Table 4). Carbon dioxide appears in two experiments (nos. 83, 84) but

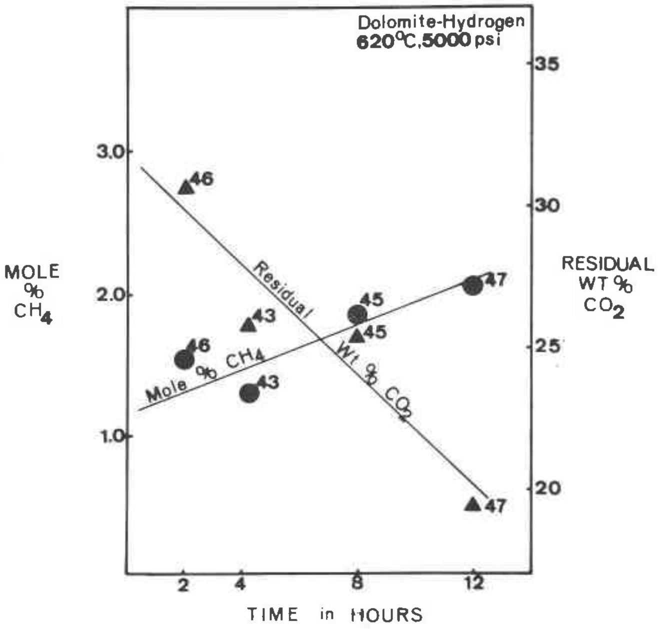

FIG. 10. Plot of mole % CH_4 generated and the residual wt % CH_2 in the solid for the dolomite-hydrogen system at 620°C; 5000 psi (H_2); for 2, 4, 8, and 12 hour experiments.

only in very small amounts. Both of these experiments were run at a lower pressure of 2000 psi. The discussion on the reaction gases for the calcite-hydrogen experiments applies also to the dolomite-hydrogen system.

The kinetics of the dolomite-hydrogen system are considerably more complex than in the calcite-hydrogen system. An evaluation of the rate constant for each successive concentration-reaction time pair at 620°C assuming the reaction is first, second or third order, shows wide scatter, and no trend for the rate constant. The wide divergence from linearity is illustrated by a plot of the Arhennius equation for a plot of the six temperature-concentration pairs. An interpretation of kinetic data into physical terms for this system is not realistic with the limited data available.

SIDERITE AND H_2

The reaction between one-half gram of 40 to 60 mesh siderite fragments and hydrogen is more complex than the preceding calcite-hydrogen and dolomite hydrogen reactions. It is also the least studied with only four experiments. These four runs were between 400 to 605°C and 2000 to 5000 psi (H_2), all for 4 hours. A "thermal soak" under helium was used in

TABLE 4. MASS SPECTROGRAPHIC ANALYSES OF REACTION GASES[a,b,c] AND WET-CHEMICAL ANALYSES OF RESIDUAL CO_2 IN UNREACTED D°LOMITE: DOLOMITE-HYDROGEN SYSTEM

Experiment No.	39	41	42	43	44	45	46	47	49	50	51	56	57	58	59	83	84
Temperature (°C)	520	525	550	620	735	620	620	620	735	735	735	735	735	735	835	605	605
Pressure (psi)	5,000	5,000	5,000	5,000	5,000	5,000	5,000	5,000	5,000	5,000	5,000	5,000	4,000	4,000	5,000	2,000	2,000
Wt. % CO_2 remaining in solid	N.A.[d]	44.3	40.2	25.6	10.1	25.4	30.7	19.4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	0.87	N.A.	N.A.
Duration of run (hours)	4	4	4	4	4	8	2	12	4	4	4	4	6	7	4	2	4
Mole % CH_4 in gas	0.01	0.02	0.04	1.20	2.34	1.82	1.53	2.05	2.00	1.88	1.77	1.80	2.86	4.76	2.12	0.46	2.64
Mole % C_2H_6 in gas	—	—	0.01	0.02	—	0.04	0.05	0.04	—	—	—	—	—	0.03	—	0.03	0.14
Mole % CO_2 in gas	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.09	0.03
Mole % CO in gas	—	—	0.04	—	—	—	—	—	—	—	—	—	—	—	—	0.72	0.13
Mole % H_2 in gas	97.70	99.90	99.30	98.70	97.60	98.00	98.40	97.80	98.00	98.10	98.10	98.16	97.10	95.20	97.86	98.6	97.0
Mole % He in gas	2.25	0.10	0.12	0.07	0.04	0.10	0.03	0.07	0.03	0.05	0.11	0.03	—	0.06	0.01	0.06	0.08

[a] Analysis calculated on water-free basis.

[b] Starting hydrogen impurities given as follows: less than 5 ppm N_2, less than 1 ppm O_2, less than 1/2 ppm CO_2, less than 1/2 ppm CO, Dew point—100°F.

[c] Detection limit 0.01%.

[d] Not analyzed.

TABLE 5. MASS SPECTROGRAPHIC ANALYSES OF REACTION GASES[a b c] AND WET CHEMICAL ANALYSES OF RESIDUAL CO_2 IN UNREACTED SIDERITE SIDERITE-HYDROGEN SYSTEM

Experiment No.	86	87	89	40
Temperature (°C)	605	455	400	525
Pressure (psi)	2,000	2,000	2,000	5,000
Duration of run (hours)	4	4	4	4
Mole % CH_4 in gas	0.15	4.34	4.45	1.45
Mole % C_2H_6 in gas	—	0.42	0.28	0.12
Mole % C_3H_8 in gas	—	0.23	0.10	0.03
Mole % C_4H_{10} in gas	—	0.05	0.03	—
Mole % CO_2 in gas	—	—	—	0.04
Mole % H_2 in gas	99.80	94.90	95.10	95.30
Mole % He in gas	0.04	0.08	0.09	3.07

[a] Analysis calculated on water-free basis.

[b] Starting hydrogen impurities given as follows: less than 5 ppm N_2, less than 1 ppm O_2, less than ½ ppm CO_2, less than ½ ppm CO, Dew point—100°F.

[c] Detection limit 0.01%.

each case to bring the bomb up to temperature before venting and replacing hydrogen for the reaction gas. Because of the low temperature for thermal dissociation of siderite, in those experiments at higher temperatures some siderite undoubtedly decomposed and the decomposition gas, presumably CO_2, was expelled along with the helium. For this reason the mole percent of gaseous hydrocarbons determined in the reaction gas for these experiments are minimum values (Table 5).

The solid reaction products for experiments 40 (525°C, 5000 psi), 86 (605°C, 2000 psi), and 87 (455°C, 2000 psi) are iron (Fe) and wüstite (FeO). The solid reaction produced from experiment 89 (400°C, 2000 psi) is magnetite. In all of the experiments the reaction gases were sampled and replaced with helium at the reaction temperature. Minute and rare flecks of what optically appeared to be graphite were observed, but no certain identification was made.

The limited data available suggests that wüstite is the primary alteration solid. The ultimate H_2O/H_2 ratio and the temperature dictate whether wüstite will be reduced to native iron or oxidized to magnetite. The simplified stoichiometric relations would be the following:

$$FeCO_3 + 5H_2 = FeO + CH_4 + 2H_2O$$

if reducing:

$$H_2 + FeO = Fe + H_2O$$

if oxidizing:[1]

$$H_2O + 3FeO = Fe_3O_4 + H_2$$

We have to date no experimental evidence that magnetite does not form directly under the appropriate conditions. The lower the temperature, the drier the hydrogen needs to be to effect reduction. In Experiment 87 run at 455°C at 2000 psi for 4 hours the solids were wüstite and iron. In experiment 89 run at 400°C at 2000 psi for 4 hours the solids were wüstite and magnetite. An extrapolation of Eastman and Evans' (1924) "best values" for the equilibrium constant from 700°C to 450°C and 400°C for the reactions,

$$FeO + H_2 = Fe + H_2O, \quad \text{and}$$

$$Fe_3O_4 + H_2 = 3FeO + H_2O,$$

yield values of the ratio H_2O/H_2 significantly higher than values obtained using the H_2O/H_2 ratios from experiment 89.

The validity of extrapolating the Eastman and Evans data to 400°C is questionable, but the magnitude of the difference between the extrapolated equilibrium ratio and our experimental H_2O/H_2 ratio allows for a considerable margin of uncertainty. The extrapolated ratio indicates that under the conditions of experiment 89, not only should magnetite not form, but wüstite should readily reduce to iron. Although our experiments with siderite never reached equilibrium, this discrepancy does suggest that relations in the Fe-C-H-O system differ significantly from the Fe-H-O system.

The reaction gases include appreciable methane and lesser amounts of ethane, propane, and butane. Water was present in all of the experiments.

The appearance of propane and butane can best be understood by considering the thermal stability of these hydrocarbons. The temperature necessary for siderite to react at an appreciable rate is low enough so that ethane, propane and butane are thermally stable. There is no direct evidence to indicate how these methane homologues form. Indirect evidence suggests that they do not form from methane. Some of the higher-temperature calcite and dolomite hydrogen runs were allowed to cool slowly under the reaction gases (methane, water, hydrogen) and the higher hydrocarbons did not form.

SUMMARY AND CONCLUSIONS

Inorganic hydrocarbons up to and including butane form directly in carbonate mineral-hydrogen reactions at temperatures as low as 400°C.

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[1] The fugacity of oxygen is proportional to P_{H_2O}/P_{H_2}.

The experimental evidence indicates that hydrocarbons form directly from a mineral surface-hydrogen reaction rather than from a subsequent reaction between generated gases and hydrogen. In general, the reaction rate is rapid at temperatures well below the "in air" calcination temperatures of the carbonate minerals.

An inverse relation exists between the complexity of the hydrocarbon formed and the temperature of the experiment. The lower the initial reaction temperature of the carbonate mineral-hydrogen pair, the more complex the hydrocarbon.

Equilibrium was not generally established in these experiments, although it must have been attained locally at higher temperatures at the reaction surfaces. An evaluation of the kinetic data for calcite-hydrogen shows the reaction to be pseudo-first order. For our experimental system the Arrhenius apparent activation energy is 18,000 cal/mole. The reactions between dolomite-hydrogen and siderite-hydrogen are more complex and an interpretation of the kinetics from our present data is not possible.

This study is pertinent to a number of geologic problems. It defines a simple process to produce inorganic hydrocarbons under conditions that could reasonably exist within the crust. These data indicate that the reactions are temperature rather than pressure sensitive and that the partial pressure of hydrogen is of greater importance than is the absolute pressure of hydrogen in initiating the reaction.

The process of limestone and dolomite assimilation by a magma is also germane. If the gases associated with a magma are reducing (hydrogen need only be a part of such a reducing gas) then CO_2 need not develop. The water generated in the reaction: carbonate mineral+hydrogen =methane+water+metal oxide or hydroxide, would inhibit the reaction; carbon dioxide would not. This water can, of course, be effectively removed from the system by being incorporated in the rock-forming minerals. The hydrocarbons may or may not leave the system. There is limited field evidence to support such a hypothesis. Petersil'ye (1962) estimates that the rocks of the Khibina massif contain 7×10^8 m^3 of inorganically derived hydrocarbon gases.

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