

KINETICS AND RELATIONS IN THE CALCITE-HYDROGEN
 REACTION AND RELATIONS IN THE DOLomite-HY-
 DROGEN 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 Romaniukhim, 1964; Petersilie, 1958; Petersilie, 1963; Petersilie, 1964; Zakrshchenskaya, 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, 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 hydroxous and anhydrous oxides and pyrolytic carbon also were investigated. None of the

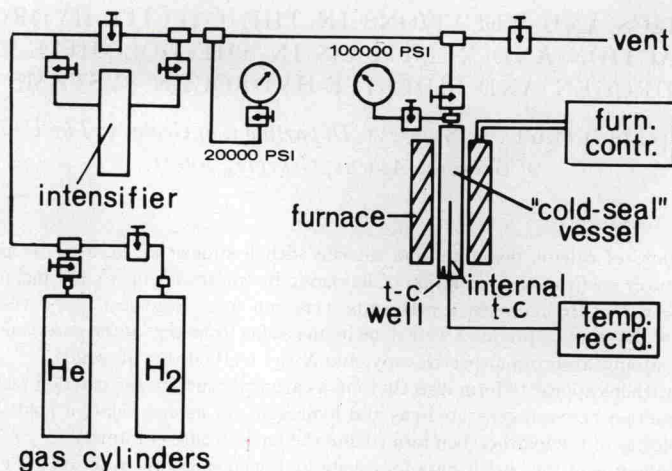


FIG. 1. Schematic drawing of the apparatus used for studies in the calcite-hydrogen, dolomite-hydrogen, and siderite-hydrogen systems.

above mentioned materials had any discernible effect upon the reaction rate. Several of the metals, particularly iron, increased the rate of pyrolytic 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 furnace 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