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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