

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

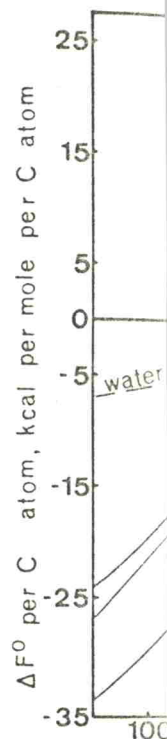


Fig. 2. Standard-state free energy change for reactions of the type: $(2n+1)C + H_2O \rightarrow 2nCO + CH_4$ of the water-gas reaction (data from Tunncliffe and P. A. Wadsworth).

experiment was run to investigate the effect of iron. It showed no discernible alteration in the reaction rate for 23 hours.

The mass spectrographic analysis was carried out in the Chemistry Department, University of Michigan, by the Consolidated Electrodynamic Corporation. The analytical sensitivity is comparable with known patterns. The compositions were interpreted by Tunncliffe and P. A. Wadsworth.

All of the starting carbonate minerals were from Ward's. The dolomite was from Radcliffe. All starting minerals were crushed, and heated in 30 per