L = liquid state
e = evaporation
f = fusion
1 = solution
o = freezing point of pure solvent

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Reaction Rate of Hydrogen with Diamond Powder

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The rate of reaction of hydrogen with 0- to 1-micron nominal size natural diamond powder was studied over the temperature range 1272° to 1372° K., and the pressure range 51 to 68 atm. The data were fitted to an Arrhenius equation to give $r = 2.01 \times 10^7 \exp[-115{,}800/RT]P^{2.343}$ grams per square meter-second. The high activation energy indicates that the reaction is not diffusion-controlled.

NATURAL diamond powder with 0- to 1-micron nominal size range as specified by the supplier was used in a study of the rate of reaction with hydrogen. The surface area determined by the standard BET method, using nitrogen as adsorbate, was 12.58 sq. meters per gram. Before any runs were made, the diamond was cleaned in hydrochloric acid to remove iron impurities, then subjected to a hydrogen precleaning at 1273° K. and 51 atm. to remove any oxides or graphite.

The hydrogen had a minimum purity of 99.95% as specified by the manufacturer. The oxygen content was less than 20 p.p.m.

APPARATUS

The most essential part of the reaction system is a high pressure, high temperature reactor through which hydrogen was continually passed over the diamond crystals. The reactor is a 36- × 2-inch, 0.5-inch i.d. Hastelloy X tube, placed within a tubular electrical resistance furnace. The reactor may be operated as high as 1373° K. and 247 atm. Because of the dangers inherent in operating with hydrogen at these conditions, the entire system was enclosed within a cement block wall. The diamond sample was placed in a quartz sample holder which, in turn, was placed within the Hastelloy X tube (Figure 1).

The remainder of the system permits accurate control and measurement of the very low hydrogen flow rates (0.5 cc. per minute at reactor conditions) through the reactor, required because of the danger of entraining the diamond particles. The flow was measured by a Hastings-Raydist mass flowmeter.

A Chromel-Alumel thermocouple was used to measure the temperature. The temperature was controlled by a Wheelco on-off controller with time proportioning. The pressure was measured by a mechanical gage.

PROCEDURE

At the start of a run, the sealed reactor was evacuated to a pressure of 10 microns of mercury and then brought to operating temperature and pressure over 2.5 hours. Once the operating temperature was reached, the flow rate was adjusted and the system held at the operating conditions. At the end of the reaction period, the furnace was turned off and the system vented to atmospheric pressure.

The reaction rates were determined by measuring the mass change of the sample. The sample holder containing the diamonds was placed within a quartz tube which was evacuated and then filled with dry air. The diamonds, sample holder, and quartz tube were then weighed. This procedure eliminated errors caused by adsorption of water vapor on the crystals. Precision was ±0.1 mg.

RESULTS

The reaction was studied over a temperature range of 1272° to 1372° K. and a pressure range of 51 to 68 atm. (Table I). Most of the uncertainty arises from the limits to which the sample can be weighed. Some uncertainty enters during the startup and shutdown periods; but since the dependency of reaction rate on pressure and temperature is so great, this inaccuracy is believed to be negligible.

This belief was substantiated by observing the rate of

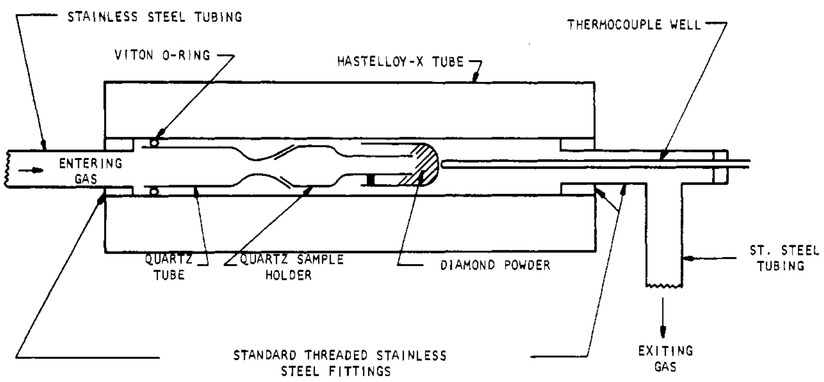

Figure 1. Schematic diagram of reaction chamber

Drawing not to scale. Copper cooling coils brazed to ends of Hastelloy X tube not shown

Table I. Summary of Rate Data

Run	Temp., °K.	Pressure, Atm.	Time, Hr.	Sample Weight, Mg.[a]	Weight Loss, Mg.	Rate × 10^9, G./Sq. M. Sec.
1	1322	51.0	4	538.4	3.5 ± 0.1	36 ± 1.0
2	1372	57.8	4	534.9	6.0 ± 0.1	62 ± 1.0
3	1272	57.8	4	526.0	0.3 ± 0.1	3.2 ± 1.1
4	1349	51.0	4	523.9	3.8 ± 0.1	40 ± 1.1
5	1272	64.6	4	520.1	0.5 ± 0.1	5.3 ± 1.1
6	1272	68.0	6	519.6	1.1 ± 0.1	7.8 ± 0.7
7	1272	64.6	12	518.5	1.2 ± 0.1	4.3 ± 0.4
8	1272	57.8	21	517.3	1.3 ± 0.1	2.6 ± 0.2
9	1272	51.0	48	516.0	2.0 ± 0.1	1.8 ± 0.1
10	1299	57.8	36	514.0	5.1 ± 0.1	6.2 ± 0.1

[a] Original specific surface area 12.58 sq. meters per gram.

reaction of hydrogen with graphite at 1273° K. and 51 atm. As found by Hedden (*1*), the rate was directly proportional to the mass. The observed rate with graphite was 1.03 × 10^{-5} gram per gram-second. The value reported by Hedden was 1.08 × 10^{-5} gram per gram-second, approximately three orders of magnitude greater than the rate for diamond at the same conditions.

An expression for the reaction rate of hydrogen with diamond was obtained by fitting the data to an Arrhenius-type expression by least squares,

$$r = 2.01 \times 10^7 \exp[-115{,}800/RT]P^{2.343} \qquad (1)$$

where r is in grams per square meter-second, T is in degrees Kelvin, R is in calories per gram-mole-° K., and P is the hydrogen pressure in atmospheres. The standard deviation of the data from the equation is 1.30 × 10^{-8} gram per square meter-second.

The values of the activation energy, frequency factor, and reaction order are empirical, and no particular theroretical significance should be attached to them; however, the large size of the activation energy would indicate that the reaction is not diffusion-controlled. The calculated rates are based on the original surface area of the diamond, 12.58 sq. meters per gram, which presumably decreased during the runs. This effect is not believed to be excessive—for example, compare runs 3 and 8, done at the same temperature and pressure.

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