

Frictional effects were too great to permit calculation of the pressure in the cylinder directly from the piston area and the applied thrust. A manganin resistance gauge (ref. (3), p. 70) was therefore used to determine the pressure for selected values of the thrust on the piston. The electrical connection G to this gauge was of the type designed by Poulter.⁴ The gauge coil (not shown in the diagram) was a small bundle of 40-gauge manganin wire, of about 100-ohms resistance. In a subsidiary experiment pressures up to 3000 atm, developed by an oil pump, were applied through a lens-ring seal at the mouth of the cylinder and the gauge constant was determined by comparison with a Bourdon gauge. This constant was then assumed to apply over the whole pressure range to 15,000 atm.⁵

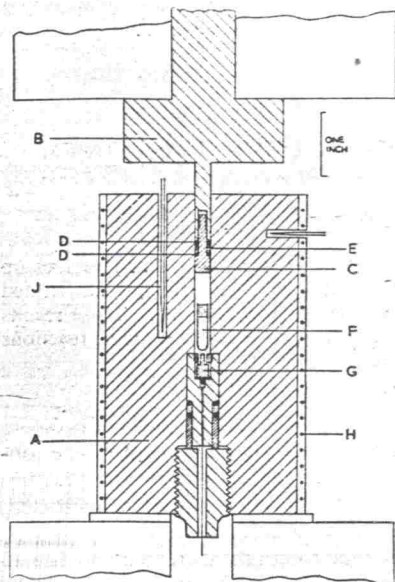


FIG. 1.—High-pressure reaction vessel.

A lagged heater H was wound around the cylinder to maintain it above room temperature. Chromel-alumel thermocouples in probe-holes J were used to determine the temperature distribution through the cylinder and it was found that a good indication of the temperature in the axial hole was given by a thermocouple in a probe-hole parallel to, and about $\frac{1}{2}$ in. distant from it. The temperature was maintained to within $\pm \frac{1}{2}^{\circ}\text{C}$ of the desired value by manual adjustment of the heater current.

Because of the friction between piston and cylinder the pressures in this apparatus were rather uncertain below 5000 atm. For that reason the measurements from 500 to 3000 atm were made in an apparatus resembling that described in part 1.¹

MATERIALS.—All the chemicals were of the highest purity available and the organic halides were further purified by drying and distillation. Dry methanol was purified by the method of Lund and Bjerrum.⁶ Sodium methoxide solutions were made by dissolving metallic sodium in pure methanol and were standardized against hydrochloric acid. Ammonium cyanate was prepared in the manner described by Warner and Stitt.⁷

PROCEDURE.—The reactions were: I, the unimolecular neutral solvolysis of *tert.*-butyl chloride in 80 % ethanol (20 volumes of water added to 80 volumes of ethanol); II, the unimolecular neutral solvolysis of *tert.*-butyl chloride in pure methanol; III, the bimolecular neutral solvolysis of ethyl bromide in 80 % ethanol; IV, the bimolecular neutral solvolysis of ethyl bromide in methanol; V, the bimolecular neutral solvolysis of ethyl iodide in methanol; VI, the bimolecular alkaline solvolysis of methyl bromide by sodium hydroxide in 80 % ethanol; VII, the bimolecular alkaline solvolysis of ethyl bromide by sodium methoxide in methanol; VIII, the conversion of ammonium cyanate to urea in water.

For each reaction an approximately N/2 solution of the reactants was made up at a low temperature and 0.2 ml of this was transferred to a small soda glass reaction tube F (fig. 1). The tube was quickly stoppered by a Neoprene plug and dropped into pre-heated petroleum ether in the pressure vessel A. Pressure was then applied to the petroleum ether as described in an earlier section. After a known time, usually several hours, the pressure was released and the reaction tube removed, rapidly cooled, broken, and washed with cold alcohol. The contents of the tube and the alcohol washings were titrated to find the extent of reaction. In reactions I-V the hydrogen halide was estimated by titration with standard barium hydroxide; in reactions VI and VII the unchanged alkali was titrated with hydrochloric acid, and in VIII the unchanged ammonium cyanate was titrated in excess ethanol with standard mercurous nitrate, using eosin as an indicator.

At 1 atm and at the highest pressure the reactions were measured over several time intervals and gave consistent rate constants for different reaction times. Because of the tedium of the experimental procedure and the strictly limited life of the pressure vessel, many of the reactions at intermediate pressures were observed over only a single time interval.