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An Apparatus for the Study of Reaction Kinetics in Solution at Pressures up to 10 000 atm

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Description of a 10 000 atm apparatus designed to follow continuously reaction kinetics by conductivity measurements. The apparatus consists of three parts: a two-stage pressure generator equipped with Bourdon manometer, a reaction chamber which is a steel block with a cylindrical hole 100 mm long and of 7 mm diameter and with high pressure electrical leadthroughs, and an electrical circuit for recording the conductivity. The reaction chamber is kept immersed in water thermostatted to within 0.05°C during measurements.

A subsequent paper deals with kinetic measurements of the hydrolysis of a series of esters at pressures up to 8 000 atm.

In the experimental study of reaction kinetics in solution at pressures above 2 000 or 3 000 atm it has been customary to let the reaction proceed for a given time at high pressure, release the pressure and analyze the mixture, after which the process is repeated for other durations. This procedure, which is motivated by the difficulties in measuring physical parameters at high pressure, is lengthy and introduces scatter in the experimental results. It may be avoided in certain cases, such as those in which the electrical conductivity of the reaction mixture is related to its composition. Although high pressure electrical connections have been developed,[1] their usefulness in this context seems to have escaped notice. The present authors have developed a high pressure reaction cell with auxiliary equipment described below that permits measurement of the conductivity of its contents at pressures up to 10 000 atm. With this apparatus it is possible to record continuously the degree of advancement at high pressure of any reaction that is accompanied by a change in electrical conductivity.

EXPERIMENTAL

Pressure generator. The block diagram of Fig. 1 shows the main components of the high pressure generator which operates in a two-stage process. In the first stage (7, see the figure) compressed air at 6 atm is used to build up a pressure of 300 atm in a mixture

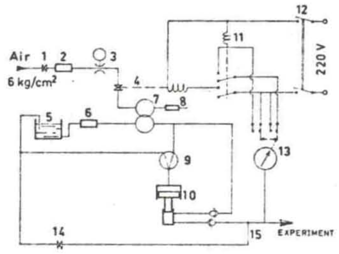

Fig. 1. Block diagram of pressure generator. 1. Valve for pressurized air; 2 mm bore. 2. Air filter. 3. Oil for lubricator. 4. Magnetic valve. 5. Oil reservoir: 2 l capacity. 6. Oil filter. 7. Air operated hydraulic pump 10–500(300). 8. Ato muffler. 9. Three-way valve (250 atm). 10. Intensifier. 11. Relay. 12. Switch. 13. Contact gauge 10 000 kg/cm². 14. 10 000 atm valve. 15. Tubing.

of 50 % Esso white spirit (isoparaffins, distillation fraction 178–203°C) and 50 % Shell Dialac which serves as the pressure transmitting medium through the rest of the system. In the second stage the pressure is increased in the ratio of 40:1 by means of a pressure intensifier (10) which is simply a rigid cylindrical floating piston having a large diameter in one end and a small diameter in the other. When one stroke is accomplished, the piston may be returned to its starting position hydraulically with the high pressure system isolated, and so the pumping may be continued indefinitely. The three-way valve (9) is used for this purpose. The high pressure is read from a Bourdon manometer (13) calibrated at the factory. The pointer of the meter is provided with a contact function so that if the indicated pressure is lower than a pre-set value, the system will start pumping automatically and continue to do so until the pre-set value has been reached. A relay (11) controlled by the contact and acting on an electromagnetic valve (4) at the compressed air inlet achieves this function. The generator is capable of maintaining constant pressure to within ±100 atm throughout the duration of an experiment. It is connected to the measuring cell by means of stainless steel tubing 8 mm O.D., 2 mm I.D.

Measuring cell. The reaction cell (Fig. 2) consists basically of a cylindrical piece of Uddeholm stainless steel 22 hardened to 350° Brinell, through which is drilled a hole 100 mm long and 7 mm diameter. One end of the hole is connected to the pressure generator through the steel tube mentioned above while the other end is closed with a demountable stopper in which three insulated steel pins are fixed.

The connections used have performed well, and the principle of their construction, as indicated by Hart and Sons [2] will be described in some detail. When two pieces having cylindrical bores and approximately the same hardness are to be joined, a third piece of harder material is inserted between them. The ratio between the hardnesses, as measured in the Brinell scale, should be approximately 4:3. The softer pieces should have flat faces perpendicular to their axes, while the hard piece should have conical end faces so that an angle of 15° remains free when the pieces are assembled. The inside diameter of the intermediate piece should not be greater than that of the adjoining pieces, and its orientation be well controlled. The seal between the two steel faces is formed when the harder one deforms the softer. This design has been modified somewhat for the junctions at the two ends of the measuring cell. The back face of the stopper is ground spherical so that it may take up the correct orientation.

The electrical leadthroughs consist of pins of Uddeholm stainless steel 31 hardened to 380° Brinell. To reduce forces, they are made rather thin, 1.3 mm diameter at maximum. To resist the pressure, they and the corresponding holes are conical with a diameter:length