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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

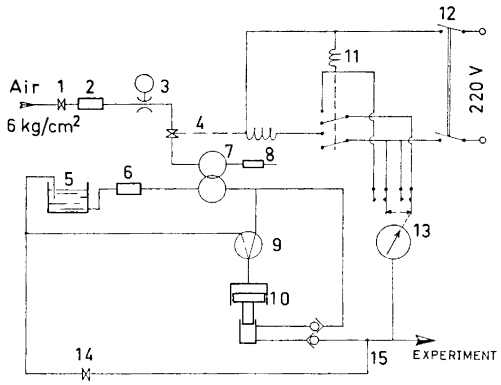

Fig. 1. Block diagram of pressure generator. 1. Valve for pressurized air; 2 mm bore. 2. Air filter. 3. Oil for lubricator. 4. Magnetic valve. 5. Oil reservoir: 2 l capacity. 6. Oil filter. 7. Air operated hydraulic pump 10—500(300). 8. Ato muffler. 9. Three-way valve (250 atm). 10. Intensifier. 11. 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

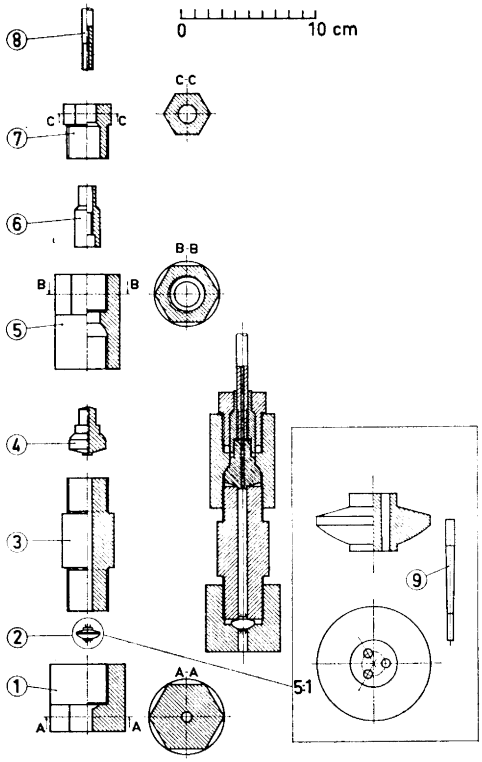

Fig. 2. Measuring cell.

		Type	°B
9. Electrodes	UHB	stls. 31	380
8. Tube			
7. Flanged nut	Bofors	CRO 861	250
6. Flanged tube		18 CrNi 8	200
5. Two-threaded union	Bofors	CRO 861	250
4. Connecting piece		nicro 812	420
3. Pressure chamber	UHB	stls. 22	350
2. Electrode holder	UHB	stls. 22	420
1. One-threaded union	UHB	stls. 22	300

ratio of 1:50. Ciba Araldite AT1 was used for insulation; this was not satisfactory in the long run, since the electrical resistance to ground fell to an unacceptable level with use. It was found, however, that admixture of finely divided glass wool in the Araldite improved the resistance value by a factor of 10 at least.

During all measurements, the cell was kept immersed in a thermostat, the temperature of which was controlled to within 0.05°C. This arrangement suffices to equalize inner and outer temperature, as will be described below. It necessitates separation of the cell from the generator, the connection consisting in a 2 mm I.D., 8 mm O.D. stainless steel tube 1.5 m long.

An indication of the pressure in the cell was obtained by means of a manganin wire, the specific resistance of which varies linearly with pressure according to Bridgman.[3] A length of about 2 m of 0.13 mm silk-spun manganin wire having a resistance of about 55 ohm was coiled up inside the measuring cell, and its ends were soldered to the leadthroughs. The assembly was then connected as one arm of a Wheatstone bridge, and its resistance measured with a precision of 0.01 ohm.

The temperature in the cell was measured by means of a chromel-alumel thermocouple made from 0.5 mm wire.

Electrical equipment. All attempts to use conductivity electrodes fixed on a glass tube inside the cell failed because of breakage. Instead, the leadthrough pins were used. In spite of their small area, they gave very reproducible and consistent results with a number of electrolytes. To lower interface resistance and polarization, all three pins were platinized, using a solution of 1 g platinum chloride and 0.01 g lead acetate in 33 ml distilled water at a current density of 10 mA/cm^2.

The conductivity was measured with a radiometer conductivity meter type CDM2, (see Fig. 3). This consists mainly of a constant voltage 3 000 c/s AC generator which

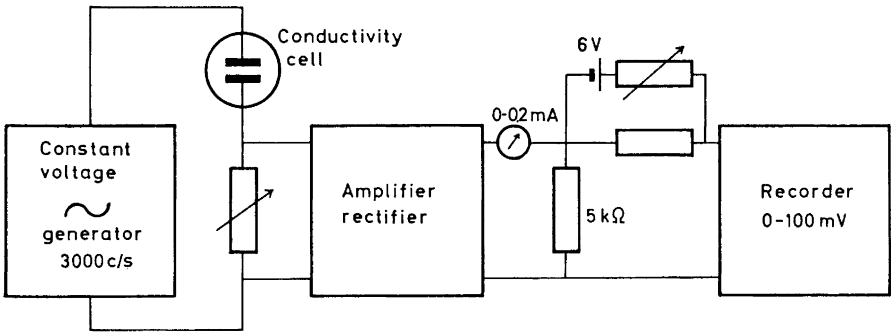

Fig. 3. Electrical circuit for conductivity recording.

sends current through the measuring cell and one of a number of standard resistors so chosen as to have a resistance of the same order of magnitude as that of the cell. The voltage drop across the resistor is amplified by a feedback amplifier whose output current, 0—0.2 mA, is fed to a meter. In order to record the conductance, the meter current is passed through a 5 kΩ external resistor, and the difference between the voltage drop across the latter and a fixed subtraction voltage (80—90 % of the former) is recorded at a sensitivity of 0—100 mV f.s.d. With this setup, the change in conductivity corresponding to completion of the chemical reaction will produce a deflection of one to two chart recorder spans. The stability and linearity of the measuring circuit were tested by substituting decade resistors for the conductivity cell, and the error was found to be smaller than 0.5 % of the total change in resistance corresponding to that of a reaction.

RESULTS

Secondary pressure measurements. Before any conductivity measurements were made, the values of pressure and temperature within the cell were measured under high pressure. In a first series of experiments, the pressure was increased gradually, and readings of the Bourdon manometer and the manganin wire resistance were taken simultaneously. The respective converted pressures agreed up to 8 000 atm, but between 8 000 and 9 000 atm, the resistance value lagged up to one minute behind the manometer reading, and above 9 000 atm the pressure did not equalize. One may conclude that in this range the liquid becomes very viscous and perhaps even non-Newtonian. In another series of experiments, the pressure was first increased stepwise from 1 to 9 000 atm and then decreased to 1 atm. The results are shown in Fig. 4, where the Bourdon manometer readings are plotted against the corresponding resistance increments of the manganin wire. The ascending part of the curve is seen to be a straight line while the descending part is curved, corresponding either to too high Bourdon values or too low resistance readings. The hysteresis effect is in all probability due to mechanical deformation of the Bourdon tube since the specific resistance is known to be a well-defined linear function of pressure, as mentioned above. The same ascending line has been found on repeated trials thus showing that the Bourdon manometer must recover between measurements.

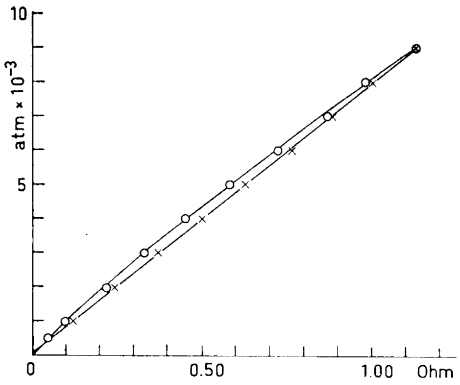

Fig. 4. Plot of Bourdon gauge reading against manganin wire resistance increase.

Temperature measurements. As mentioned earlier, compression is expected to produce a temperature change which, if sufficiently large, may seriously affect kinetic measurements. For an adiabatic, reversible compression

$$\left(\frac{\partial T}{\partial P}\right)_S = -\left(\frac{\partial S}{\partial P}\right)_T \Big/ \left(\frac{\partial S}{\partial T}\right)_P = \alpha T V / C_P = 1.86 \times 10^{-3} \text{ deg. atm}^{-1}$$

for water at room temperature and atmospheric pressure. If extrapolated, this will give the maximum temperature change that may be observed.

In practice, the system was constructed to be isothermal rather than adiabatic, so the changes would be expected to be less significant. This was confirmed by thermocouple measurements. In preliminary investigations, the thermal emf of the chromel-alumel couple proved to be pressure independent when thermal equilibrium with the surroundings was established. Further tests have shown that it is possible to keep the temperature rise well below 1°C while increasing the pressure from 1 to 10 000 atm if the process is extended to last about 8 min. If the pressure was suddenly released from 10 000 to 1 atm, the temperature decreased by about 5°C; one minute later it was about 1°C, and three minutes later about 0.1°C below that of the surroundings. The cell dimensions are obviously favourable for maintaining constant temperature, and the changes are sufficiently small to be tolerated in the type of kinetic work envisaged, in which the duration of an experiment is typically of the order of 100 min.

Conductivity measurements. When the control of pressure and temperature in the cell had indicated its satisfactory performance, a series of conductivity measurements on aqueous solutions of electrolytes were made. First, the conductivities of solutions of potassium hydroxide, sodium hydroxide, fluoride, sulphate, and acetate of various strengths were measured at room temperature and atmospheric pressure. When observed values were compared with table values, the results were all found to be mutually consistent to within 0.5 %, giving the same cell constant. Subsequently, the measurements were repeated at pressures up to 9 000 atm. Apart from the hysteresis effect that may be

assigned to the Bourdon manometer, the conductivity results were as reproducible as at atmospheric pressure.

These preliminary measurements show that the measuring cell gives results comparable to those obtained with ordinary conductivity measuring equipment at atmospheric pressure. The results at high pressure are sufficiently reproducible to give confidence in the performance of the apparatus. A series of kinetic measurements have been performed on the hydrolysis of a number of esters at various pressures up to 8 000 atm. The consistent results obtained have confirmed that the apparatus described is capable of measuring the course of reactions. The results will be published in a subsequent paper.

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