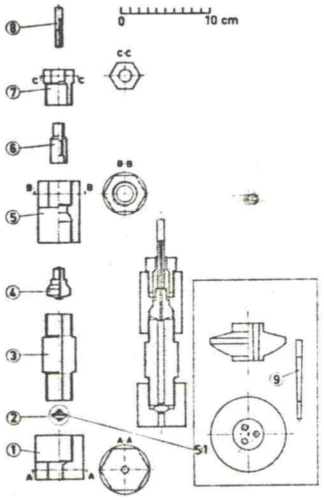

Fig. 2. Measuring cell.

		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

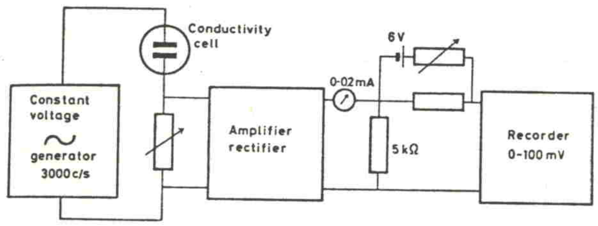

Fig. 3. Electrical circuit for conductivity recording.

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.