



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

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

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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