made simultaneously by a Solartron high input-impedance data-logging system linked to an Addo tape-punch and a Frieden Flexowriter for printed output. Also included in the potential measuring system was a Wayne–Kerr vibrating reed electrometer (M141) and a precision potentiometer for some of the very high input-impedance measurements.

RESULTS AND DISCUSSION

(a) *Stability of cell emf with time*

It was necessary first to demonstrate that the cell emf at any particular temperature was constant over long periods of time, because of the following adopted procedure of measurement. When a certain temperature was reached and thermal equilibrium attained, the pressure of the cell was fixed and the cell emf observed, generally for 1–2 h. A new pressure was then fixed and its effects followed. This procedure was repeated until the whole pressure range had been covered. A number of different examples of cell-emf/time observations are given in Fig. 2. Here are shown, in the upper set of curves, data from a typical pressure run, the example chosen being

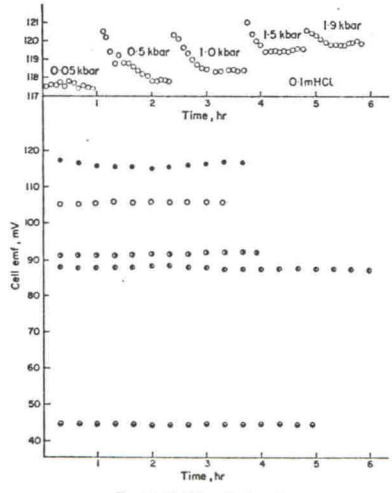

FIG. 2. Stability of cell emf
●, 4·5 M CsCl, 50 bar 200°C;
○, 0·1 M CsCl, 50 bar 200°C;
◑, 0·1 M HCl, 50 bar 150°C;
◐, 0·1 M CsCl, 50 bar 150°C;
◒, 4·5 M HCl, 50 bar 25°C.

for 0·1 M HCl as solution, temperature of 200°C and pressure range from 0·050 K bar to 1·7 K bar.

The lower plots of cell emf, which are almost invariant with time, show very good stability over periods up to 6 h at any particular temperature and pressure, the variation in cell emf being usually less than ±0·05 mV/h. The upper curves show the temporary heating effects caused in the cells due to changing the pressure, which are indicated by rapidly falling portions to the curves. The true thermal equilibriated portions of the curves are again almost invariant with the time axis.

Temperature and pressure hysteresis of the cell appears to be very small, as the example in Fig. 3 shows. Here is given a plot of cell emf against pressure for a cell

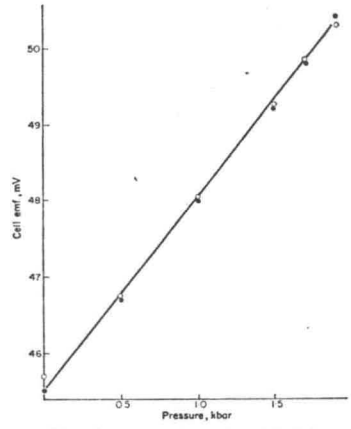

FIG. 3. Effect of temperature hysteresis on 4·5 M KCl cell at 25°C.
○, before temperature excursion to 90°C, measurements at 25°C; ●, after temperature excursion to 90°C, measurements at 25°C.

at 25°C before and after a temperature excursion to about 100°C. This observation may appear remarkable since it has been shown that both electrodes suffer some temperature hysteresis. Changes not larger than a few tenths of a mV in systems involving the skin-calomel electrode are known to exist.[10] Changes of several mV in the standard electrode potential are known also for the silver/silver-chloride electrode after some temperature excursions.[12] In both of these cases, however, the experimental information was gained from cells whose construction was not the same as for the present work. The principal difference was that both electrodes used here were contained in their own cell compartments each of which had an adequate supply of calomel skin or silver chloride and isolated from the main bulk of solution by sintered plugs.