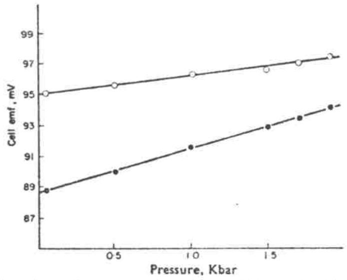

FIG. 6. Dependence of pressure and type of electrolyte on cell emf at 150°C.
○, cell with 4·5 M CsCl; ●, cell with 4·5 M KCl.

1·43 kcal/mol respectively, whilst ΔV for these three temperatures (also at 1 Kbar) is $-2{\cdot}0_9$, $-2{\cdot}2_3$, $-1{\cdot}0_1$ cm^3. dE/dT $0{\cdot}3_8$ mV/deg and dE/dP $2{\cdot}1_9$, $2{\cdot}3_5$, $1{\cdot}6_0$ mV/Kbar, used for these calculations, were calculated from linear and quadratic fits of the relevant data given in Table 1.

From the cell-emf values given in Table 1, taking the values at the lowest molality of HCl it is possible to calculate the standard electrode potential of the skin-calomel electrode. This is done by simple subtraction, if the standard electrode potentials of the silver/silver-chloride electrode are known with sufficient precision. Lietzke, Greeley, Smith and Stoughton[15] and recently Izaki *et al.*[16] have made measurements to derive the standard electrode potential of the silver/silver-chloride electrode up to at least 200°C.

Table 2 shows the derived values of standard electrode potential of the calomel

TABLE 2. STANDARD ELECTRODE POTENTIALS OF THE SKIN-CALOMEL ELECTRODE FROM 25–200°C

	E°, Hg_2Cl_2, Hg, mV				
Authors	25°C	70°C	100°C	150°C	200°C
Various[5–10]	267·93 to 268·23	—	—	—	—
This study (using Lietzke *et al.*[15])	$268{\cdot}0_5$	$249{\cdot}5_5$	$232{\cdot}9_4$	$195{\cdot}9_5$	$144{\cdot}3_5$
This study (using Izaki *et al.*[16])	$267{\cdot}8_4$	$248{\cdot}6_5$	$231{\cdot}7_3$	$194{\cdot}8_0$	$142{\cdot}7_8$

electrode over a range of temperature, from the present work. The standard electrode potential may be represented by

$$E^{\circ}_{Hg_2Cl_2,Hg(t^\circ C)} = 276{\cdot}261 - 0{\cdot}30535t - 8{\cdot}7170 \times 10^{-4}t^2 - 4{\cdot}594 \times 10^{-6}t^3 \text{ mV},$$

with a scatter of $\pm 0{\cdot}6$ mV; this is the result of least-squares fit of the combined sets of results of Table 2, including the averaged value at 25°C from previous work.[5–10] The rather large scatter is due to the large difference, *ca* 2 mV at 200°C, between the E°s of Lietzke *et al.*[15] and those of Izaki.[16] Selection of only one or other of the E°s would reduce this scatter, but no preference can really be made at the present time.

(d) *Measurements involving the Orion chloride-reversible electrode*

The Orion electrode (O.E.) was tested at 25 and 70°C and at 1–1900 bar. Table 3 shows values found for cells II and III at concentrations of 0·1 and 5 M HCl;

O.E./HCl (M)/Hg_2Cl_2, Hg (II)

O.E./HCl (M)/AgCl, Ag (III).

The potentials were measured simultaneously, at 1 s intervals; therefore, they should give the same potential as cell (I).

TABLE 3. EXPERIMENTAL CELL EMFS FOR CELLS (II) AND (III), USING THE CHLORIDE-REVERSIBLE ORION ELECTRODE

		Pressure, Kbar						
		0·001	0·050	0·50	1·00	1·50	1·70	1·90
0·1 M HCl								
25°C	E_{II}, mV	−5·1	—	+3·1	—	+2·65	−0·9	+3·8
	E_{III}, mV	−50·3	—	−42·4	—	−45·5	−49·9	−44·8
	$\Delta E \equiv E_1$	+45·2	—	+45·5	—	+48·2	+49·0	+48·6
70°C	E_{II}, mV	—	−6·3	−6·3	−5·3	−5·1	−4·4	4·2
	E_{III}, mV	—	−67·0	−68·1	−67·8	−69·3	−68·1	−68·1
	$\Delta E \equiv E_1$	—	+60·7	+61·8	+62·5	+64·2	+63·7	+63·9
5 M HCl								
25°C	E_{II}, mV	−1·7	—	+2·7	+6·9	+10·5	+11·8	+13·2
	E_{III}, mV	+45·6	—	+42·2	+39·1	+36·3	+35·7	+34·7
	$\Delta E \equiv E_1$	+43·9	—	+44·9	+46·0	+46·6	+47·5	+47·9
70°C	E_{II}, mV	+4·8	—	—	+2·5	+37·5	+51·5	+48·7
	E_{III}, mV	+52·4	—	—	+56·4	+22·9	+10·3	+13·2
	$\Delta E \equiv E_1$	+57·2	—	—	+58·9	+60·4	+61·8	+61·9

Thus, for example, taking the value of $E_{II} - E_{III}$ at 25°C, 0·1 M HCl and 0·5 kbar as 45·5 mV there is a 0·2 mV discrepancy with the value shown in Table 1. Similar discrepancies are apparent for other pressures and temperatures. However, the results in Table 3 demonstrate that any "asymmetry" potential the Orion electrode may possess is reasonably constant for short periods of time and that the electrode does function correctly as a chloride-reversible electrode under these conditions.

(e) *Effect of nature of cation and concentration of electrolyte on cell potential*

The Nernst equation for cell (I) does not depend on concentration or type of cation of the chloride electrolyte, as (1) shows. By reference to Table 1 it is seen that there is a variation in the cell emf for any particular concentration, temperature or pressure for the three different solutions studied. Thus the values given for 4·5 M HCl, KCl and CsCl at 100°C and 0·050 Kbar are 70·0, 71·1 and 69·3 mV; 76·0 and 73·6 mV were recorded for HCl at 100°C for 0·1 M HCl and 4·5 M HCl at 1·5 Kbar.

There are three possible reasons for this behaviour. The first may be disposed of quickly as being the most unlikely—that the anomalous results are a consequence of the presence of small amounts of bromide. Guntelburg[17] warned of the dissimilar extent of sources of error imposed upon the silver/silver-chloride and classical calomel electrodes due to bromide impurity. In the present case precautions, already