TABLE 1. EXPERIMENTAL CELL (I) EMFS AT TEMPERATURES AND PRESSURES

| | Temperature °C | Pressure international kilobars | | | | | |
		0·050	0·500	1·000 Cell emf mV	1·500	1·700	1·900
Molality	25	45·5	45·7	47·2	48·6	48·8	48·9
	70	60·8	61·8	62·5	64·3	63·5	63·8
0·1 M HCl	100	72·8	73·9	74·6	76·0	76·6	77·2
	150	92·3	94·1	95·7	97·1	97·6	98·0
	200	116·1	116·4	116·9	118·1	118·6	118·9
	25	44·7	45·7	47·1	48·2	48·8	49·3
	70	57·9	59·5	60·7	61·9	62·4	63·0
4·5 M HCl	100	70·0	71·3	72·3	73·6	74·2	74·6
	150	86·6	87·5	88·4	90·1	90·6	91·0
	200	—	—	—	—	—	—
	25	45·3	46·4	48·0	49·5	49·9	50·3
	70	59·4	60·7	61·5	62·6	63·2	63·8
0·1 M KCl	100	72·7	73·4	74·6	75·4	75·8	76·2
	150	89·2	90·3	91·5	92·6	93·0	93·4
	200	109·4	109·6	110·1	110·1	110·0	110·2
	25	—	46·7	48·0	49·3	49·9	50·3
	70	60·5	61·3	62·2	63·0	63·3	63·4
4·5 M KCl	100	71·1	—	73·5	74·5	75·8	—
	150	88·8	90·0	91·3	92·9	93·4	94·0
	200	106·2	107·8	107·8	112·3	114·1	115·6
	25	44·7	45·8	47·4	48·7	49·2	49·9
	70	60·5	61·1	62·4	63·4	64·1	64·5
0·1 M CsCl	100	71·9	73·3	74·4	75·2	75·8	76·2
	150	87·6	88·9	89·9	90·8	91·3	91·9
	200	104·5	105·6	106·1	106·8	107·0	—
	25	41·2	43·1	44·6	45·9	46·3	46·9
	70	59·5	60·8	62·3	63·6	64·3	64·8
4·5 M CsCl	100	69·3	70·8	72·2	73·5	74·2	74·8
	150	95·1	95·6	96·3	96·6	97·0	97·4
	200	117·6	122·4	120·5	120·6	120·6	120·8

are very close to the thermochemical value. The results of Lietzke and Vaughen for 0·1 M HCl should be regarded with caution since they exhibit the greatest curvature, and also are furthest from the almost straight line plot produced from thermochemical data. It would not be remarkable to think that the system that has the least contamination in the solution as a whole should have a curve closer to the line derived from the thermochemical data. These reservations concerning published work are prompted by the fact that the thermodynamic calculations are based on the reaction of cell (1), ie

$$Ag_{(s)} + \tfrac{1}{2}Hg_2Cl_{2(s)} \rightarrow AgCl_{(s)} + Hg_{(l)}, \qquad (1)$$
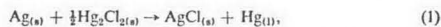
and do not involve the electrolyte, thus not involving liquid-junction pds or hydrolysis.

It would appear that both the Lietzke and Vaughen work and the present suffer from the possibilities of contamination—the former, the more so, because of a less rigorous attempt to confine the dissolved electrode materials, and because rather larger amounts of calomel are generally used in the classical form of the calomel electrode; on this point the results of the present work should be preferred. Lietzke and Vaughen in their paper attribute the curvature to hydrolysis: this factor is
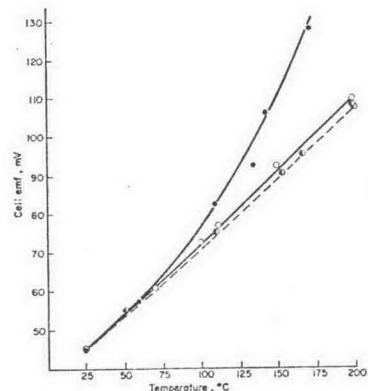
FIG. 5. Cell (1) emf as a function of temperature.
O, this work 50 bar 0·1 M HCl; ●, Lietzke and Vaughen,[4] SVP 0·1 M HCl; ◐, Lietzke and Vaughen,[4] SVP 1·0 M HCl; --- Calculated value based on thermochemical data.[14]

discussed again in the last section of this paper. There is also the possibility that the thermochemical data are incorrect; some of the references given in the Bulletin[14] are very old.

If the data given in Table 1 are fitted by a least-squares procedure to linear or quadratic expressions in temperature or pressure, a relatively high degree of fit can be achieved. The least-square fitting calculations were carried out on an English Electric KDF9 computer. The scatter given for these calculations in the present work is significantly less than that from the Lietzke and Vaughen work, if scatter is defined as $\delta = \pm[\Sigma(\text{observed potential} - \text{calculated potential})^2/\text{D.F.}]^{1/2}$, D.F. being the number of degrees of freedom. The Lietzke and Vaughen data give, 0·1 M HCl call at 25°C, $\delta = \pm 6 \cdot 6$ mV and $\pm 3 \cdot 9$ mV, with $(dE/dT)_{(SVP)}$ $0 \cdot 5_3$ and $0 \cdot 1_8$ mV/deg for a linear and quadratic fit, whilst the work here reported gives $\delta = \pm 2 \cdot 3$ mV and $\pm 2 \cdot 5$ mV, with dE/dT $0 \cdot 38$ and $0 \cdot 3_6$ (50 bar) and $0 \cdot 3_8$ (1·9 Kbar) mV/deg. It seems that, as a general trend, the cell-emf isotherms become more nearly linear as the pressure increases. No experimental comparison can be made for the fits of cell potential with pressure, for lack of published data. The cell-emf/pressure relationship at least up to 2 Kbar seems to be almost linear. Figure 6 demonstrates this property with an example of a plot of cell emf against pressure for CsCl and KCl at 4·5 M and 150°C. If however, a linear or a quadratic expression is used to fit the data for the 0·1 M HCl cell, we obtain $\delta = \pm 0 \cdot 6_5$ and $\pm 0 \cdot 7_8$ and $(dE/dP)_{25°C}$ $2 \cdot 2_0$, $1 \cdot 3_5$ (50 Kbar) $3 \cdot 0_9$ (2 Kbar) mV/Kbar.

Employing the temperature and pressure differentials of the 0·1 M HCl cell to calculate ΔH and ΔV for (1) gives at 25, 100 and 200°C, and 1 Kbar, ΔH 1·52, 1·57,