

THE BEHAVIOUR OF CELLS USING SILVER/SILVER-
CHLORIDE AND SKIN-CALOMEL ELECTRODES
AT TEMPERATURES FROM 25°C TO 200°C
AND 1 BAR TO 2 KBAR PRESSURE*

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Abstract—Electromotive force measurements have been carried out on cells employing the skin-calomel, the thermal electrolytic silver/silver-chloride electrodes and aqueous electrolyte solutions of HCl, KCl, CsCl, at concentrations of 0.1 and 4.5 molality. The cells were measured between 25 and 200°C and at pressures up to 2 Kbar. Discrepancies in cell emf are detected between various workers and the present work ranging from a few tenths of a mV at 25°C to several tens of mV at 200°C. These differences are explained in terms relating to the creation of liquid-junction pds due to solubility and cation complex formation of calomel in these cells.

The skin-calomel electrode in a new and improved form is shown to be a reliable electrode and the standard electrode potentials are derived for the first time at these elevated temperatures. Thermodynamic data pertinent to the over-all cell reactions are also discussed.

Résumé—Des mesures de f.e.m. ont été effectuées sur des cellules formées d'une électrode à pellicule de calomel, d'une électrode Ag/chlorure d'argent thermo-électrolytique et d'une solution électrolytique aqueuse de HCl, KCl ou CsCl, de molarité 0,1 ou 4,5. Ces cellules ont été étudiées entre 25° et 200°C sous une pression pouvant atteindre 2 Kbar. Les écarts entre f.e.m. trouvées par différents auteurs et dans le présent travail s'échelonnent entre quelques dixièmes de mV à 25°C et plusieurs dizaines de mV à 200°C. Ces différences sont expliquées par la création de d.d.p. de jonction, dues à la solubilité et à la formation de complexes du calomel dans de telles cellules.

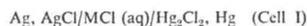
Cette électrode nouvelle à pellicule de calomel apparaît particulièrement fidèle et ses potentiels standard ont ainsi été obtenus pour la première fois à des températures aussi élevées. Discussion complémentaire des données thermodynamiques convenant aux réactions globales de la cellule.

Zusammenfassung—Elektromotorische Kraftmessungen wurden an Zellen unter Verwendung von Oberflächenkalomel, den thermisch elektrolytischen Silber/Silberchlorid Elektroden und wässrigen, elektrolytischen Lösungen von HCl, KCl, CsCl bei Konzentrationen von 0,1 und Molalität von 4,5 vorgenommen. Die Zellen wurden zwischen Temperaturen von 25 und 200°C und Drücken bis zu 2 Kbar gemessen. Abweichungen in Zellen E.M.K. wurden unter verschiedenen Arbeitern und der gegenwärtigen Arbeit festgestellt, die sich von ein paar Tausendstel eines mV bei 25°C bis auf mehrere Zehnfache eines mV bei 200°C erstreckten. Diese Unterschiede werden in Form ausgedrückt, die sich auf die Bildung von Flüssigkeitsberührungspunkt P.D.'s infolge der Löslichkeit und Kationkomplexbildung von Kalomel in diesen Zellen beziehen.

Die Oberflächen-Kalomelektrode in einer neuen und verbesserten Form erweist sich als eine zuverlässige Elektrode, und die normalen Elektrodenpotentiale werden zum ersten Mal für diese erhöhten Temperaturen abgeleitet.

Thermodynamische, zu den allgemeinen Zellreaktionen gehörige Daten werden auch besprochen.

GERKE¹ in 1922 was the first to measure accurately cells involving the silver/silver-chloride and the classical calomel electrode employing 1 M hydrochloric acid in one series of measurements, and 1 M potassium chloride in another as electrolyte solution. He measured the cells between 5 and 35°C. The cell can be written generally as



where M is either H⁺ or K⁺.

In work connected with the estimation of the standard electrode potential of the

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classical calomel electrode, Pouradier and Chateau² were able to redetermine the emf of this cell over a larger range and more frequent intervals in temperature than Gerke. Their measurements ranged from 5 to 70°C. However they used only potassium chloride solutions, and had to rely on the standard electrode potentials of silver/silver-chloride given by Harned and Ehlers.³ The temperature range of study of cell (I) was extended eventually to 200°C by Lietzke and Vaughen.⁴ They reported that the cell became unreliable at 70°C if concentrations greater than 1 M potassium chloride were used. The classical calomel electrode was again used in their work.

The introduction of the skin-calomel electrode by Hills and Ives⁵ and its continued improvement and use reported by Hills,⁶ Grzybowski,⁷ Gupta, Hills and Ives, quoted in 1957 but not published until 1963, and Schwabe and Ziegenbalg,⁸ did not exploit its use in Gerke-type cells. It was not until 1967, in papers by Covington, Dobson and Wynne-Jones¹⁰ that experimental redeterminations of cell (I) with the skin-calomel electrode were attempted. In this work further improvements were made in the preparation and use of the electrode up to 55°C.

In all the studies referred to above, important discrepancies between the different workers' measured cell emfs exist at certain temperatures. Not all the differences can be equated to errors in standard electrode potentials or methods of preparation of electrodes.

The purpose of the work reported in the present paper was to seek the source of some of these discrepancies and to extend the range in temperature of the Gerke-type cells using the skin-calomel electrode to at least 200°C. The experiments were also designed to be carried out at high pressures within the 1–2 Kbar range. The Lietzke and Vaughen work was carried out only at SVP, moreover they did not explain completely the reasons for the failure of the cell at high concentrations. For this latter reason a series of solutions of various salts at high and low concentrations were used.

In 1967, Orion Research Incorporated, USA, introduced a membrane chloride-ion-activity electrode which was marketed to be used at least up to 100°C. Because little had been published at the time about the behaviour of this electrode, and nothing at all on the effects of pressure, one of these electrodes, model No. 94-17, was also incorporated in some of the cells, in addition to the calomel and the silver/silver-chloride electrodes.

EXPERIMENTAL TECHNIQUE

The skin-calomel and the thermal electrolytic silver/silver-chloride electrodes used in the work reported in this paper have been described previously.¹⁰ Solutions were prepared with bromide-free constant boiling hydrochloric acid, three times recrystallized Analar grade potassium chloride, or caesium chloride, and triple-distilled water.

The cell containers made in Teflon, shown in Fig. 1 and also described elsewhere,¹¹ had a thin-walled, pressure-sensitive Teflon bag screwed into the main body. The over-all dimensions of the cell container were 20 cm long by 3.5 cm dia., and the total volume of cell contents was approximately 16 cm³. The electrodes were contained in threaded, cylindrical Teflon units, fitted at one end with a half-inch length of FOS sintered Teflon. These units were screwed into the main cell body, making a three-compartment cell. One of the cell vessels allowed the introduction of the Orion chloride-sensitive electrode into the central compartment. The internal electrolyte solution of the Orion was covered with silicone oil before use. The cell container was

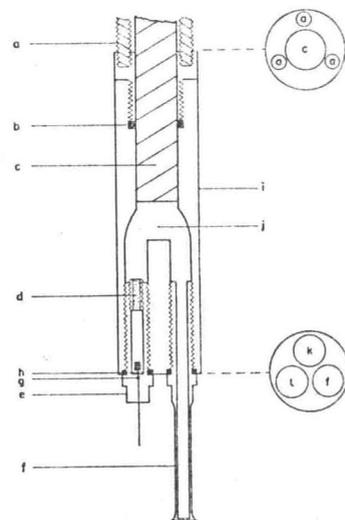


FIG. 1. Design of cell container.

- a, brass studs
- b, Viton O-ring
- c, Orion electrode
- d, Teflon FOS sinter
- e, Teflon electrode holder
- f, pressure-sensitive Teflon bag
- g, electrode seal
- h, excess electrode material
- i, Teflon main body
- j, electrolyte solution
- k, skin-calomel electrode
- l, silver/silver-chloride electrode.

supported in the pressure vessel by a length of brass studding screwed into the pressure vessel head at one end and into the body of the cell at the other.

The pressure vessel was a 500-ml Pressure Products vessel and filled with MS 550 silicone oil. Hydraulic pressure was provided by a C. S. Madan, single-action air-hydropump and measured on high precision Heise gauges fitted with an internal potentiometer. The pressure vessel was maintained at various temperatures by an air-fluidized sand bath. The cell temperatures were measured by a Thermocoax, Cr/Al thermocouple, introduced through the base of the pressure vessel via an Aminco "T" coupling.

Continuous measurement of the cell potential, temperature and pressure were

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

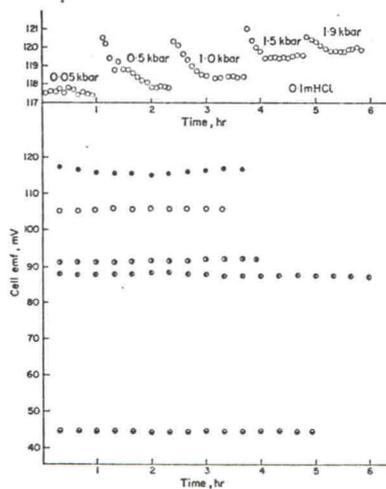


FIG. 2. Stability of cell emf
 ●, 4.5 M CsCl, 50 bar, 200°C;
 ○, 0.1 M CsCl, 50 bar, 200°C;
 ◐, 0.1 M HCl, 50 bar, 150°C;
 ◑, 0.1 M CsCl, 50 bar, 150°C;
 ○, 4.5 M HCl, 50 bar, 25°C.

for 0.1 M HCl as solution, temperature of 200°C and pressure range from 0.050 Kbar to 1.7 Kbar.

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 equilibrated 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

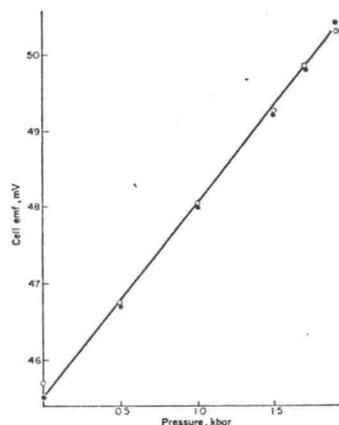


FIG. 3. Effect of temperature hysteresis on 4.5 M KCl cell at 25°C.
 ○, before temperature excursion to 90°C, measurements at 25°C; ●, after temperature excursion to 90°C, measurements at 25°C.

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.

The close confinement of any dissolved electrode species perhaps allows the recrystallization, if any, to proceed more rapidly than if the species were distributed in a relatively large bulk of solution as is the usual case. This physical arrangement should, for the same reasons, also tend to re-establish the mercuric-mercurous complex equilibria for the calomel electrode once a new temperature is reached.

(b) *Effect of solubility of electrode materials on cell emf*

At the commencement of the present series of measurements, it was observed that in some runs, after long periods of time of high stability and low drift at various temperatures, an increase in temperature of a few degrees caused the emf of the cell to fall dramatically to a lower but constant value. This type of observation is clearly presented in Fig. 4, where two curves are shown of cell potential against temperature

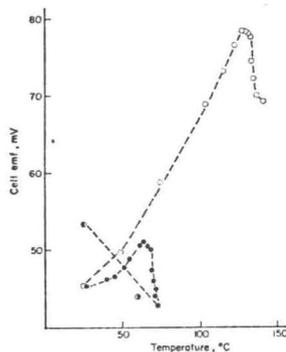


Fig. 4. Effect of solubility of calomel on Gerke cell emf with temperature change. ●, 1 \times excess calomel; ○, 5 \times excess calomel; ●, Final value at 25°C; ○, Final value at 60°C.

which possess very sharp maxima. The magnitude of the fall in the two examples are very much the same, *ca* 10 mV, but occurring at temperatures of 70° and 140°C. The effect of cooling is even more unusual, as the lower curve in Fig. 4 shows that, after falling to approximately 43 mV at 70°C, when the cell was cooled to room temperature the potential followed an increasing linear dependence in temperature, the final cell potential being several mV higher than it was originally at 25°C. Thus in the example given a cell commenced at 25°C with a potential of 45 mV and after being taken to 70°C fell to 43 mV and then when allowed come to 25°C gave 53 mV. A single point given on the figure also shows the potential of the cell when the same cell was taken again to 60°C. Another usual feature of the cell, when it is in the lower potential state, is that, when a pressure run is carried out, $(dE/dp)_T$ is two to three times more than when it is in the normal state. Thus when possessing almost linear temperature dependence or regions before the onset of maxima, $dE/dp_T = 2.49 \times 10^{-3}$ mV/bar is found, whereas 5.8×10^{-3} mV/bar is found in the lower state.

Some relationship with the solubility of calomel can be suggested if the upper curve in Fig. 4 is considered. The upper curve is the result of having approximately five times more by weight of "free" calomel skin in the electrode compartment than in the cell giving the lower curve. Apparently then, quite an excess of calomel skin is required "free" in the electrode compartment. The amounts are of course relative to the particular size of electrode compartment; however for the cells used here, a minimum of *ca* 1g of calomel skin was found necessary to prevent maxima appearing if the cells were taken to 200°C, the volume of each electrode compartment being approximately 3 cm³ and the approximate total volume of cell 20 cm³. It will be seen later, however, that this quantity is also subject to variation depending on the concentration and nature of the electrolyte.

Nothing has been said about the solubility of silver chloride because it is always understood that it is considerably less than that of calomel. Forbes¹³ showed, however, that silver chloride is slightly soluble in the presence of alkaline chloride solutions of differing concentration. Care was always taken to ensure that adequate supplies of solid silver chloride were contained in the electrode compartment. There are other effects that could become apparent if solubilities are not taken into account. One may ask, for example, could the effect of solubility cause the electrode itself to behave improperly, because of removal of silver chloride from the surface to such an extent that the electrode reaction cannot proceed. This possibility could be realized if the electrode were thinly coated, and if no free silver chloride were present. In principle, the silver/silver-chloride reaction needs only a very thin layer of silver chloride on the silver surface; in practice even with the best electrometer available, drawing extremely small currents (10^{-14} A), polarization must occur during a measurement; therefore the thicker the layer the better. If most of the silver chloride layer is allowed to dissolve, non-reversible behaviour may set in. Varying and erratic potentials may then be developed at the electrode, giving a cell potential different from that appropriate to the thermodynamic equation, unless different electrode reactions are invoked. Similar arguments could be considered for the calomel electrode, but there they are of greater complexity. For all measurements succeeding the detection of the maxima discussed earlier, on the upward journey and in any temperature run, observation was continually made to ensure no maxima were encountered.

(c) *Temperature and pressure dependence of cell (I) and comparison with previous workers*

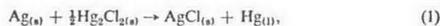
The experimental results of the present study, at two different concentrations 0.1 and 4.5 M of electrolyte for the three salts studied, are given in Table 1 at different temperatures and pressures. The potential of the cell appears to increase both with temperature and pressure. For the purpose of comparison, experimental values of Lietzke and Vaughn at 0.1 M HCl are represented by the uppermost curve in Fig. 5, and a set of calculated values of the cell by the lowest curve; both are shown as a function of temperature. The centre curve is a plot of the data from the present work, taken from Table 1, at 50 bars, also at 0.1 M HCl concentration.

It is clear from the figure that the results of Lietzke and Vaughn at 0.1 M HCl disagree, more than the results presented in this paper, with the calculated values based on thermochemical data, found in Bulletin 476, United States Bureau of Mines, Kelley.¹⁴ Values of Lietzke and Vaughn for 1 M HCl, also shown in Fig. 4,

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

Molality	Temperature °C	Pressure international kilobars					
		0.050	0.500	1.000	1.500	1.700	1.900
		Cell emf mV					
0.1 M HCl	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
	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
4.5 M HCl	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
	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	—	—	—	—	—	—
0.1 M KCl	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
	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
4.5 M KCl	25	—	46.7	48.0	49.3	49.9	50.3
	70	60.5	61.3	62.2	63.0	63.3	63.4
	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
0.1 M CsCl	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
	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	—
4.5 M CsCl	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
	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), i.e.



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

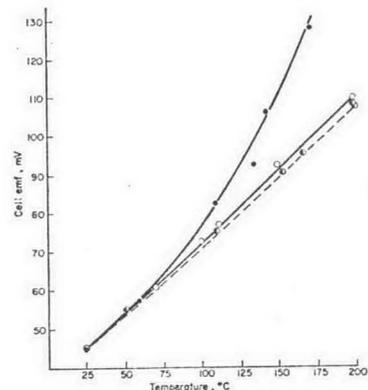


Fig. 5. Cell (I) emf as a function of temperature. \circ , this work 50 bar 0.1 M HCl; \bullet , Lietzke and Vaughen,⁴ SVP 0.1 M HCl; \bullet , Lietzke and Vaughen,⁴ SVP 1.0 M HCl; --- Calculated value based on thermochemical data.¹¹

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 Bulletin¹¹ are very old.

If the data given in Table I 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 $\delta = \pm[\sum(\text{observed potential} - \text{calculated potential})^2/D.F.]^{1/2}$, D.F. being the number of degrees of freedom. The Lietzke and Vaughen data give, 0.1 M HCl cell at 25°C, $\delta = \pm 6.6$ mV and ± 3.9 mV, with $(dE/dT)_{(SVP)}$ 0.5₃ and 0.1₃ mV/deg for a linear and quadratic fit, whilst the work here reported gives $\delta = \pm 2.3$ mV and ± 2.5 mV, with dE/dT 0.38 and 0.3₈ (50 bar) and 0.3₈ (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 $\delta = \pm 0.6_3$ and $\pm 0.7_8$ and $(dE/dP)_{25^\circ\text{C}}$ 2.2₀, 1.3₃ (50 Kbar) 3.0₀ (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,

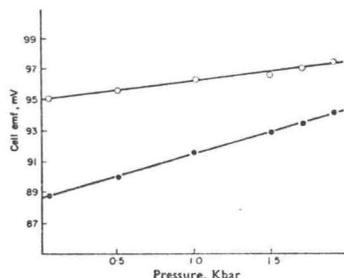


FIG. 6. Dependence of pressure and type of electrolyte on cell emf at 150°C.
O, cell with 4.5 M CsCl; ●, cell with 4.5 M KCl.

1.43 kcal/mol respectively, whilst ΔV for these three temperatures (also at 1 Kbar) is -2.0_9 , -2.2_3 , -1.0_1 cm³. dE/dT 0.3 mV/deg and dE/dP 2.1₉, 2.3₅, 1.6₀ 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 Stoughton¹⁵ 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

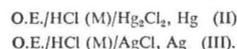
Authors	$E^{\circ}, \text{Hg}_2\text{Cl}_2/\text{Hg}, \text{mV}$				
	25°C	70°C	100°C	150°C	200°C
Various ¹⁻¹⁹	267.93 to 268.23	—	—	—	—
This study (using Lietzke <i>et al.</i> ¹⁵)	268.0 ₄	249.5 ₄	232.9 ₄	195.9 ₄	144.3 ₄
This study (using Izaki <i>et al.</i> ¹⁶)	267.8 ₄	248.6 ₄	231.7 ₄	194.8 ₄	142.7 ₄

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

$E_{\text{Hg}_2\text{Cl}_2/\text{Hg}}^{\circ} = 276.261 - 0.30535T - 8.7170 \times 10^{-4}T^2 - 4.594 \times 10^{-6}T^3$ mV, with a scatter of ± 0.6 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.⁶⁻¹⁰ 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;



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_{111}, mV	-5.1	—	+3.1	—	+2.65	-0.9	+3.8
		E_{11}, mV	-50.3	—	-42.4	—	-45.5	-49.9	-44.8
		$\Delta E = E_1$	+45.2	—	+45.5	—	+48.2	+49.0	+48.6
70°C		E_{11}, mV	—	-6.3	-6.3	-5.3	-5.1	-4.4	4.2
		E_{111}, mV	—	-67.0	-68.1	-67.8	-69.3	-68.1	-68.1
		$\Delta E = E_1$	—	+60.7	+61.8	+62.5	+64.2	+63.7	+63.9
5 M HCl	25°C	E_{11}, mV	-1.7	—	+2.7	+6.9	+10.5	+11.8	+13.2
		E_{111}, mV	+45.6	—	+42.2	+39.1	+36.3	+35.7	+34.7
		$\Delta E = E_1$	+43.9	—	+44.9	+46.0	+46.6	+47.5	+47.9
70°C		E_{11}, mV	+4.8	—	+2.5	+37.5	+51.5	+48.7	
		E_{111}, mV	+52.4	—	+56.4	+22.9	+10.3	+13.2	
		$\Delta E = E_1$	+57.2	—	+58.9	+60.4	+61.8	+61.9	

Thus, for example, taking the value of $E_{11} - E_{111}$ 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 (I) 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. Guntelburg¹⁷ 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

described in a preceding section, were made to ensure the presence of bromide was kept to the absolute minimum.

The second and perhaps the more probable reason, but not the most easily understood, is that relying on the observed difference in solubilities of calomel in the solutions. Covington, Dobson and Wynne-Jones¹⁹ were the first to recognise the possibility and significance of differences in cell potentials from comparisons made with their experimental results of measured cells at different concentrations and different 1:1 electrolytes. In their paper reference was made to the work of Richards and Françon¹⁸ on solubility of calomel at 25°C in solutions of different concentrations and type of electrolyte. It is found that calomel is more soluble in CsCl than KCl or HCl and the least soluble in HCl and low concentrations. For example, at 25°C the amounts of mercuric chloride found¹¹ in 2 N solutions of electrolyte saturated with calomel were 0.015, 0.28 and 0.70 g/l for HCl, KCl and CsCl respectively. In section (b) also it is demonstrated that the solubility can be quite high. In the cells under discussion there will be at times very considerable amounts of mercurous and mercuric ion species. These ions are known to undergo complex formation. The net result would be an alteration in the concentration of chloride and cation in various parts of the cell, principally in the calomel electrode compartment. Since this electrode compartment is separated from the rest of the cell by a very fine and long Teflon sinter, a concentration gradient would be set up. Thus, because of the perhaps very considerable dissimilar concentrations existing, liquid-junction pds could be established and contribute to the over-all cell potential. These apparent liquid junctions can be maintained for lengthy periods and under varying conditions, as the reproducibility of the experimental results demonstrates.

Referring back to the solubility values quoted above, it may be seen that they are equivalent to only a ca 0.003 M solution of HgCl_2 . Since the highest concentration of alkaline salt solution is 4.5 M, the contribution of the charge carried by the mercuric species would be very much less than that by the ions from, say, CsCl. Liquid-junction potentials would, therefore, be significant only at concentrations approaching 0.003 M CsCl. However, the value of 0.003 M HgCl_2 is the concentration of this species alone, and the total concentration of mercuric species in the form of complexes present may well be very much higher. Because no solubility data is available other than the work of Richards and Françon at 25°C, a semi-quantitative estimation of the total dissolved calomel was carried out not only at 25°C but at some higher temperatures by a series of simple solubility measurements. In these measurements varying quantities of solid calomel were sealed in glass tubes containing similar amounts of 4.5 M KCl solutions; Teflon-covered magnets were also contained in the tubes to facilitate stirring. The tubes were heated in an oil bath by a combined heater and magnetic stirrer. Temperatures were noted when the last trace of solid disappeared in each of the tubes. Observations were noted, but only with difficulty, on cooling the tubes of the first reappearance of solid crystals. A temperature range between 25 and 135°C only was possible with this simple arrangement, but an idea of the temperature dependence of solubility can be inferred from the data produced.

A plot of solubility of calomel in 4.5 M CsCl solution as a function of temperature is given in Fig. 7. It is seen that at 25°C the amount of calomel is equivalent to 0.01 M whereas at 135°C the value has risen to 0.5 M. It is also to be noted that the curve of the solubility rises very rapidly when the temperature exceeds 60°C or so; therefore

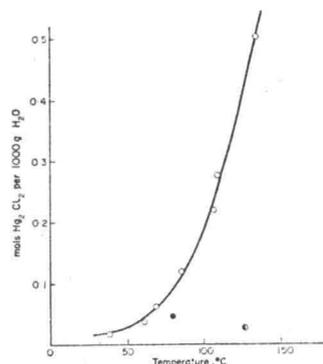


FIG. 7. Solubility of calomel in 4.5 M CsCl solution as a function of temperature. ○, solubility of Hg_2Cl_2 ; ●, solubility of Hg_2Cl_2 in 4.5 M KCl; ◐, solubility of AgCl in 4.5 M CsCl.

at 200°C the solubility could be at least ten times this amount. The graph also shows, by single points, first, the much lower value for the same concentration of KCl, and second, the even lower value for the solubility of silver chloride in 4.5 M CsCl.

The precise formula of the complex species present cannot be ascertained. If we take the empirical formula of the cation complexes, from the chemical analysis of Richards and Françon, CsHg_2Cl_6 , CsHgCl_5 , CsHgCl_4 , Cs_2HgCl_3 , Cs_3HgCl_2 , as a working basis, or consider the complex ions such as CsHgCl_4^- and CsHgCl_3^{2-} from the conductance studies of Foote and Martin,¹⁹ we see that in any of these complexes the proportion of Cl ion to cation or mercuric species is high. This means that the effect on the total change of the difference between the chloride-ion activity in the calomel electrode compartment and that in the main bulk of solution in the cell may be many times that of the calomel solubility. It could be equivalent at least, at 130°C, to a difference of 1 M Cl^- . At these levels of concentration difference the possibility of liquid-junction pd now becomes more likely. To substantiate the possibility of liquid junction pds and to demonstrate their magnitude, a plot of these values as a function of temperature is shown in Fig. 8. The ordinate was obtained by subtracting the calculated value of the cell emf from the values of observed at various temperatures at 50 bar. The thermodynamic data for Ag, AgCl, and Hg_2Cl_2 used for these calculations are taken from the values published by Kelly¹⁴ and are generally based on thermochemical evidence.

The values given in Fig. 8 are for 4.5 M CsCl, this being the electrolyte and concentration that would be expected to show the greatest effect. Values for 0.1 M HCl are also given, to show the least effect. Cell emfs from the work of Lietzke and Vaughen⁴ were treated in a similar manner and are also shown on the graph. It is seen that the points generally lie in almost straight lines and as would be expected CsCl shows a

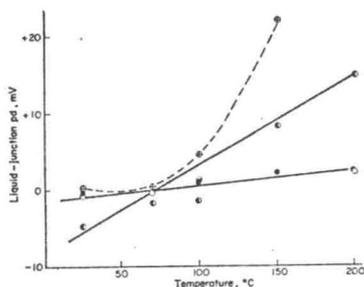


FIG. 8. Variation of liquid junction pd with temperature and with type and concentration of electrolyte.
 O, 0.1 M HCl; ●, 0.1 M KCl; ●, 4.5 M CsCl; ○, Lietzke and Vaughen,⁴ 0.1 M HCl.

greater apparent liquid-junction pd than HCl over the same temperature range. The slope of these lines is approximately 0.1 mV/deg and 0.02 mV/deg, with a total change of 20 mV and 3 mV between 25 and 200°C, respectively.

A third possibility to account for the differences in cell emf shown in Table I could arise from differences in the electrode potential of the calomel electrode itself. The solubility product $K_s = a_{\text{Hg}_2^{2+}} \cdot a_{\text{Cl}^-}^2$ should be obeyed. If K_s is constant for a certain temperature and a_{Cl^-} is changed then $a_{\text{Hg}_2^{2+}}$ must alter. This change in $a_{\text{Hg}_2^{2+}}$ will cause the electrode potential of the calomel electrode to alter.

A further observation on the differences in cell emf obtained for the three types of electrolyte studied, is that in general, the values of cell emf for CsCl tend to be lower than those for KCl or HCl, at least for the highest concentration and lower temperatures. Moreover the emf shown for HCl are generally not in the order of the solubility calomel is least soluble in HCl. This observation shows perhaps the somewhat different characteristic behaviour of the skin-calomel electrode in acid solution as opposed to neutral chloride solutions. This apparently different behaviour has been a persistent though not frequently explored property of the skin-calomel electrode since its original inception.⁵ Some mercuric complex species known to exist¹⁹ in strong acid solutions are certainly protonated; this may account for the characteristics. A relationship between apparent liquid-junction pds and solubility has already been suggested. This solubility must be also directly associated with the extent of complexing and hence involved with stability constants and the further effects of temperature. It would be interesting, therefore, to study the apparent liquid-junction pds over a temperature and pressure range. Attempts could be then made to see if there is any relationship with the changes that are thought to occur in dielectric constant, viscosity or density of "pure" HCl, KCl or CsCl solutions over these temperature and pressure ranges.

Unfortunately, little is known of the dielectric constant of these electrolyte solutions over the large range of temperature and pressure studies here.²⁰ Adequate information is given in the literature only of the dielectric constant of pure water.

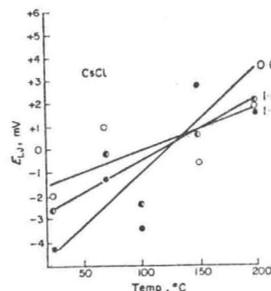
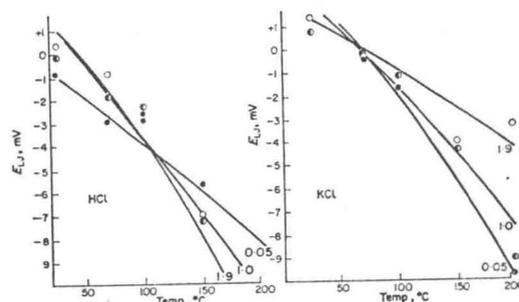


FIG. 9. Variation of apparent liquid junction pd with temperature and pressure.

●, 0.050 Kbar
 ●, 1.00 Kbar
 ○, 1.90 Kbar.

It is known, at least for temperatures up to 40°C, that the dielectric constants of solutions of these salts decrease with increase in concentration and temperature, whilst the dielectric constant of water decreases with increase in temperature, and increases with increase of pressure. These facts demonstrate the well known powerful effect these alkali cations, and high pressures, have on the structural character of water—the decrease of dielectric constant indicating an increase in association constant of a complex or decrease in ionization constant in the case of water. The decrease of complex mercury-cation association or decrease in apparent liquid-junction pd should follow increases in dielectric constant of the solution. Unfortunately what occurs at lower temperatures may not occur at high temperatures or pressures.

Similar qualitative arguments could be invoked for changes connected with viscosity and density; whilst they may prove interesting, if the complete data became available, generally nothing more could be deduced of a quantitative nature.

An unusual result is found if the data in Table I are treated finally in another manner. Assuming that the data derived from the low concentrations of HCl follow (1), the pressure/cell-emf data should represent most closely the changes in compressibility for the components of (1). Therefore $(E_{4.5MCl} - E_{0.1MHCl})$ would represent the apparent liquid-junction pd corrected for pressure at any temperature. A plot of $E_{l,j} = (E_{4.5MCl} - E_{0.1MHCl})$ against temperature, at 0.05, 1.0 and 1.9 Kbar, is given in Fig. 9. Although the scatter seems rather high certain observations are unassailable. For the HCl curve, an increase in pressure causes the negative slope to increase, whilst for KCl, it causes a decrease. CsCl gives a positive slope, decreasing as the pressure increases. Thus following from the argument above, since CsCl mixtures show the greatest lowering of dielectric constant with increase of concentration, *ie* the extent of complexing is raised, the CsCl curve should show the least effect: but the evidence from the figure is to the contrary.

(f) *The over-all cell reaction*

It is certain that reactions other than that required by the Nernst relationship for cell (I) are operable under certain circumstances. Lietzke and Vaughen⁴ considered the hydrolysis of the calomel as a major factor in causing divergences from (1). Their experimental evidence showed that the lower the concentration, the more apparent the curvature and positive deviations. The present data show less divergence from (1) than the Lietzke and Vaughen data. It has been demonstrated in section (c) that the electrode potentials as a function of temperature now reported are closer to the thermochemical calculated values. It should not be forgotten that two entirely different forms of calomel electrode were used in the measurements. Further, Lietzke and Vaughen have suggested that if



or



were operable, very high potentials could be developed—222 mV for process (2) and 703 to 780 mV for (3), depending on concentration and temperature. In the present work, the extent or concentration of the species in these equations must be at a minimum, at least for 0.1 M HCl solutions.

To conclude, no clear explanation can be given for the Lietzke and Vaughen curvature, nor their reported failure of electrode systems in solutions of KCl greater than 1 M. The chemical evidence for hydrolysis cited by these workers is circumstantial. Hydrolysis may be operable, but at concentrations much lower than were studied or reported.

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