

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

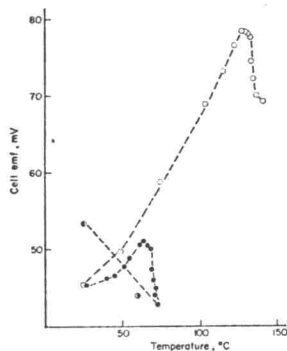


Fig. 4. Effect of solubility of calomel on Gerke cell emf with temperature change. ●, 1 × excess calomel; ○, 5 × excess calomel; ○, Final value at 25°C; ●, Final value at 60°C.

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. For the purpose of comparison, experimental values of Lietzke and Vaughen 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 Vaughen 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 Vaughen for 1 M HCl, also shown in Fig. 4,