

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-Jones¹⁰ 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

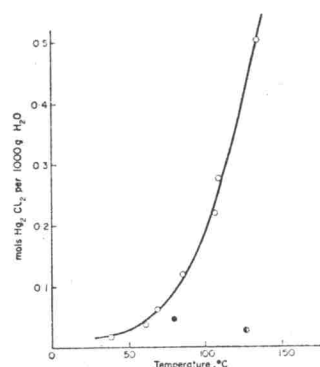


FIG. 7. Solubility of calomel in 4.5 M CsCl solution as a function of temperature. $\circ$, solubility of Hg_2Cl_2 ; $\bullet$, solubility of Hg_2Cl_2 in 4.5 M KCl; $\bullet$, solubility of AgCl in 4.5 M CsCl.

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_7 , Cs_3HgCl_8 , as a working basis, or consider the complex ions such as CsHgCl_4^- and CsHgCl_5^{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, 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