

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 $(E_{4.5\text{MCl}} - E_{0.1\text{MHCl}})$ would represent the apparent liquid-junction pd corrected for pressure at any temperature. A plot of $E_{1,2} = (E_{4.5\text{MCl}} - E_{0.1\text{MHCl}})$ 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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