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 1 could arise from differences in the electrode potential of the calomel electrode itself. The solubility product $K_s = a_{Hg_2^{2+}} . a_{Cl^-}^2$ should be obeyed. If K_s is constant for a certain temperature and a_{Cl^-} is changed then $a_{Hg_2^{2+}}$ must alter. This change in $a_{Hg_2^{2+}}$ 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 exist[19] 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.
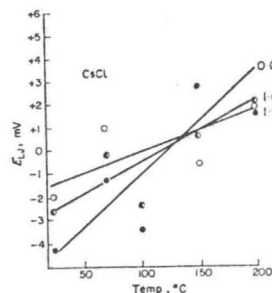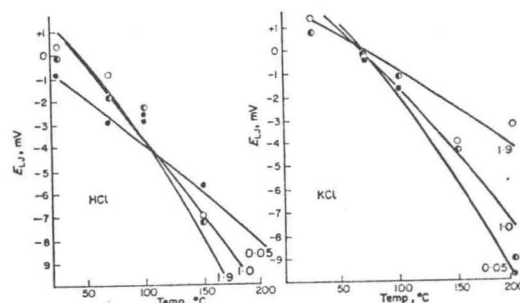
FIG. 9. Variation of apparent liquid junction pd with temperature and pressure.
●, 0·050 Kbar
◐, 1·00 Kbar
O, 1·90 Kbar.

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.