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THE ADSORPTION OF POTASSIUM HALIDES AT

THE MERCURY WATER INTERFACE.

A Thesis presented for the Degree of
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ABSTRACT OF THE THESIS.

Theories of the electrical double layer are critically reviewed and a recent theory of the double layer which takes into account the variation of the specific adsorption of the ions is discussed in detail. On this theory an equation for the differential capacity, which provides a satisfactory explanation for the differential capacity curves is derived. The theory is applied to the interface of mercury with aqueous solutions of potassium halides. The method for calculating the components of charge at the interface is outlined.

The methods available for studying the electrode solution interface are briefly summarised and the reasons for the choice of the electrocapillary method are adduced. The thermodynamic theory of electrocapillarity is considered and the equations for computing surface excesses of anions and cations at a polarisable electrode are derived. The experimental technique used in the determination of electrocapillary curves is detailed and the values of the charge and the surface excesses for the cations and the anions are obtained. Data are tabulated for 17 electrocapillary curves comprising six concentrations each for potassium chloride and potassium bromide solutions and five concentrations for potassium iodide solutions at 25°C. The corresponding charge potential curves and the surface excess curves for cations and anions are illustrated. The limitations in graphical differentiation, used in determining charge values and surface excess values are discussed.

It is shown that the observed surface excesses are in good agreement with calculated values for 1.0N potassium chloride, 0.1N potassium chloride, bromide and iodide solutions. Evidence for the correctness of the characteristic anionic capacities assigned according to this theory for chloride, bromide and iodide ions is adduced.