classical calomel electrode, Pouradier and Chateau[2] were able to redetermine the emf of this cell over a larger range and more frequent intervals in temperature than Gerke. Their measurements ranged from 5 to 70°C. However they used only potassium chloride solutions, and had to rely on the standard electrode potentials of silver/silver-chloride given by Harned and Ehlers.[3] The temperature range of study of cell (I) was extended eventually to 200°C by Lietzke and Vaughen.[4] They reported that the cell became unreliable at 70°C if concentrations greater than 1 M potassium chloride were used. The classical calomel electrode was again used in their work.

The introduction of the skin-calomel electrode by Hills and Ives[5] and its continued improvement and use reported by Hills,[6] Grzybowski,[7] Gupta, Hills and Ives, quoted in 1957 but not published until 1963, and Schwabe and Ziegenbalg,[9] did not exploit its use in Gerke-type cells. It was not until 1967, in papers by Covington, Dobson and Wynne-Jones[10] that experimental redeterminations of cell (I) with the skin-calomel electrode were attempted. In this work further improvements were made in the preparation and use of the electrode up to 55°C.

In all the studies referred to above, important discrepancies between the different workers' measured cell emfs exist at certain temperatures. Not all the differences can be equated to errors in standard electrode potentials or methods of preparation of electrodes.

The purpose of the work reported in the present paper was to seek the source of some of these discrepancies and to extend the range in temperature of the Gerke-type cells using the skin-calomel electrode to at least 200°C. The experiments were also designed to be carried out at high pressures within the 1–2 Kbar range. The Lietzke and Vaughen work was carried out only at SVP, moreover they did not explain completely the reasons for the failure of the cell at high concentrations. For this latter reason a series of solutions of various salts at high and low concentrations were used.

In 1967, Orion Research Incorporated, USA, introduced a membrane chloride-ion-activity electrode which was marketed to be used at least up to 100°C. Because little had been published at the time about the behaviour of this electrode, and nothing at all on the effects of pressure, one of these electrodes, model No. 94-17, was also incorporated in some of the cells, in addition to the calomel and the silver/silver-chloride electrodes.

EXPERIMENTAL TECHNIQUE

The skin-calomel and the thermal electrolytic silver/silver-chloride electrodes used in the work reported in this paper have been described previously.[10] Solutions were prepared with bromide-free constant boiling hydrochloric acid, three times recrystallized Analar grade potassium chloride, or caesium chloride, and triple-distilled water.

The cell containers made in Teflon, shown in Fig. 1 and also described elsewhere,[11] had a thin-walled, pressure-sensitive Teflon bag screwed into the main body. The over-all dimensions of the cell container were 20 cm long by 3·5 cm dia., and the total volume of cell contents was approximately 16 cm³. The electrodes were contained in threaded, cylindrical Teflon units, fitted at one end with a half-inch length of FO5 sintered Teflon. These units were screwed into the main cell body, making a three-compartment cell. One of the cell vessels allowed the introduction of the Orion chloride-sensitive electrode into the central compartment. The internal electrolyte solution of the Orion was covered with silicone oil before use. The cell container was

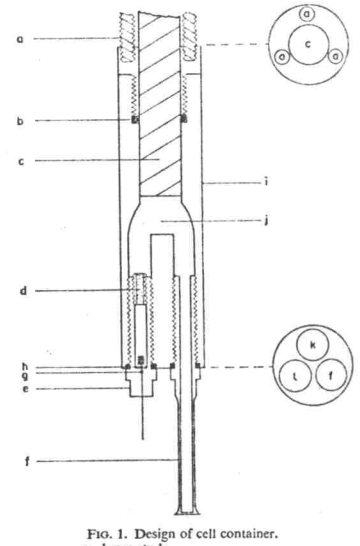

Fig. 1. Design of cell container.
a, brass studs
b, Viton O-ring
c, Orion electrode
d, Teflon FO5 sinter
e, Teflon electrode holder
f, pressure-sensitive Teflon bag
g, electrode seal
h, excess electrode material
i, Teflon main body
j, electrolyte solution
k, skin-calomel electrode
l, silver/silver-chloride electrode.

supported in the pressure vessel by a length of brass studding screwed into the pressure vessel head at one end and into the body of the cell at the other.

The pressure vessel was a 500-ml Pressure Products vessel and filled with MS 550 silicone oil. Hydraulic pressure was provided by a C. S. Madan, single-action airo-hydropump and measured on high precision Heise gauges fitted with an internal potentiometer. The pressure vessel was maintained at various temperatures by an air-fluidized sand bath. The cell temperatures were measured by a Thermocoax, Cr/Al thermocouple, introduced through the base of the pressure vessel via an Aminco "T" coupling.

Continuous measurement of the cell potential, temperature and pressure were