VARIATION OF THE DIFFUSION COEFFICIENT OF FERRIC ION (0.002 M IN 1-N SULPHURIC ACID) WITH TEMPERATURE AND CALCULATION THEREFROM OF THE ENERGY AND ENTROPY OF ACTIVATION

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Received February 10, 1962
(Communicated by Prof. K. S. G. Doss, F.A.Sc.)

INTRODUCTION

There are practically no reliable experimental data available \(^1\) for the diffusion coefficients of individual ions in solutions, containing relatively large concentrations of indifferent salts. Though attempts have been made to determine the diffusion coefficient of various kinds of ions in supporting electrolyte by polarographic method using dropping mercury electrode or linear diffusion electrode, \(^1\) yet the values obtained are likely to be influenced by the suppressor or the other constituents present in the supporting electrolyte. Out of the various methods described under experimental technique for the determination of diffusion coefficient of solutes in liquid, the magnetically stirred porous diaphragm cell method as described by Hammond and Stokes \(^2\) has been reported to yield results of good accuracy. As both surfaces of the diaphragm are continuously swept due to stirring of solutions of both sides, an approximately steady state is reached in the diaphragm and the application of the steady state method developed by Clack (1908-24) can be extended to such a case.

EXPERIMENTAL

A H-type cell, fitted with a fritted glass diaphragm D, of porosity 1G4 in the bridging arm, was used as shown in Fig. 1. The compartment ‘A’ was filled up with the solution of known concentration of the salt of which the diffusion was to be studied, and simultaneously the solvent was poured into compartment ‘B’, so that the layers of liquids in both the columns might stand at the same level, above the entire diameter of the porous diaphragm. The cell was allowed to stand for 30-40 min., so that a steady gradient of the salt might be set up in the porous diaphragm. Then the
solutions of both the compartments were thrown away and the compartments were refilled with the same solutions. The cell was kept immersed in Townson and Mercer X 27 auto-boost thermostat maintained at the desired temperature. The solutions of both the compartments were freed from any traces of air by bubbling nitrogen for a few minutes through the two capillaries provided. The stirrer of the compartment ‘A’ was set in motion. After allowing sufficient time for the steady state to be fully established (i.e., two to three hours), the measurement of variation of concentration of the diffused salt at different intervals of time in compartment ‘B’ was made conductometrically or by an electrochemical method. For conductometric measurements the sidearm ‘C’ of the cell carried a conductivity cell whereas for E.M.F. measurements, the side arm ‘C’ held a calomel electrode. Before proceeding to the study of diffusion of ferric ion, the characteristic cell constant was determined by studying the diffusion of 0.05 N KCl, whose diffusion coefficient as determined by Hartley and Runnicles was $1.89 \times 10^{-6} \text{ cm.}^2 \text{ sec.}^{-1}$ at $25^\circ \text{C}$. The concentration of the