EXPERIMENTAL TECHNIQUES
Sample Preparation

E. Merck reagent grade calcium nitrate tetrahydrate and sodium thiosulfate pentahydrate, BDH analytical reagent grade magnesium nitrate hexahydrate and magnesium chloride hexahydrate, SD analytical reagent grade nickel chloride hexahydrate, and recrystallized (twice from double distilled water) sodium nitrate (BDH reagent grade) were used (each from single bottle) in preparing the solutions. The water used in preparing the solutions was double distilled from alkaline potassium permanganate in a quartz distilling unit. The specific conductance of this water was found to be less than $10^{-6}$ mho cm$^{-1}$. The exact concentrations of the solutions were volumetrically determined by the EDTA titration method. Erichrome Black T was used as an indicator in the cases of Ca(NO$_3$)$_2$·H$_2$O, Mg(NO$_3$)$_2$·H$_2$O, and MgCl$_2$·H$_2$O systems, whereas Murexide indicator was used in estimating Ni$^{2+}$ in NiCl$_2$·H$_2$O systems. The exact concentrations of sodium thiosulfate solutions were determined by titrating against standard potassium dichromate solution. In the case of sodium nitrate solutions exact concentrations were calculated directly by weighing. All the titrations were carried out at 25°C.
Temperature Control

All the measurements were made in a thermostated water bath (Ultra-Thermostat Type NBE). The thermostat consists of an electronic relay (10 amps, 220 volts), an immersion heater of variable heating capacity (270, 400, 800, and 1200 watts), a circulating pressure pump cum stirrer, and a contact thermometer (0.03 amp, 250 volts). The bath temperature was measured with a calibrated check thermometer. The temperature of the thermostat remained stable to ± 0.02° during the course of density, viscosity, and conductance measurements.

Density Measurement

Density measurements of all the solutions were made in a glass dilatometer of ~ 7.0 ml capacity with a stem of about 7 cm length and graduated to 0.01 ml divisions. Each mark on the stem of the dilatometer was calibrated using conductivity water as a reference liquid. For filling the dilatometer with test solutions a hypodermic syringe with a needle of ~ 10 cm length was used.

Viscosity Measurement

The viscosities of all the electrolytic solutions
were measured using a Hoppler BH-2 falling sphere viscometer to 0.5%. This viscometer consists of a cylindrical tube of 15.936 mm inner diameter fixed at an inclination of 10° from the vertical axis. The cylindrical viscometer tube is jacketed with a larger tube through which water from the Ultra-Thermostat was circulated. The temperature of the circulated water in this outer jacket was measured with a Labortherm-N thermometer (GDR). In order to measure the viscosity of a solution, the viscometer tube was first filled with the test solution and a sphere of suitable dimension (depending on the viscosity of the test solution) was slid into this tube. The time required for the sphere to travel a path of 100 mm, which is designated by two marks on the cylindrical tube, was noted. This is repeated till constant value for the time of fall of the sphere was obtained. The viscosity of the solution was then calculated from the formula

\[ \eta = \frac{t}{2} \left( \rho_1 - \rho_2 \right) \]

where \( \eta \) is the dynamic viscosity in cP, \( t \) the time of fall of the sphere in second, \( \rho_1 \) the density (g. cm\(^{-3}\)) of the sphere used, \( \rho_2 \) the density (g. cm\(^{-3}\)) of the solution, and
\( K(\text{cp. cm}^3\text{g}^{-1}\text{s}^{-1}) \) the constant factor characteristic of the sphere used. In this viscometer, since the solution is sealed, the condensation of water vapour at low temperatures and the loss of water at high temperatures are prevented.

In the case of molten salt systems viscosity measurements were made using Cannon-Ubbelohde suspended-level viscometers of viscometer constants \( 4.98 \times 10^{-3} \text{ cm}^2\text{s}^{-2} \) and \( 8.42 \times 10^{-2} \text{ cm}^2\text{s}^{-2} \).

**Conductance Measurement**

The conductances of all the electrolytic solutions were measured using a Philips PR 9500 conductivity bridge and a dip-type conductivity cell with platinized platinum electrodes of cell constant \( 1.081 \text{ cm}^{-1} \). For measuring the conductivity of molten salts a conventional conductivity bridge (ELICO CM 82T Type) and a dip-type conductivity cell of cell constant \( 1.198 \text{ cm}^{-1} \) were used. In both the cases the accuracy of conductance measurements was found to be \( \sim 0.1\% \).

For measuring conductance the sample ( \( \sim 20 \text{ ml} \) ) was taken in a 35 x 100 mm glass tube into which the conductivity
cell was properly fitted. The sample tube was then placed in the thermostat and the electrodes were connected to the conductance bridge.

All the measurements (density, viscosity, and conductance) were made in a descending order of temperature.