CHAPTER - III

EXPERIMENTAL

3.1 GENERAL INTRODUCTION

This chapter deals with the preparation, storage and testing of (Li, Na, K)NO_3 eutectic used in the electrochemical experiments and also of the salts of the electroactive species that have been studied and their purification. The experimental part is further expanded by the addition of description of the apparatus for electrochemical techniques, which has been fabricated in the laboratory. The apparatus can be used successfully for employing the techniques of cyclic voltammetry, chronopotentiometry, chronoamperometry and sampled current voltammetry.

3.2 PREPARATION OF THE EUTECTIC

In literature there are several methods described for preparation of congruently melting eutectics. Most of the eutectics have been used for latent heat storage. Several of these have been patented and even the composition of these eutectics has not been mentioned. An excellent review by Kaufman[97] gives a compilation of the data for these eutectics.

In spite of the fact that the ternary eutectic used in the present work viz. (Li, Na, K)NO_3 has been used and described by several authors (References are given later), the actual preparation of the eutectic was found to be difficult. The method adopted for the same as well as for the storage of the material is described here in detail.

In the compilation of the data regarding the congruently melting materials for thermal energy storage, Kaufman[97] has mentioned about the low melting nitrate eutectic, the composition of which is given as

	$LiNO_3$	+ $NaNO_3$	+ KNO_3
wt %	23.3	+ 16.3	+ 60.4
mole %	30	+ 17	+ 53

As regards the preparation of this eutectic, no specific method has been mentioned. The storage of the eutectic also poses a problem due to the inherent hygroscopic nature of the eutectic. The methods for preparation and storage of the eutectic given below were found most suitable and satisfactory for our purpose. The testing of the eutectic by its physical characteristics like density, melting point etc. confirmed its purity.

The chemicals used for the purpose were

Sodium Nitrate - GR Sarabhai Chemicals

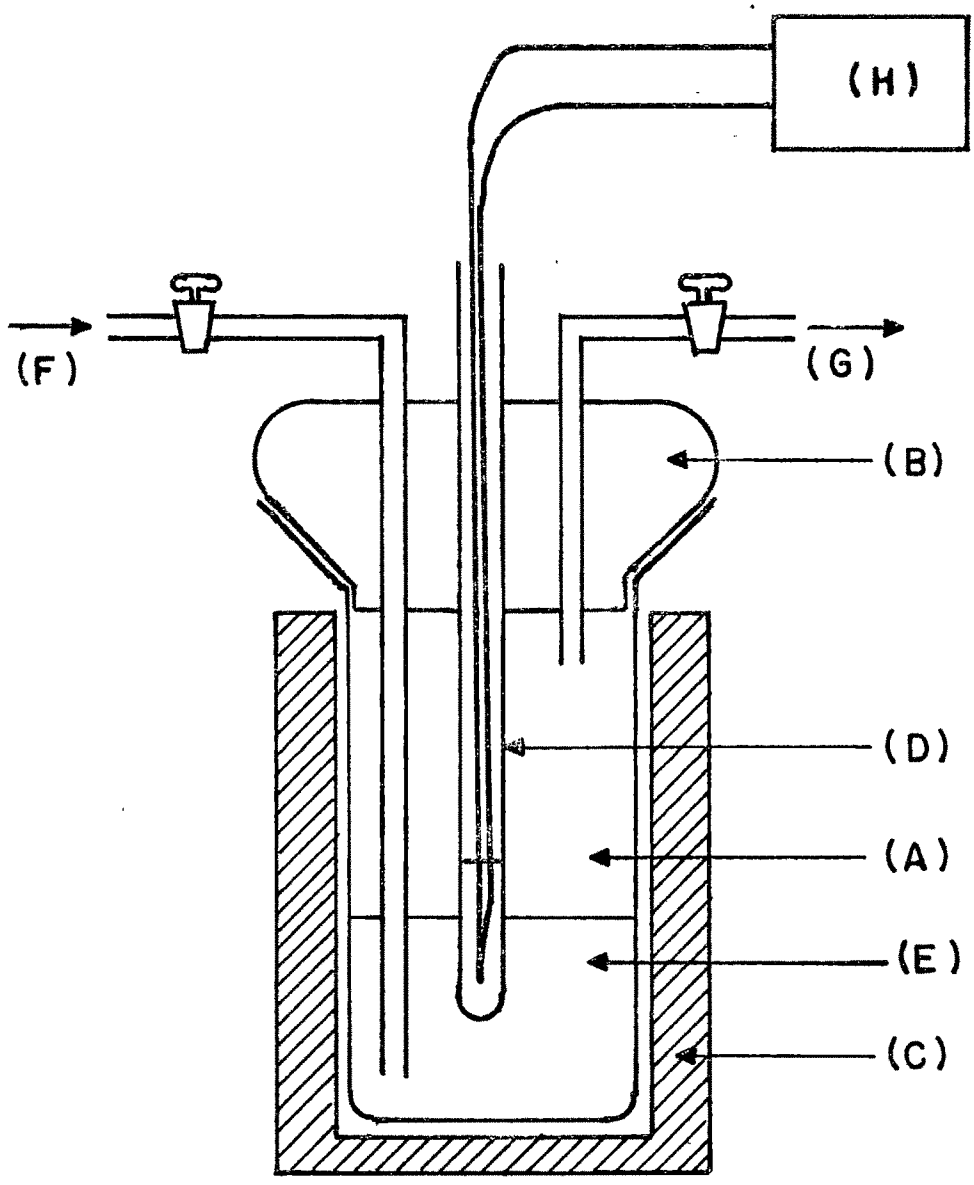
Potassium Nitrate - GR S.D. Chemicals

Lithium Nitrate - AR B.D.H

All the salts were dried at 393 K under vacuum for 12 hours and stored in big vacuum desiccators and taken out just before mixing directly in a dry box. Vacuum was maintained in the desiccator throughout so as to keep moisture level and contact of atmosphere to the minimum.

For preparation of eutectic calculated weights of potassium nitrate, sodium nitrate and lithium nitrate salts were taken in proportions mentioned above and thoroughly mixed in a moisture free argon environment inside a glove box. The homogenity of the mixture was ensured by repetitive mixing of the solid and then the mixture was transferred to the specially made silica vessel that is shown in Fig. 3.1. It was found necessary to use silica containers for all the operations as otherwise nitrate melt etched the borosilicate glass and extracted impurities from it. This vessel (A) having an air-tight lid (B), made of teflon had two tubes, an inlet (F) and an outlet (G) for passing dry argon gas, while the heating was going on. The whole assembly was lowered in a furnace (C) and after starting the argon flow, the furnace was heated slowly, sudden heating being avoided. The temperature of the furnace was raised slowly till the solid mass melted to a clear, transparent liquid and at this point the temperature was measured. The temperature was about 394 K, the melting point for the eutectic. The temperature was then raised to 404 K and was held constant there for several hours, constantly purging with dry argon so as to completely homogenise the eutectic. The temperature of the furnace was controlled by a controller (H).

The eutectic, while in liquid condition, was then transferred into capsules and allowed to cool in desiccator.



(A) SILICA VESSEL (B) TEFLON LID (C) FURNACE (D) THERMOCOUPLE WELL (E) EUTECTIC (F) INLET FOR ARGON (G) OUTLET FOR ARGON (H) TEMPERATURE CONTROLLER

FIG.3.1. ASSEMBLY FOR PREPARATION OF EUTECTIC.

The capsules were then sealed. The solid mass was used as and when required by breaking the capsule and powdering the solid mass under dry conditions. The capsules were otherwise stored in vacuum desiccators.

To test the homogenity of the eutectic, the melting point was taken using a gallenkamp melting point apparatus and compared with the values cited in the literature[97]. The homogenity and composition of the melt was initially and occasionally checked by plotting the heating and cooling curves in cycles in a differential scanning calorimeter. The melt condition was considered satisfactory if the eutectic melted within $\pm$ 2 K of melting point.

The purity of the melt was tested electrochemically by measuring voltammetric residual current over useful potential range. The melt is considered to be pure provided the magnitude of the residual current is negligible relative to the magnitude of the current during experimentation[98].

The respective salts of electroactive ions viz. lead nitrate, nickel nitrate, ferric nitrate, cobalt nitrate and cupric nitrate were dehydrated by drying under vacuum for several hours at 395 K. The water content of these salts was tested by Karl - Fisher and other methods and found to be negligible.

The density of the eutectic melt was determined from buoyant effect on a lead weighted pyrex bob. The bob hung from

one arm of an analytical balance and dipped into the melt which was heated in a resistance-wound vertical tube furnace. The density d_s of the melt at different temperatures was determined to be

$$d_s = 2.103 - 7.9 \times 10^{-4} t \qquad 3.1$$

where t is the centigrade temperature.

For determining the concentration of the solute in the melt, a known weight of the solvent was taken and its volume determined using Equation 3.1. A part of the melt was weighed after the experiment and dissolved in diluted nitric acid. The concentration of the electroactive solute was then determined by atomic absorption spectroscopy and the molar concentration computed.

3.3 APPARATUS

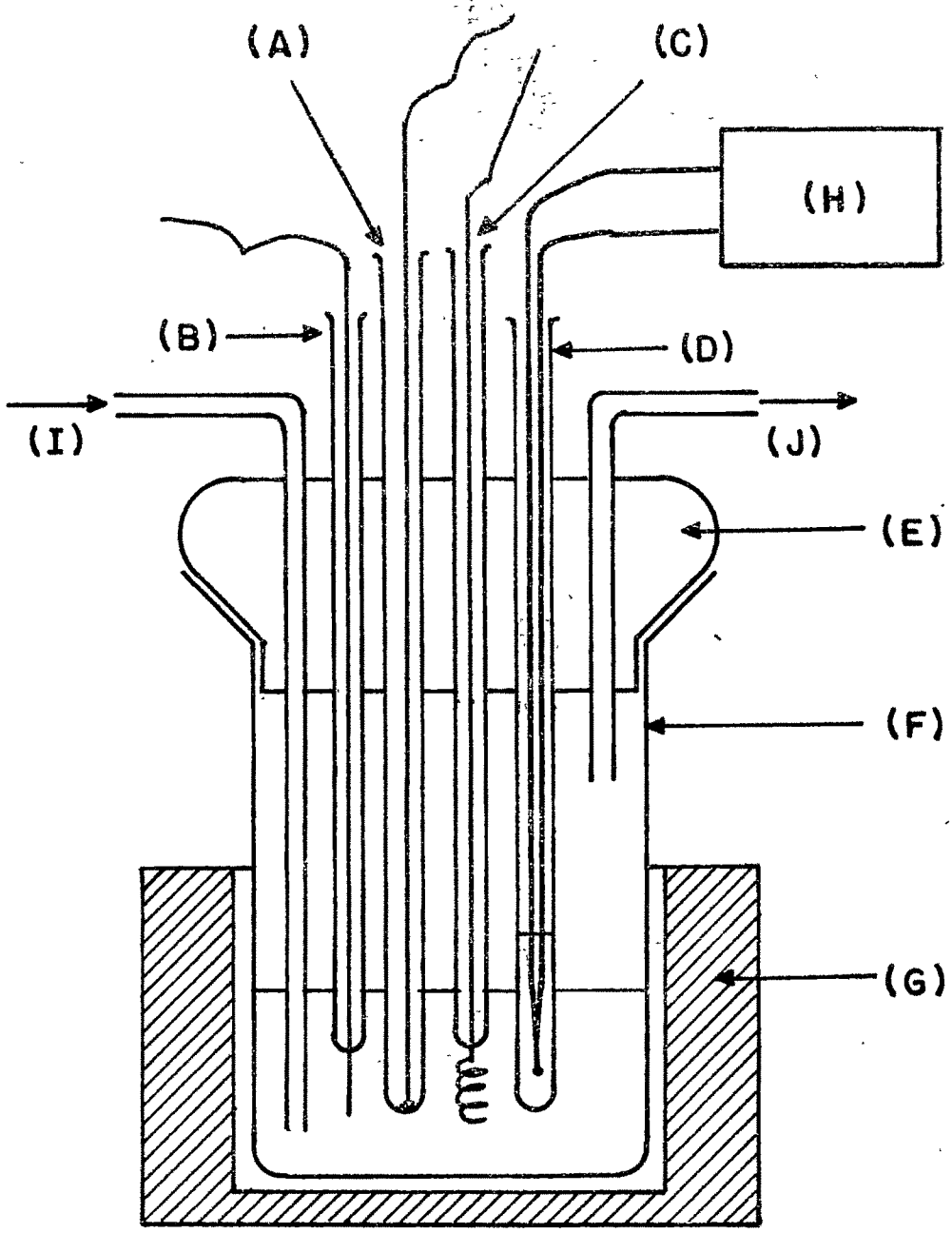
In this section, the details of cell design of the electrolysis cell used in all the electrochemical experiments are given. The fabrication, pretreatment and measurement of the electrode area of platinum microelectrode used as working electrode is described, along with the preparation of Ag/Ag^+ reference electrode. A brief description of the assembly for the control of temperature is also given.

3.3.1 Cell Design

Unlike the electrochemical experiments conducted in aqueous solutions, where temperature is almost always room

temperature, the electrochemical experiments in molten salts need special cell design because the experiments are carried out at higher temperature and during one single experiment the temperature should remain constant with very little variation if at all it varies. Silica glass, quartz and teflon were used throughout while designing the cell.

The basic diagram of the cell is given in Fig. 3.2. A quartz vessel (F) was fitted with a teflon lid (E) through which six holes were drilled. The three electrode system comprising of working electrode (A), reference electrode (C) and auxiliary electrode (B) was inserted with proper spacing of three holes, which in turn decided the spacing between the electrodes. The inlet (I) for the inert gas was a quartz tube reaching near the bottom of cell to ensure passage of gas through out the eutectic. The other hole served as outlet (J) (inert gas). The inert gas before entering the cell system was purified in the following manner. The gas was passed first through a soda lime trap for removing carbon dioxide, then through a tube containing BASF catalyst heated to 800 K and then dried using P_2O_5 and silica gel traps. The temperature was measured using a thermocouple dipping in paraffin oil contained in a well (D) . The temperature of the cell was maintained at any desired temperature within the range of $\pm$ 1 K. The cell was heated in a resistance furnace (G) and



(A) WORKING ELECTRODE (B) AUXILIARY ELECTRODE (C) REFERENCE ELECTRODE (D) THERMOCOUPLE WELL (E) TEFLON LID (F) QUARTZ CELL (G) FURNACE (H) TEMPERATURE CONTROLLER (I) INLET FOR Ar (J) OUTLET FOR Ar.

FIG. 3.2. THE CELL ASSEMBLY.

the temperature of the cell maintained constant through a temperature controller cum pyrometer (H).

3.3.2 The Electrode System

A three electrode system consisting of a working electrode, a reference electrode and an auxiliary electrode was used in all the four techniques, viz., cyclic voltammetry, chronopotentiometry, chronoamperometry and sampled current voltammetry. The working electrode used was a platinum disc electrode while the reference electrode was an Ag/Ag^{+} electrode and the auxiliary electrode a thin platinum wire.

In the following pages is given a short description of the various types of electrodes used in nitrate and other melts together with the reasons for the above choice. The methods of preparation of these electrodes are also detailed below.

3.3.3 Working Electrodes

The choice of the working electrode is mainly governed by the operating temperature, inertness of the electrode material to the fused salt being used and the degree of convenience desired. Various types of working electrodes have been tried. A summary of these is given below.

Liquid metal electrodes[99] are ideal, when possible, because they provide homogeneous smooth surface and uniform

current distribution can be obtained if interfacial tensions are suitable. The dropping mercury electrode has been extensively used, specially in low melting eutectics of binary[100] and ternary[101,102] molten alkali nitrates and in chlorides,[103] ammonium formate, urea, chloroaluminates, thiocynates, acetates etc. upto 453 K. Mercury electrodes have found limited application because they react with several molten salt solutions e.g. molten nitrates above 423 K and also because mercury boils at 638 K. Dropping bismuth[104], lead[105] and silver electrodes have been used with limited success at higher temperatures of 673 K to 773 K. However their use has been restricted to study the deposition of ions of metals less noble than that of the electrode. Also molten metals are partially dissolved in molten salt system and are reported to react with them[104]. It is also quite difficult to have a dropping metal electrode with strictly definite and constant dropping rate in practice. Most workers therefore have preferred to use solid microelectrodes rather than liquid metal electrodes for polarography and other electrochemical investigations in molten salts.

An ideal microelectrode should be very noble and provide conducting surface of known area and geometry. It should also be rugged and durable and the coefficient of expansion of the insulating material should match with that of the metal. The most widely used stationary solid electrodes are platinum[101,106,107], iridium, platinum - rhodium alloy, silver, gold, molybdenum,

tungsten, tantalum, pyrolytic graphite[108,109] and vitreous carbon[110]. Platinum, gold, silver etc. have the advantage over others since they retain their noble metal characteristics in many purified molten salts and are often used in the fabrication of electrodes.

The electrode area and the geometry of the electrode are two important factors for indicator electrodes. The cylindrical electrodes have wire-end protrude out of seal. In planar electrode the seal is ground flush so as to expose only cross-section of wire and spherical electrodes have the wire fused to form a bead. Platinum, gold, tungsten metal wires sealed into glass have commonly been employed. The maximum working temperature would be about 20-50 K lower than the softening point of glass used. Platinum sealed into soda-lead glass (corning 0120) has been used upto 748 K[111]. Similarly platinum and tungsten wires sealed into pyrex and other borosilicate glass have been employed upto 873 K[112].

During the fabrication and due to exposure to the atmosphere, the electrode may have a rough surface and it may be covered with oxide layer formed. So the electrode before use have to be polished to a mirror surface with fine emery or metallurgical alumina.

It is also necessary to give a chemical pre-treatment to the electrode before each set of experiments to avoid any erronaeous results.

The fabrication and pretreatment of platinum microelectrode is given as follows. The disc type electrode was fabricated by first sealing a platinum rod such that a little length of the rod was protruding out of the seal. This protruding part was then carefully cut with the level of the seal so as to expose a uniform disc of platinum. The electrode was then polished to a mirror surface with fine emery and later with metallurgical alumina. Continuity of the electrode was checked and found to be as desired.

In the case of all solid electrodes a chemical pretreatment of the electrode is essential. The platinum disc electrode was given the pretreatment as follows. After thorough polishing of the electrode surface till it shined like a mirror, the electrode was cleaned with 1 : 1 nitric acid by dipping it into nitric acid for a few minutes and then rinsed with distilled water repeatedly. The electrode then was subjected to a potential of +1.4 V vs saturated calomel electrode in 1 : 4 HNO_3 for few minutes. Since the application of extreme anodic potentials results in the formation of platinum oxide on electrode surface with evolution of hydrogen, care was taken not to suddenly exceed this potential. Then the potential was slowly raised till the evolution of hydrogen was visible. The electrolysis was continued for five minutes. The potential was then brought down to zero when the evolution of hydrogen stopped. This was then continued for two minutes. Now the potential was

raised to a small positive value so as to completely remove hydrogen absorbed on electrode surface. After the completion of pretreatment the electrode was washed, dried completely.

For each set of experiments the pretreatment was given to the electrode to minimise the error arising from electrode poisoning.

3.3.4 Area of the Electrodes

Although it is difficult to define true area of a solid microelectrode, for linear diffusion conditions one is mainly concerned with apparent or projected area of the microelectrode. The proportionality of electrolysis current with apparent or projected area of the microelectrode has been shown.

Various methods have been suggested to find out area of the electrode. Simplest is the measurement of area with micrometer screw. Geometrical area most of the time approximates the projected area.

The most popular method which was used in the present work to find out the microelectrode area is as follows. Since chronopotentiometry in aqueous solution is in all other aspects similar to that of fused salts, experiments were conducted with Cd^{++} in 0.1 M aqueous KCl as supporting electrolyte. The deaeration of aqueous solution was done with bubbling of argon. A number of experiments with varying currents and hence with

the transition time in the range of 1 to 100 s was made and the area of the electrode was calculated using Sand's equation where the diffusion coefficient of Cd^{++} in 0.1 M KCl was taken as 0.76×10^{-5} $cm^2 s^{-1}$. This value of the diffusion coefficient for Cd^{++} ions in 0.1 N potassium chloride at 298 K has been determined by Rullfs[113] using several electroanalytical methods. Thalmayer[114] et. al has suggested a similar calibration procedure where the effective area is calculated by chronopotentiometric measurements of Tl^+ in aqueous KNO_3 solution at 298 K with a known diffusion of Tl^+. When using this procedure or applying Sand's equation generally, it should be borne in mind that the equation is only strictly applicable to planar diffusion. Equations have been developed and correction factors computed for cylindrical[115] and spherical[116] diffusion conditions. In the case of all solid electrodes measurement of area is a serious problem[74]. The change in the nature and area of the electrode surface due to metal deposition during electrolysis should be avoided as far as possible.

3.3.5 Reference Electrodes

The reference electrodes used in molten salts are discussed in detail in the form of a general review by R. Laity[117]. Another review by Alabyshev et. al[118] gives a good understanding of reference electrodes in molten salts.

There is no universal reference electrode for the use in molten salts because of different operating temperatures and the different properties of various melts. An electrode reversible to a given ion in one salt system is likely to be reversible to the same ion in most others, provided they do not contain ions with which it might react.

One of the most important factors that favours the reversibility of an electrode is high temperature. For an electrode to be reversible it must pass current easily in either direction. The more slowly the forward and reverse reactions occur the more nearly the electrode approximates the ' ideal polarized electrode ' which acts as a capacitor in adopting any potential applied to it. Thus the reversibility of an electrode depends upon the velocities of oxidation and reduction reactions taking place even when no net current is being passed i.e. the magnitude of the exchange current. Now rates of all reactions are accelerated by increasing temperature; this favours reversibility in molten salts.

Reference electrodes consisting of a metal and its own ions in the melt have been extensively used because of their easy preparation and usually good reproducibility and reversibility. In contrast to this gas electrodes are difficult to prepare and are seldom used in electroanalytical studies in molten salts.

The Ag^+ / Ag half cell has been widely used as reference electrode in molten nitrates[135] and molten cholorides[136,137]. The couple may be the most satisfactory and practical reference electrode because silver has only one oxidation state and there is no problem associated with oxide formation (Ag_2O is unstable at high temperatures) and the couple is stable at high temperatures[117,138]. But the main drawback of this electrode is continuous recrystallisation of silver at high temperatures.

A larger concentration of the metal ion in the melt in contact with metal foil or rod gives the desired depolarizability systems Ag / Ag^+ [139] and Pt / Pt^{++} [100,111,140] have been used as reference electrodes for polarography and were found to be reversible, reproducible and stable with time.

The Pt / Pt^{++} reference electrode has been extensively used in LiCl - KCl eutectic at 723 K. $MgCl_2$ - NaCl - KCl eutectic at 698 K [100] and $MgCl_2$ - KCl [120] eutectic at 748 K. A platinum foil spot welded to a platinum wire is suspended inside a glass frit and Pb^{+2} ($\sim$0.01 - 0.1 M) is generated coulometrically, its formation being the only anodic reaction in the melt at low current densities. The performance of this electrode is very good, but instability has been observed at temperatures above 773 K.

Al^{+++}/Al electrode is a common reference electrode in molten chloroaluminates[119]. Aluminium wire is immersed in the melt which contains Al^{+++} and is separated from main compartment by an asbestos wick.

Several workers have used platinum[112,120-126] silver[127,128], lead[129], bismuth pools and even graphite[130] dipping into the melt. Much polarographic data regarding decomposition potentials, half wave potentials etc. vs these metals as reference electrode have been presented, the potential of each electrode having been considered constant and arbitarily given a zero value. In the absence of a known potential determining equilibrium the function of such a system as reference electrode has not been unambigously interpreted. The possibility arises from anodic generation of a small concentration of metal ions in the vicinity of the electrode surface, but it has also been suggested in the case of halide melts that platinum functions as an oxygen electrode due to the trace of moisture which could be held in melt at relatively high temperatures[131,132]. To some extent, such an electrode may be reversible, stable and reproducible, but it can be regarded as non-polarizable only to a first approximation. The data obtained with such a reference electrode are therefore useful only on a relative basis.

Quite frequently a large noble metal electrode (133,134) is used as a quasireference electrode (QRE) in electroanalytical work . Such an electrode is equivalent to mercury pool electrode in conventional polarography. Such QRE is normally used in three electrode systems.

In the ternary eutectic (Li, Na, K) NO_3 Steinberg and (102) Nachtrieb even used calomel electrode as reference electrode but obviously this electrode cannot be used above the temperature of 473 K .

3.3.6 Preparation of Ag/Ag^+ Reference Electrode

On the basis of the above discussion it was found expedient in the present work to use a Ag/AgCl electrode. The preparation of such an electrode is described below.

A piece of 18 SWG silver wire was sealed in a soft glass tube and the portion outside the sealing was coiled in a spiral. The inside wire extended upto the outside of the tube was used for contact purposes. The spiral was cleaned thoroughly with nitric acid and then washed thoroughly with distilled water to remove last traces of nitric acid. The electrode was then anodised in an electrolyte comprising of 0.1 M of hydrochloric acid with the current density of about 0.4 mA cm^{-2}. The anodising was continued for about 30 minutes, sufficient to give a proper coating of silver chloride on the wire. The electrode was then washed with conductance water

repeatedly and was left in conductance water for two days.

The electrode, so prepared was tested for its reversibility by comparing it with saturated calomel electrode and also by carrying out cyclic voltammetric experiments for aqueous cadmium solution in aqueous potassium chloride as supporting electrolyte.

In the present case the above electrode was made to dip in nitrate melt contained in a quartz tube fitted with a frit. A small quantity of potassium chloride was added to the melt in order to provide Cl^- ions. This electrode served well, giving reproducible values. After use the electrode was taken, washed thoroughly and kept in conductance water.

Reversibility of this reference electrode was indicated by almost immediate return to equilibrium after short anodic or cathodic polarisation. Stability was good to 2 to 3 mV on successive experiments. The sintered porous pyrex frit, while helping to establish electrical contact, prevented contamination of the melt from reference electrolyte and indication was rarely given of any significant assymetry of potential.

3.3.7 Control and Measurement of Temperature

For maintaining a constant temperature environment recourse was taken to a sand bath which was heated by a Nichrome wire wound electrical resistance furnace. Nichrome wire was

wound around a porcelain tube which was covered with special cement. The tube was placed in an aluminium enclosure and insulated with alumina bubbles. The sand bath was placed in the furnace tube and the electrolytic cell in the sand bath. The temperature of the bath was controlled by a proportional temperature controller - Indotherm - 457, the sensing element being a Chromet - Alumel thermocouple. For the measurement of temperature in the electrolytic cell, a thin cylindrical tube containing paraffin oil and a calibrated Chromel - Alumel thermocouple was used. Temperatures could be controlled to $\pm$ 2 K in the bath with this system.

3.4 LABORATORY FABRICATED PROGRAMMABLE POTENIOSTAT WAVE FORM GENERATOR

The potentiostat - wave form generator which was used for the techniques of cyclic voltammetry, sampled current voltammetry and chronoamperometry was fabricated in the laboratory, itself. The performance was excellent and the maintenance was easy as the fabrication was done in the laboratory, itself. The potentiostat wave form generator was capable to provide potentials between + 5 and - 5 V and was also capable of switching from one potential value to another preset potential value. The triangular potential sweep generator could generate scan sweeps of 10 to 100 mV s^{-1}.

3.4.1 Circuit Diagram

The circuit diagram of the apparatus is given in

Fig. 3.3. The circuit is based on the work done by Bhagat and Santhanam[141]. However, the use of high performance integrated circuit operational amplifiers is incorporated in the present apparatus.

The main component of the operational amplifier IC - 2, is AD 517 low cost laser trimmed precision I.C. operational amplifier and is responsible for the control of current through the electrolysis cell. The potential developed on the reference electrode by this current is detected by voltage follower, IC - 3 and also AD 517.

There are three inputs to control operational amplifier IC - 2 which are summed at the inverting input of IC - 2. These inputs are

(A) The initial potential supplied by the helipot HP_2 or HP_3.

(B) The ramp input supplied by the integrator IC - 1 (AD 515) and

(C) The potential of the reference electrode

The control operational amplifier IC - 2 controls the current through the cell in such a way that the sum of the three inputs at the summing point is zero. The magnitude of the current is measured by measuring the voltage drop across a standard resistor R_m placed in series with the cell.

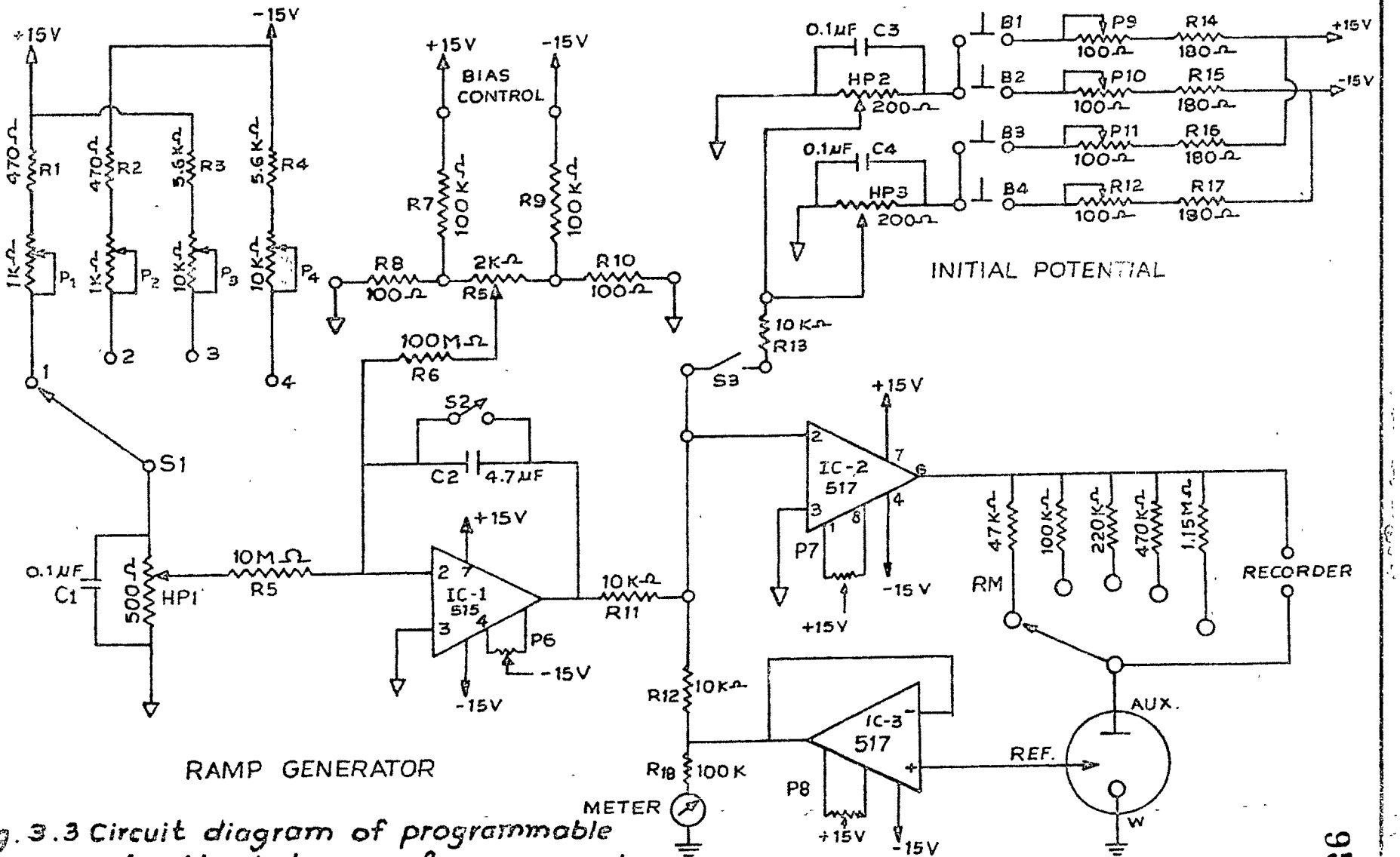


Fig. 3.3 Circuit diagram of programmable potentiostat-wave form generator.

3.4.2 The Voltage Sweep Generator

The helipot HP, has a total voltage of + 5 V or - 5 V across it when it is connected to + 15 V or - 15 V DC supply through R_1, P_1 or R_2, P_2 respectively. The polarity of this voltage is selected by the switch S_1. The wiper of HP_1 has a voltage V_1 which can be varied between 0 and $\pm$ 500 nA through 10 megaohm resistor, R_5. This current flows through C_2, the feed - back capacitor of the operational amplifier IC - 1 to produce a highly linear output voltage ramp V_c having a slope from 0.0 to 100 mV sec^{-1}. The bias voltage V_b applied through a resistor R_6 produces a bias current I_b equal to the input bias current of the negative input terminal of the operational amplifier IC - 1. The potentiometer P_6 is used to adjust the input off - set voltage of the operational amplifier IC - 1 to zero. The switch S_2 is usually kept closed keeping the integrating capacitor discharged and is opened only to start the voltage sweep.

To get a fine control of the lower sweep rates between 0 and 20 mV s^{-1}, the potentiometers P_3 and P_4 are adjusted to produce a voltage drop of + 1.0 V and - 1.0 V across helipot HP_1 when switch S_1 is connected to positions 3 and 4 respectively.

3.4.3 The Reference Voltage Follower

The potential of the reference electrode must be measured without drawing any current from it. This is done by

using a voltage follower based on a field effect transistor (FET) input operational amplifier AD 517. This gives extremely high input impedance (approx $10^{14}\Omega$) and has extremely low bias current. The potentiometer P_8 is used to adjust the off-set to zero. The output V_R is connected to the summing junction of IC-2 through a resistor of R_{12} of 10 KΩ.

3.4.4 Initial Voltage Circuit

In electrochemical experiments it is sometimes required to switch from one preset potential to another. This function is incorporated in the apparatus by using two separate helipots HP_2 and HP_3 for two different potentials.

The voltage V_1 is supplied by the helipot HP_2 which is connected to + 15 V or - 15 V d.c. supply through P_9 and R_{14} or P_{10} and R_{15}. The voltage of + 5 V or - 5 V is supplied by HP_3 by connecting it to + 15 V or - 15 V d.c. supply through P_{11} and R_{16} or P_{12} and R_{17} respectively. The voltage V_1 is fed to the summing junction, S, of control amplifier IC-2 through resistor R_{13} of 10 KΩ.

3.4.5 Calibration of Initial Set-up

The apparatus was calibrated as follows.

1. The potentiometer P_1 and P_2 were adjusted to produce voltage drop of + 5 V to - 5 V across helipot HP_1 when switch S_1 is connected to positions 1 and 2 respectively.

2. The potentiometer P_9 and P_{10} are adjusted to produce a voltage drop of +5 V or -5 V across the helipot HP_2 likewise P_{11} and P_{12} also adjusted to produce a voltage drop of +5 V or -5 V across the helipot HP_3.

3. The input offset of operational amplifier IC-1 is adjusted to zero with P_6.

4. The bias current of operational amplifier IC-1 is nutralized by making V_I zero, putting on S_2 to start the integrator of the input bias current of IC-1 and adjusted P_5 so that output voltage V_c remaining constant to zero.

5. The reference electrode and working electrode are shorted and P_8 is adjusted to zero the offset of op. amp. IC-3.

6. The offset voltage of operational amplifier IC-2 is adjusted to zero by P_7.

For adjusting the forward and reverse sweep rates, the reference and auxiliary electrodes are shorted and the output signal across the reference electrode and the working electrode is recorded on a strip chart recorder Philips Model PM 8100. The triangular wave of voltage vs time is recorded. The wiper of the helipot HP_1 is set for the full length and the potentiometers P_1 and P_2 are adjusted in such a way that both the forward and reverse waves have the same slope of

100 mV s^{-1}. In the same way P_3 and P_4 are adjusted to yield the triangular waves with slope of 20 mV s^{-1} for the full length of the helipot HP_1.

3.4.6 Constant Current Source for Chronopotentiometry

This apparatus also was fabricated in the laboratory and was a stabilised d.c. supply of 30 V. The resistors for fabrication were so chosen as to minimise heat effects. The current could be adjusted from 50 μA to 1 mA and maintained constant even though load resistance varied from 0 to 12 KΩ. The value of the constant current obtained from the source was accurately measured by measuring the fall of potential across a standard 1 KΩ resistance in series on a model strip chart potential recorder. The value of the resistance of the assembled cell was found out by conductometric method and it never exceeded 1 KΩ and hence the value of standard resistance was chosen as 1 KΩ.

In order to use the apparatus for current reversl, chronopotentiometry, a provision for reversing the direction of the current was provided DPDT key mounted on a 1 cm thick perspex sheet to avoid loss of current.

3.4.7 Measuring Circuit

Cyclic voltammograms were recorded on a Philips PM-8100 model strip chart recorder which had a high input resistance of 1 M in the range of 0.01 mV - 10 V. The

response was less than 1 sec. for full scale deflection. The chart speed was constant with specified time and was checked with a precision chronometer. The available chart speeds ranged from 0.04 s mm^{-1} to 24 s mm^{-1} range. The voltage span for 250 mm width chart could be adjusted with the help of a standard weston cell.

The same recorder was used for sampled current voltammetry, chronoamperometry and chronopotentiometry. Occasionally, an Omniscribe Recorder was also used with due precautions.

3.5 PROCEDURE

For all these techniques, the procedure adopted were the same. The cell assembly was used for all the four techniques, with modifications only for the application of voltage and the measuring system.

For assembling the cell, the cell was cleaned with nitric acid several times and then rinsed with tap water and finally distilled water. The cell was then washed with alcohol and dried in an oven at 383 K for 2 hours. The temperature of the oven was then raised to 473 K in order to bake the cell free of adsorbed moisture. The cell was then transferred to a vacuum desiccator kept over P_2O_5.

A known weight of the eutectic was then transferred into the cell after breaking an evacuated capsule containing

the solid melt. Known quantity of the electroactive salt in the anhydrous form was then added in the melt and the cell was placed in the heated sand bath, precautions being taken to avoid contact of the melt with atmosphere. As soon as the eutectic melted the electrode assembly was fitted to the cell and the bubbling of argon gas was started. The cell was kept for 24 hrs. in the melted condition of eutectic with the bubbling of argon through out. This ensured the complete homogenisation and solubility of the electroactive salt and would help the complete removal of moisture from the melt. The electrode connections were then made to the potentiostat or the constant current source, as the case may be and the recorder, this procedure was adopted for all the techniques.

Description of the parameters measured, the shape of the curves and all other particulars are given in chapter IV.