

CHAPTER-II

EXPERIMENTAL

The present investigation comprises the study of transport processes such as electro-kinetic effects of solutions involving acetonitrile and thermodynamic properties such as activity coefficients of cadmium chloride and cadmium sulphate in water and aqueous acetonitrile, thermodynamic functions of transfer of cadmium chloride and cadmium sulphate from water to aqueous acetonitrile. The experimental part of these studies has been discussed under the following sections for convenience of presentation.

#### II.1 Reagents

#### II.2 Determination of electro-kinetic parameters

#### II.3 Determination of thermodynamic parameters

### II.1 REAGENTS

The reagents acetonitrile, nitromethane, acetone, cadmium chloride, cadmium sulphate, mercurous chloride, mercurous sulphate, water and mercury were purified as described below:

#### Acetonitrile (ACN)

Acetonitrile (BDH), after standing over anhydrous calcium oxide for about 48 hours was shaken vigorously with phosphorous pentoxide ( $P_2O_5$ ) and was distilled. The first fractions were discarded and the middle fraction was refluxed

again over calcium oxide and refractionated to obtain the acetonitrile for the present studies. The density of acetonitrile at 25°C used for the study was 0.7770 gm/ml which is comparable with the standard value<sup>1</sup>.

### Nitromethane (NM)

Nitromethane (BDH) was first dried by keeping over anhydrous calcium chloride for about 24 hours. Then it was purified by simple distillation over fused calcium chloride and was stored in air tight bottles for the present studies. The physical constants of nitromethane at 25°C, such as density, viscosity and specific conductance, determined were 1.130 gm ml<sup>-1</sup>, 0.614 (cp) and 2.0x10<sup>-6</sup> ohm<sup>-1</sup> cm<sup>-1</sup> respectively. The density and viscosity values are in agreement with the literature values<sup>1</sup> viz.,  $d = 1.1300 \text{ gm ml}^{-1}$   $\eta = 0.612 \text{ cp}$ .

### Cadmium Chloride

Cadmium chloride (A.R.) was used as such.

### Cadmium Sulphate

Cadmium sulphate was crystallised<sup>2</sup> from distilled water by partial evaporaton in a desiccator.

### Mercurous Sulphate

Mercurous sulphate was prepared by treating mercurous nitrate with sulphuric acid. Mercurous nitrate was prepared

as described elsewhere<sup>3</sup>. According to this method, mercury was treated with cold dilute nitric acid. A low temperature and dilute nitric acid favour the formation of crystals with a large proportion of water of crystallisation. The rate of formation of crystals of mercurous nitrate increases if the mercury and the acid are heated on a water bath. Crystals of mercurous nitrate so obtained were treated with dilute sulphuric acid to obtain mercurous sulphate. The acidified mercurous nitrate solution was dropped from dropping funnel with constant shaking in a beaker containing sulphuric acid of 1-6 percent strength. The contents were then allowed to settle and solution was decanted to remove excess of sulphuric acid. Mercurous sulphate so obtained was repeatedly washed with distilled water to remove last traces of sulphuric acid. It was then dried before use.

### Mercurous Chloride

Mercurous chloride used was of A.R. grade. It was used after drying over phosphorous pentoxide in vacuum desiccator.

### Conductivity Water

Water needed for preparing various solutions was obtained by distilling thrice in an all glass double distillation unit supplied by "Scientronic Instruments India Limited". The specific conductance of the distilled water was of the order of  $10^{-6} \Omega^{-1} \text{cm}^{-1}$ .

**Mercury**

Mercury was of Analar grade and was used without further purification.

**II.2 DETERMINATION OF ELECTRO-KINETIC PARAMETERS**

The design of the apparatus and its experimental set up is shown in **Figure II.1**

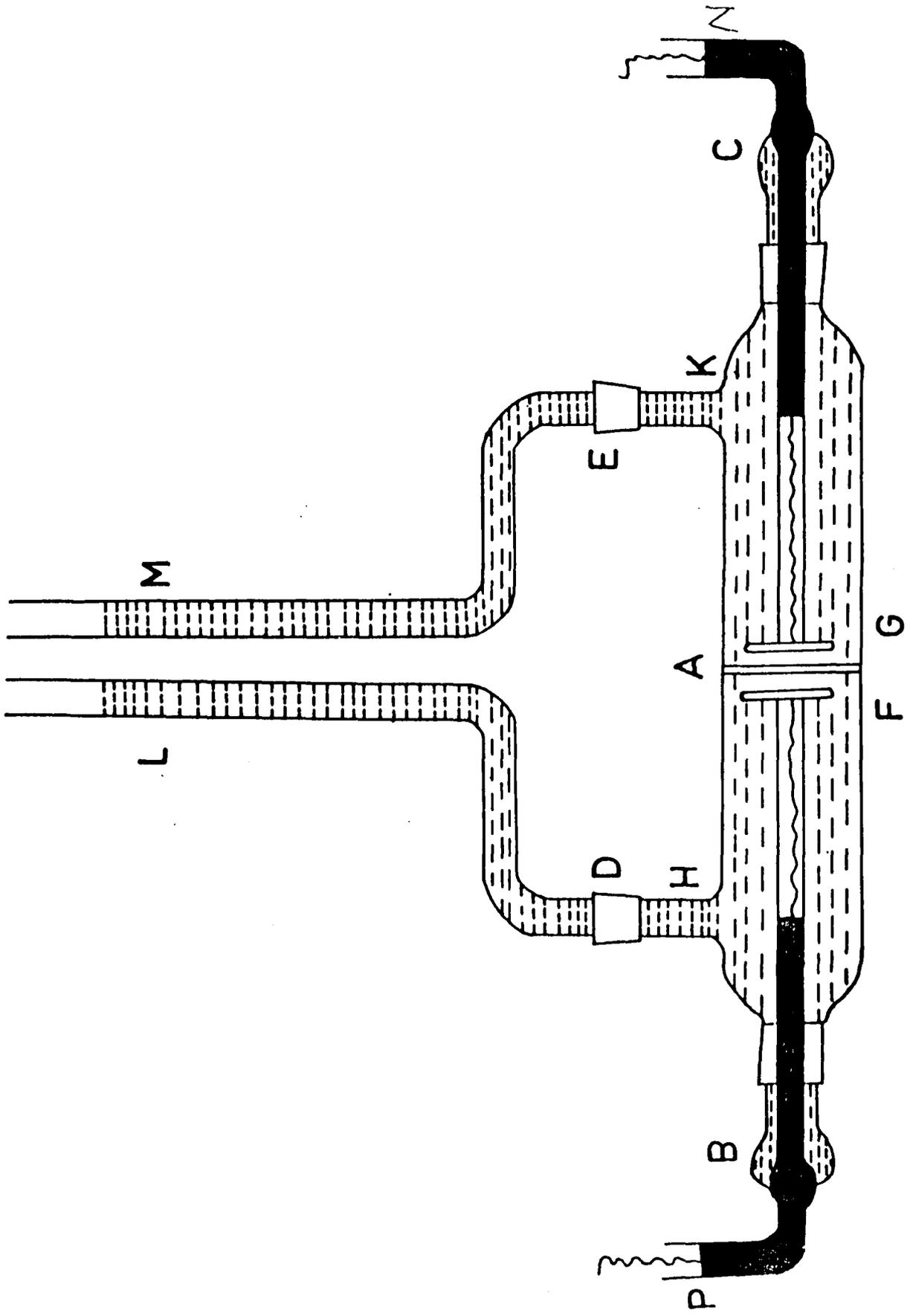


FIG.1. APPARATUS FOR STUDYING ELECTRO-OSMOSIS

## [SECTION A]

### The Apparatus

The apparatus consists of a pyrex tube of length 24 cm and of diameter 2.55 cm in the middle of which is fused a sintered glass disc A of porosity  $G_3$ . This tube has two standard B-24 female joints B and C at the ends. Perforated platinum discs F and G are fixed to the standard B-24 male joints with the help of platinum wires. The entire length of each electrode, except the perforated disc is sealed in a glass tube of diameter 0.50 cm in order to insulate it from the liquid medium. The length of these glass tubes is adjusted in such a way that the platinum discs approached very close (within 2 mm) to the sintered disc, when the standard joints are kept in position. The main pyrex tube bears two side tubes H and K to which tubes L and M of  $0.0836 \text{ cm}^2$  cross sectional area are connected through standard taper joints D and E in such a way that both the tubes are kept parallel and close together. These tubes are graduated in cm scale.

### Temperature Control

The apparatus shown in **Figure II.1** was set up in an air thermostat, the temperature of which could be controlled upto  $\pm 0.05^\circ\text{C}$ . A thermometer, a mini fan, an electric heater and an electronic relay helped to control the temperature of the thermostat. For the present study, all measurements were made at  $25^\circ\text{C}$ .

### Experimental Procedure

The apparatus was washed thoroughly with concentrated nitric acid and finally with conductivity water. Conductivity water was forced through the disc under pressure in order to remove last traces of the acid. The apparatus was filled by adding the solution under investigation on one side of the disc and then forcing it to the other side under a pressure gradient by means of a vacuum pump. This ensured the complete filling of the capillaries of the disc. The tubes L and M were then introduced and the solution under investigation was introduced into them by means of a syringe to bring the solution to a desired level. Mercury was introduced into the tubes P and N to make the contacts of the electrodes. The apparatus was suitably mounted inside the thermostat where it was allowed to attain a constant temperature. A constant D.C. Voltage was then applied and the level of the solution goes up in one limb and down in the second limb. The time required for the level of the solution in the tube L and M to reach different levels was recorded. The time required to reach one level was recorded six times and the average of these six readings were used for calculations and analysing the data. The time was recorded by means of a stop watch capable of reading upto 0.1 second. Such experiments were repeated for three values of the voltages varying from 40 to 60 volts at 25°C.

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The electro-osmotic pressure can be determined with the help of the apparatus described in **Figure II.1** Since electro-osmotic pressure is the hydrostatic pressure difference in the two tubes L and M, the electro-osmotic experiments allowed to continue till the flow due to electro-osmosis stops.

## [SECTION B]

### Sources of Error and Precautions Taken

The various sources of error and factors responsible for affecting reproducibility are discussed in the following:

#### (i) Polarisation of the Electrodes

Evolution of gases can take place at the electrodes on account of the possibility of polarisation at the electrodes. There is, therefore, likelihood of gas bubbles sticking to the sides of the electrodes which may introduce significant error in the flow of the solution. It was found negligible because of the small magnitude of the current passing through the electro-osmotic cell.

#### (ii) Incomplete Wetting of the Sintered Disc

The rate of flow of the solution depends on the actual number of capillaries transmitting the liquid. Accordingly, if all the capillaries may not be wetted, poor reproducibility can result from one experiment to another. This was avoided

to a greater extent by introducing the solution after evacuation of the apparatus and preparation of the solutions from degassed water.

### **(iii) Absorption of Carbon Dioxide from the Atmosphere**

Since zeta-potential is known to be very sensitive to impurities<sup>4,5</sup>. Absorption of gases such as carbon dioxide etc. is likely to affect the zeta potential and hence affecting the reproducibility of the results. This was minimised by using the guard tubes of lime and sodium hydroxide.

## **[SECTION C]**

### **Measurement of Density**

The density measurements needed for the calculations of phenomenological coefficients and other parameters were made with the help of a bicapillary pycnometer (shown in **Figure II.2**) described in the following:

### **Caliberation and Working of the Pycnometer**

Before fabrication of the pycnometer, the capillaries (A and B) were caliberated by measuring the length and weight of a mercury thread. The length of the thread was measured with the help of a travelling microscope capable of reading

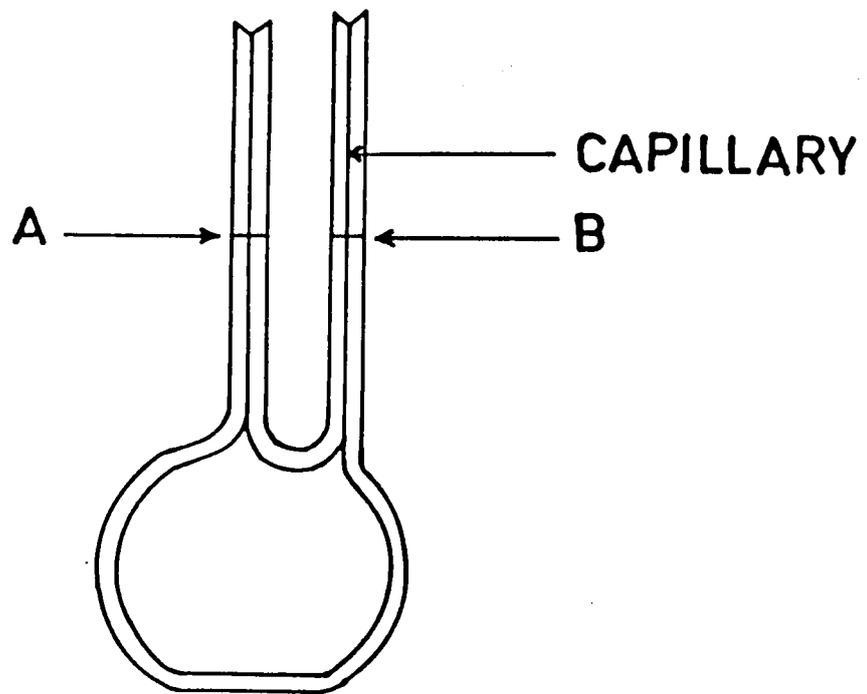


Fig. II.2. Pycnometer

upto 0.001 cm. The capillaries had small bores to avoid the evaporation of the volatile component during the course of the measurements. Different reference marks were etched on both the limbs A and B of the pycnometer.

Before calibrating, the pycnometer was cleaned by filling it with chromic acid solution and then flushing it with distilled water under pressure. It was then dried first with hot air blower and finally dried by placing it in a vacuum oven and weighed repeatedly until a constant weight was obtained. The calibration was done with water having a specific conductance  $1.3 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ . The pycnometer was filled with water by means of a syringe having a long needle and then it was mounted suitably in the thermostat. The difference in the level of the liquid and the reference marks were read with the help of a cathetometer capable of reading upto 0.001 cm. The experiment was repeated four times and the volume thus determined was reproducible within  $\pm 0.001$  ml. The volume of the pycnometer at  $25^\circ\text{C}$  was found to be  $11.738 \pm 0.001$  ml.

### Procedure

The pycnometer before each reading was cleaned thoroughly with distilled water and then with pure acetone and was then dried with hot/<sup>air</sup>blower followed by drying it in a vacuum oven.

The pycnometer, after filling with the solution whose density is required to be determined, was dried with a flannel cloth. No air bubbles were left trapped in the solution in the pycnometer. After filling the pycnometer, it was suitably mounted inside the thermostat. It was allowed to attain a constant temperature before the difference of the liquid level from the reference mark was noted. This difference was noted again with the help of a cathetometer. The pycnometer was then removed and weighed. The accuracy of the experiment was checked by determining the density of pure acetonitrile at 30°C. It was found to be  $0.77154 \text{ gm cm}^{-3}$  which is in good agreement with the literature<sup>6</sup> value of  $0.77148 \text{ gm cm}^{-3}$ .

### II.3 DETERMINATION OF ACTIVITY COEFFICIENT AND THERMODYNAMIC FUNCTIONS OF TRANSFER

The determination of activity coefficient and of the thermodynamic functions of transfer of cadmium chloride and cadmium sulphate from water to acetonitrile + water mixtures have been carried out from the electromotive force measurements of the cell (I) and (II).



The method of measurement of the electromotive force of the cells (I) and (II) has been discussed under the following

sections for convenience of presentation:

- A. Preparation of amalgams
- B. The Apparatus
- C. The Experimental Procedure
- D. Sources of Error

A) Preparation of Amalgams

Saturated cadmium amalgam<sup>7</sup> was prepared by dissolving cadmium in nine times its weight of pure mercury with gentle heating. A higher cadmium content should be avoided, however, as the amalgam then becomes inconveniently stiff, the amalgam was stored under 0.1M perchloric acid. Prior to use it was washed with perchloric acid to remove traces of cadmium (II).

B) The Apparatus

The e.m.f. cell used for the study is shown in **Figure II .3**. The cell consists of two pyrex glass tubes, each 20 cm long and 2.5 cm in diameter, at the bottom of which are fixed two platinum wires. The two tubes are joined together at the centre by another tube which is provided with a stop cock. Contact of the platinum wires with the inside solution of the cell was made with mercury. The platinum wire in one limb of the cell was covered with the amalgam and that in the other limb in case of cell (I) with  $\text{Hg}/\text{Hg}_2\text{Cl}_2$  (s) and in case of

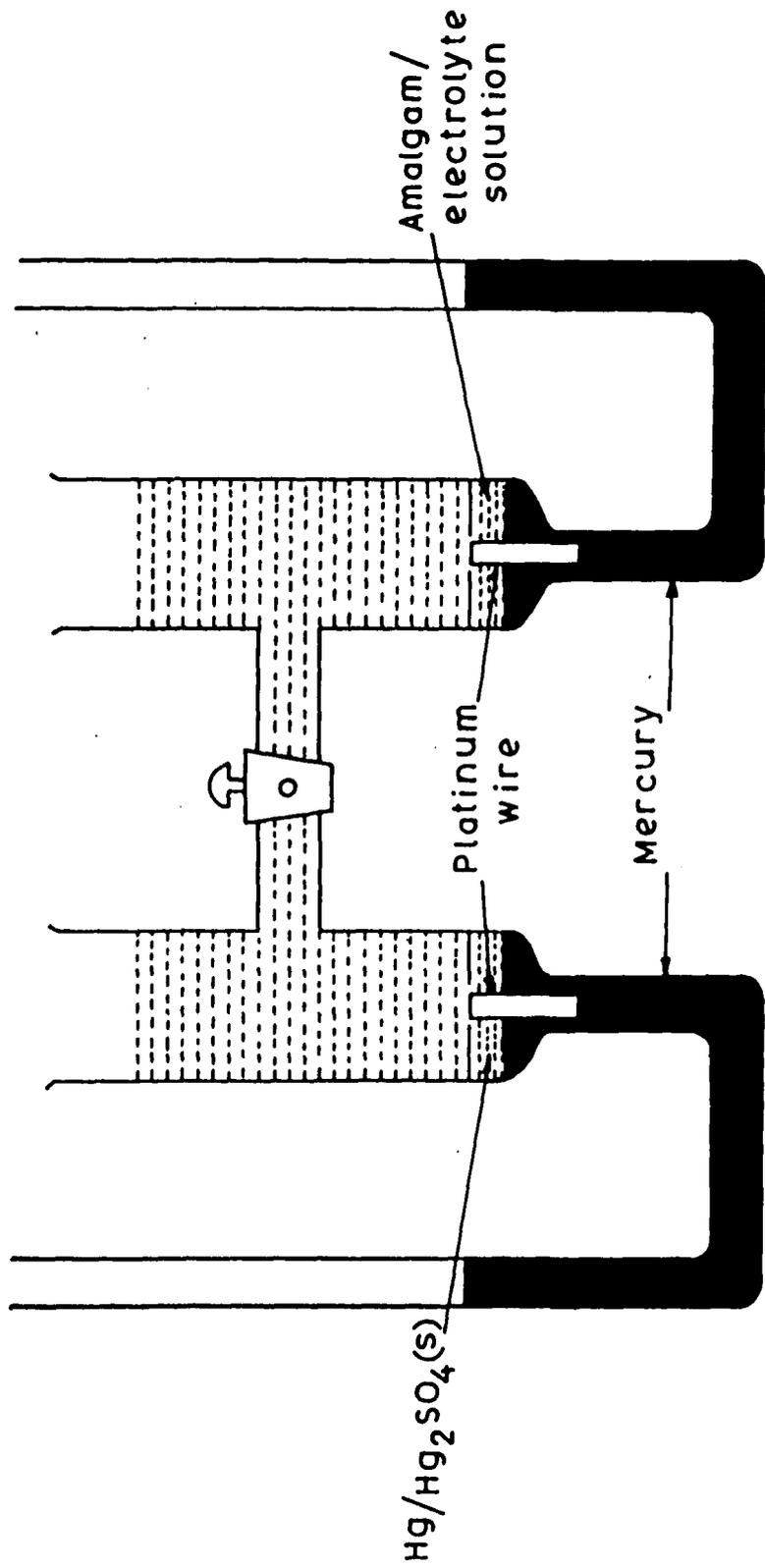


Fig.II.3 E.M.F. CELL

cell (II) with  $\text{Hg}/\text{Hg}_2\text{SO}_4$  (S). The cell was then covered with the electrolyte solution under investigation.

### C) The Experimental Procedure

The cell was washed with distilled water and then mercury was dropped such that it covers the platinum wire at the bottom of each limb of the cell. In case of cell (I) the solution under investigation saturated with mercurous chloride and in cell (II) solution saturated with mercurous sulphate was poured into the left limb while the right limb of the cell was covered with the solution saturated with the amalgam. A 1/10th degree thermometer was dipped well inside the cell in order to read the temperature of the solution. The cell was then placed in the water thermostat the temperature of which could be controlled upto  $\pm 0.1^\circ\text{C}$ . The cell was connected to the digital potentiometer through long flexible wires.

The e.m.f. measurements were made with digital potentiometer having an accuracy 0.05mV. The potentiometer was standardised against a certified weston standard cell maintained at a constant temperature. All measurements were made at 298, 303, 308, 313 and 318K.

Experiments were repeated at different concentrations. The equilibrium of the cell was set up after 30 minutes in case of cadmium chloride and after 2 hours in case of cadmium sulphate after which the e.m.f. remained constant. This is in

accordance with the observations of Wiebe and Winkler<sup>8</sup>. The constant e.m.f. thus observed was recorded and used for the estimation of activity coefficients and the various thermodynamic functions of transfer from water to the respective acetonitrile + water media. The concentrations of the solutions were occasionally checked after the experiments. No significant change was observed. Duplicate experiments were performed simultaneously in each case and the duplicates generally agreed within  $\pm 0.5\text{mV}$ .

#### D) Sources of Error

The various sources of error involved in the determination of e.m.f. measurements of the solutions are as follows:

##### (i) Impurities:

The presence of impurities in the solution may have critical effects on e.m.f. measurements due to ready transport of surface active material to the metal solution interface of an electrode. To avoid this conductivity water and extra pure acetonitrile were used for the preparation of the solutions.

##### (ii) Connections to the Electrodes:

These connections often involve glass metal seals. Leaky metal glass seals as well as dirty or wet mercury contact tubes, in which unsuspected secondary cells can be so easily set up, are obviously to be excluded. This has been avoided by using pure, dry mercury for connections.

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