CHAPTER III

EXPERIMENTS

3.1 Material

3.1.1 Conductivity Water

The conductivity water was prepared by first double distilling the tap-water using "Double distillation water still model 3 DWS" followed by deionisation through the "Elgastat type B 114" unit. The specific conductance of this water is usually between 1.0×10^{-6} and 8×10^{-7} ohm cm^{-1}.

3.1.2 Chemicals

All chemicals listed below were used without further purifications.

Name	Grade of purity	Manufacturer
Chloroplatinic acid	A.R.	FLUGA
Hydrobromic acid	A.R.	MERCK
Mercury	A.R.	B.D.H
Mercurous chloride	A.R.	Mallin krodt
Mercuric nitrate	A.R.	MERCK
Nitric acid	A.R.	MERCK
Potassium bromide	A.R.	MERCK
Potassium chloride	A.R.	MERCK
Potassium hydrogen phthalate	A.R.	MERCK

(continued)

Name	Grade of purity	Manufacturer
Silver dioxide	L.R.	B.D.H
Silver nitrate	A.R.	MERCK
Sodium hydroxide	A.R.	EKA KEMI
Zinc rod	A.R. 99.99%	B.D.H.
Zinc chloride	A.R.	MERCK
Zinc bromide	A.R.	MERCK

3.1.3 Preparation of Constant Boiling Point Hydrochloric Acid

The constant boiling-point hydrochloric acid was prepared by distilling hydrochloric acid solution having a density of about 1.1 g cm^{-3} which was obtained from dilution of approximately 400 cm^3 of the concentrated acid with 480 cm^3 deionised water. The 500 cm^3 portion of acid solution was distilled at the delivery rate of 3 to 4 cm^3 of the distillate per minute. The first 375 cm^3 of the distillated acid was discarded. Further 50 cm^3 of portion was collected and was used in the subsequent experiments.

3.1.4 Preparation of Calomel

The precipitated calomel was prepared according to the method given by Hill and Ives (12). Five grams of mercurous nitrate were moistened with 1 cm^3 of concentrated nitric acid and dissolved in 100 cm^3 of distillated water. This solution was then added dropwisely to about 500 cm^3 of 0.1 mol dm^{-3} hydrochloric acid and mechanically stirred by a glass paddle. The addition was completed within 10 minutes and the suspension was stirred for a further hour.

The precipitate was then allowed to settle and the supernatant solution was decanted and replaced by a further 50 cm^3 of 0.1 mol dm^{-3} hydrochloric acid. The solution was then stirred for further 24 hours, during period of which the two portions of 50 cm^3 hydrochloric acid solution was subsequently added. The precipitated calomel was finally filtered onto a sintered glass crucible, rinsed quickly with four portions of cold distilled water, and transfered to a vacuum desiccator.

3.2 Preparation of the Electrodes

3.2.1 The Calomel Electrode.

The diagram of the calomel electrode was shown in Fig.(3.1 a). It was prepared according to the method of Hills and Ives (12). A small amount of dry precipitated calomel was ground together with a little mercury, until a grey skin was formed over the mercury. This grey skin was spreaded evenly over the whole surface of a pool of mercury in the cell vessel, and the 0.1 mol dm^{-3} potassium chloride solution saturated with calomel was poured carefully on the top.

3.2.2 The Hydrogen Electrode.

The hydrogen electrode , Fig(3.1b), consists of a platinum plate, the surface of which is able to catalyze the reaction

$$H^+(aq.) + e^- \rightleftharpoons 1/2\ H_2(g)$$

It was prepared according to the method of Hills and Ives (12). The platinum electrode was first cleaned with concentrated nitric acid and was throughly rinsed with deionised water. Cathodic electrolysis of this electrode was carried out in a very dilute sulfuric acid solution at a current density of 10 $mA.cm^{-2}$. It was then washed in deionised water and platinized without delaying from 2% chloroplatinic acid solution containing a small amount of lead acetate for about 1 minute at a current density of 50 $mA.cm^{-2}$.

3.2.3 The Silver-Silver Halide Electrode.(Ag,AgX; X = Cl^-, Br^-)

The silver-silver halide electrodes used in this work were of thermal electrolytic type. They were prepared according to the procedure suggested by Janz (12). The electrode base was spiral Pt wire (1 mm.diameter) of 2-3 turns. This was sealed into a 4-6 mm.diameter glass tubing with the end of the wire protruding inside the tube for mercury contact. The Pt spiral was cleaned by boiling in concentrated nitric acid, followed by rinsing and boiling in deionised water. The dry and clean platinum spiral was then coated with a paste of silver oxide to form a ball of a suitable dimension. It was first heated slowly to 100°C, at which it was held for 1/2 - 1 hour to permit superficial drying. The temperature was then raised at a uniform rate (60°C. per hr.) to 450°C.,at which it was held for 1/2 hour. The electrode was allowed to cool within the furnace to avoid thermal shock. For second coating, a paste of much thinner consistency was used. Reduction of a second coat of silver oxide was proceeded in the same way. A batch of 3-4 electrodes was prepared simultaneously. These electrodes were stored in a desiccator until required for chloridisation (or bromidisation).

The silver electrode was chloridized (or bromidized) by making it as an anode with platinum spiral as a cathode. About 15% of silver was converted to silver chloride by passing a current of a 10 $mA.cm^{-2}$ through a solution of 1 mol dm^{-3} constant boiling-point hydrochloric acid. The electrode was then aged by storing in N_2-saturated 1 mol dm^{-3} hydrochloric acid for at least one week before use.

For bromidisation, however, about 8% of silver was converted to silver bromide by passing a current of 1 $mA.cm^{-2}$ through a solution of 0.1 mol dm^{-3} potassium bromide. The electrode was aged and stored in N_2-saturated 0.05 mol dm^{-3} potassium bromide for 24-48 hours before use.

Bias potentials between these electrodes were found to be within ±0.1 mV. or less.

3.2.4 The Zinc Amalgam Electrode.

The electrode was made by sealing a zinc rod (0.5 cm. diameter) of 99.99% purity, which was fitted with a copper wire lead, into the ground glass cone with "Aradite" epoxy resin. The zinc electrode was then cleaned with dilute nitric acid and deionise water. Amalgamation was carried out in N_2 atmosphere by immersion of the zinc electrode in a 0.05 mol dm^{-3} mercury(II)chloride solution containing 0.1 cm^3 of concentrated nitric acid (the pH of the solution was 2.6) for 30 minutes. The electrode was then stored in a dry state under hydrogen atmosphere.

3.3 Stock Solution and their Analyses.

3.3.1 The Zinc Chloride and Zinc Bromide Solutions

The stock solutions of zinc chloride ($ZnCl_2$) and zinc bromide ($ZnBr_2$) were prepared by dissolving the dry salt with deionised water. It was found necessary to prepare them at different concentrations due to precipitation of the insoluble oxychloride upon dilution. In such cases, small amount of 0.1 mol dm^{-3} solution of hydrochloric acid (or hydrobromic acid) were added dropwisely until the precipitate was redissolved. The concentrations and the pH of the stock solutions were listed in Tables 3.1 and 3.2, respectively.

Table 3.1 The concentrations and the pH of the $ZnCl_2$ stock solutions.

concentration ($mol.dm^{-3}$)	pH
3.5	3.30
2.0	4.07
1.0	4.70
0.6	5.16
0.3	5.40
0.1	5.85

Tabel 3.2 The concentrations and the pH of the $ZnBr_2$ stock solutions.

concentration ($mol.dm^{-3}$)	pH
3.7	3.37
2.0	4.18
1.0	4.90
0.6	5.30
0.3	5.69
0.1	6.05

The concentrations of the stock solutions were determined by gravimetric silver chloride (silver bromide) method (13). The mean deviation over four analyses of the stock solutions was ±0.05%. The pH values as listed in Tables 3.1 and 3.2 showed no indication of hydrolysis of zinc halide solutions.

3.3.2 The Hydrochloric and Hydrobromic Acid Solutions

The concentrations of hydrochloric acid solutions were standardized by acid-base titration using sodium hydroxide which was pre-standardized with a primary standard solution of potassium hydrogen phathalate. Precipitation titration was used to standardize the hydrobromic acid solutions by using silver nitrate as precipitant and the eosin as an indicator (14).

3.4 Preparation of the Solutions.

Solutions of the desired concentrations were prepared by weight dilution of the appropriate amounts of the stock solutions with deionised water.

3.5 Instruments

3.5.1 Potentiometer

Potentiometer model 701 A/Orion research digital ionalyzer was used for electromotive force measurements (emf). The input impedance is about 10^{13} ohm and the input offset current less than 2 pico A. The accuracy of the emf readings for the range ±1999.9 millivolts (mV.) is about ±0.1 mV. or 0.05% of the reading value. The emf scale was calibrated with the standard Weston cell type 1268 (its emf. value was 1.0184 volts) which was standardized by standard Weston cell type 1149 j from National Physical Laboratory KK. The emf. reading of 1.0173 volts correspond to the value of 1.0184 volts. Therefore, the correction of +1.1 mV. was applied to all of the emf readings.

3.5.2 Temperature Control Unit

It is usually important to have a good temperature control for precise electromotive force measurements. In this work the temperature of the solution was controlled by immersion of the cells in the thermostat bath. The temperature of thermostat bath was set accurately at 25.00±0.01°C. by means of a Beckmann contact thermometer which remained constant to ±0.01°C. The calibrated ASTM thermometer R 37382 with the range of 19°C. to 35°C., graduated in 0.02° C., was used to indicate the thermostat temperature. Its calibration with a standard thermometer from National Physical Laboratory KK. showed that a temperature of 25.00°C. corresponds to the thermometer reading of 25.05°C.

3.6 Electromotive Force Measurement

In making the electromotive force measurements, the solution was introduced into the glass vessel and was suspended in the thermostat bath, maintained at 25.00°C.±0.01°C., for about 1/2 hour to attained thermal equilibrium. During which period, the oxygen freed nitrogen gas (or hydrogen gas) which was saturated with the cell solution, was passed through the cell to sweep out the air and to saturate the solution with nitrogen gas (or hydrogen gas). The electrodes were rinsed with small portions of the same solutions before putting in positions. The emf of the cell was recorded when the reading was steady within 0.1 mV. for at least 1/2 hour.

The emf of the cell

$$\mathrm{Zn\text{-}Hg} \;/\; \mathrm{ZnX_2}(m_1),\ \mathrm{KX}(m_2) \;/\; \mathrm{AgX,Ag}$$

(where X = Cl^-, Br^-) was investigated in this work. The standard potential of silver-silver halide electrodes were determined by measuring them with a secondary reference hydrogen electrode in the cell

$$\mathrm{Pt,H_2}(P) \;/\; \mathrm{HX}(C) \;/\; \mathrm{AgX,Ag}$$

The hydrogen electrode was standardized against, the primary reference calomel electrode in the cell

$$Pt,H_2(P) / HCl(C) // KCl(0.1\ M.) / Hg_2Cl_2,Hg$$

Table 3.3 shows the list of systems under investigation.

Table 3.3 The list of systems under investigation

cell	solution	concentration range
I. Pt,H_2(P) / HCl(C) // KCl(0.1M.) / $HgCl_2$,Hg	HCl	0.01-0.06 mol dm^{-3}
II. Pt,H_2(P) / HCl(C) / AgCl,Ag	HCl	0.005-0.05 mol dm^{-3}
III. Pt,H_2(P) / HBr(C) / AgBr,Ag	HBr	0.005-0.05 mol dm^{-3}
IV. Zn-Hg / $ZnCl_2(m_1)$,$KCl(m_2)$ / AgCl,Ag	$ZnCl_2$	0.001-3.22 mol kg^{-1}
	$ZnCl_2$ + KCl	$ZnCl_2$: 0.03-0.90 mol kg^{-1}
		KCl : 0.5 mol kg^{-1}
V. Zn-Hg / $ZnBr_2(m_1)$,$KBr(m_2)$ / AgBr,Ag	$ZnBr_2$	0.001-3.50 mol kg^{-1}
	$ZnBr_2$ + KBr	$ZnBr_2$: 0.025-0.90 mol kg^{-1}
		KBr : 0.5-1.0 mol kg^{-1}

where m_1 = concentration of zinc halide in mol.kg^{-1}

m_2 = concentration of potassium halide in mol.kg^{-1}

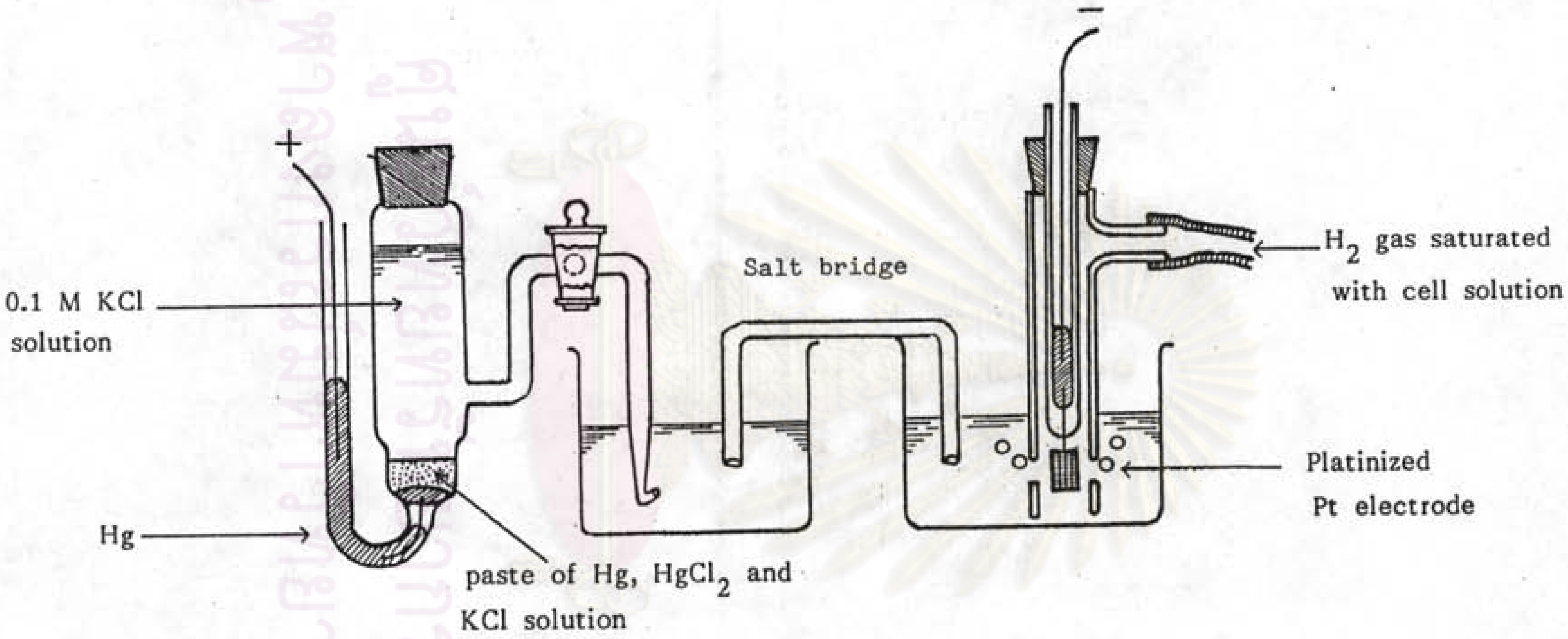
C = concentration of solution in mol.dm^{-3}

P = pressure of hydrogen gas

The diagrams of cell I and cells II, III are shown in Fig.3.1 and Fig.3.2, respectively.

For calibration of silver halide electrodes, the oxygen freed hydrogen was bubbled through the cell solution onto the hydrogen electrode with the rate of about 10 bubbles per minute.

The diagrams of cell IV and cell V are shown in Fig.3.3. The emf. measurements of these cells are carried out for the solutions of ZnX_2 alone (m_2=0) and for the mixture of ZnX_2 and KX at total zinc : total halide ratios of 1:2 to 1:20. The cell emfs. were usually stable within 1 hour but for solutions below 0.1 mol kg^{-1} longer time interval were required. No sign of electrolysis was observed during the measurement. The reproducibility of the measurement was ± 0.1 mV.



a) Calomel electrode

b) Hydrogen Electrode

Figure 3.1 The diagram of cell Pt, H_2 (P) / HCl (C) // KCl (0.1 M) / $HgCl_2$, Hg

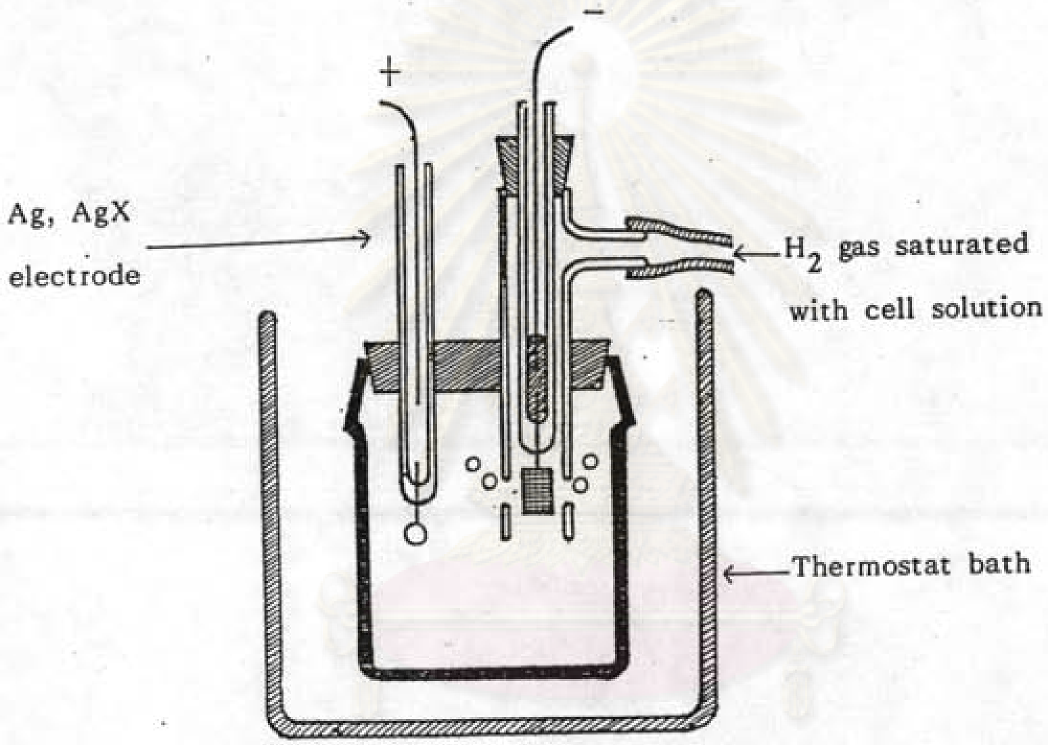


Figure 3.2 The digram of cell Pt, H_2 (P) / HX (C) / AgX, Ag

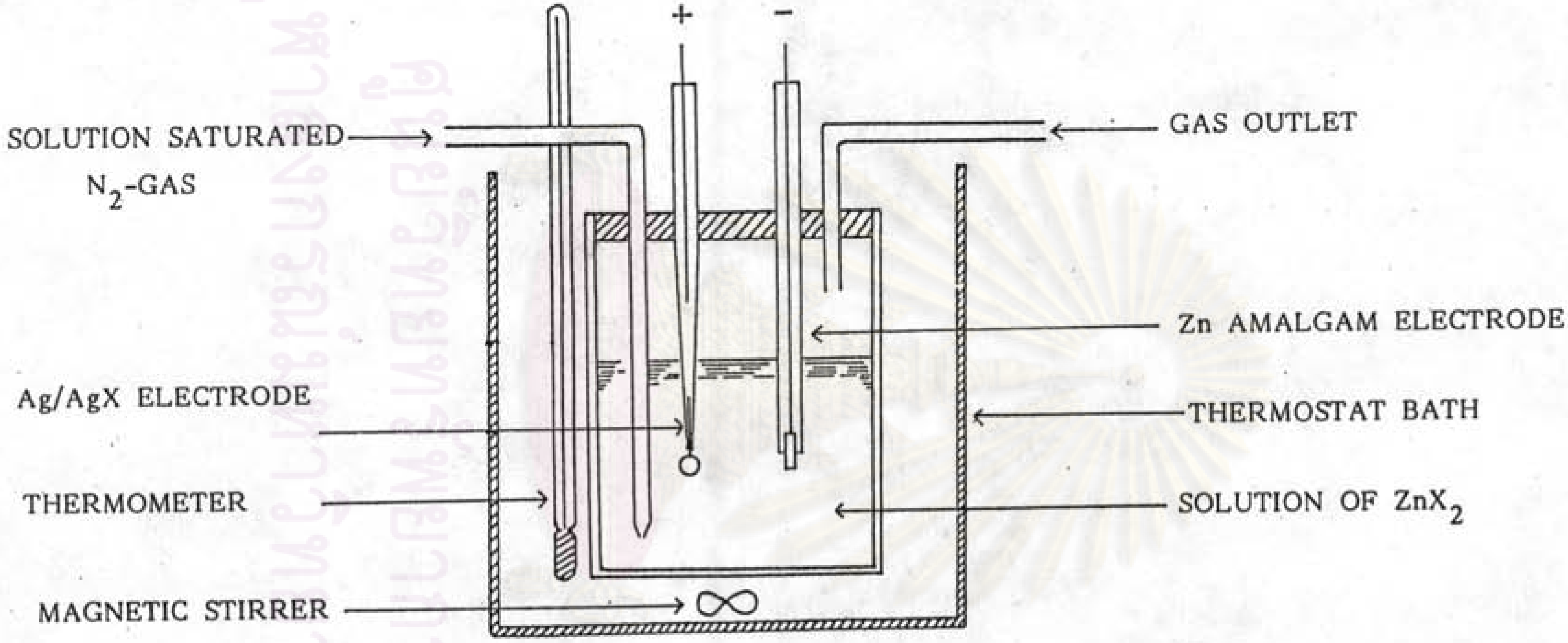


Figure 3.3 The diagram of cell Zn-Hg / ZnX_2 (m_1), KX (m_2) / AgX, Ag