CHAPTER II
LITERATURE REVIEW

2.1 Reference Electrode Theory

In all electrochemical experiments, the reactions of interest occur at the surface of the working electrode. Therefore, controlling the potential across the interface of the electrode surface and solution are of interest. However, it is impossible to measure this interfacial potential without placing another electrode in the solution, so it is required to have a reference electrode in which its potential remains constant and calculable. Hence, any changes in the measured potential can be attributed to the electrode of interest.

Ordinary reference electrodes have the components shown in Figure 2.1. In order to maintain the electrode reaction at equilibrium, a glass or polymeric body separates the filling solution from the test environment. The ionic communication with the test solution needs to be controlled, often through a porous frit. The electrode interface itself is composed of a metal coated with a metal salt. This arrangement leads to a robust equilibrium condition. The potential of the reference electrode is independent of the amount of salt as long as some metal salt is present on the electrode surface. The composition of the fill solution is important in maintaining the reference electrode at equilibrium.

Theoretically, any reaction could be used as a reference, as long as it can be maintained in equilibrium at the electrode surface. An ideal reference electrode is designed to produce the same potential independent of solution in which it is placed. It is confirmed that the correction algorithm of electrode potential is independent of the solution composition for a wide range of neutral and alkaline solutions (Bosch *et al.*, 2003).

A large variety of reference electrodes were reviewed by Ives and Janz (1961) a number of year ago. Three of the most commonly used electrodes in aqueous solution are the saturated calomel electrode (SCE), the silver/silver-chloride electrode (Ag/AgCl), and the mercury/mercury-sulfate electrode (Hg/Hg_2SO_4). As there is no absolute standard for measurement of electrochemical potential, the equilibrium potential of the H_2/H^+ reaction is defined as zero when placed in a solution of unit activity of H^+ and H_2. Since there maybe any number of reference electrodes chosen for measurement due to their distinct advantages in particular solutions, it is necessary to be able to convert from one reference electrode scale to another. Table 2.1 shows standard electrode potential versus SHE for some common reference electrodes.

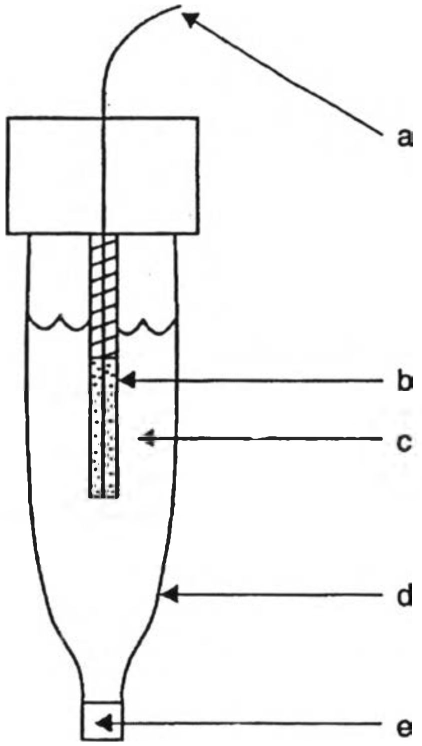

Figure 2.1 Components of typical commercial reference electrode:

a) electrical connection,
b) metal-metal salt electrode,
c) filling solution that maintains electrode interface equilibrium,
d) glass or polymeric electrode body,
e) porous frit

Table 2.1 Satandard potentials (E^o) and temperature coefficients for Cells of the Type: $(Pt)/H_2,H^+$ (a=1) : $KCl/MCl(satd)/M$ (Sawyer *et al.*, 1974)

		Standard potential (V at °C)							$\frac{dE^o}{dT}$ (mV/deg at 25 °C)
MCl/M	KCl Molarity	10	15	20	25	30	35	40	
AgCl/Ag	3.5 M (at 25°C)	0.215	0.212	0.208	0.205	0.201	0.197	0.193	-0.73
	Satd	0.214	0.209	0.204	0.199	0.194	0.189	0.184	-1.01
Hg_2Cl_2/ Hg	0.1 M (at 25 oC)	0.336	0.336	0.336	0.336	0.335	0.334	0.334	-0.08
	1.0 M (at 25 oC)	0.287	-•	0.284	0.283	0.282	-•	0.278	-0.29
	3.5 M (at 25 oC)	0.256	0.254	0.252	0.250	0.248	0.246	0.244	-0.39
	Satd	0.254	0.251	0.248	0.244	0.241	0.238	0.234	-0.67
TlCl/Tl	Satd	-0.565	-0.569	-0.573	-0.577	-0.581	-0.585	-0.589	-0.79

• Values are not available

2.2 Effects on High Temperature Electrode Potential

There are many parameters that may affect the measured electrode potential, since it is the sum of all potentials present in the system. The potential of Ag/AgCl electrode can be calculated directly from the Nernst equation, if the concentration and temperature are given. Concentration effects are described in Section 2.2.1 and the effects of temperature in Section 2.2.2. The effects of liquid junction potential and thermal liquid junction potential are described in Sections 2.2.3 and 2.2.4 respectively.

2.2.1 Concentration Effects

The potential of any electrode is determined by the Nernst equation, which relates actual potential to the standard potential, temperature and activities of the redox components. The Nerst equation of a Ag/AgCl electrode is given by:

$$E_{AgCl} = E^{o}_{AgCl} \quad \frac{RT}{nF} \ln a_{Cl} \tag{2.1}$$

where E_{AgCl} = potential of the Ag/AgCl electrode reaction at temperature T
E^{o}_{AgCl} = standard potential of Ag/AgCl electrode reaction at temperature 298 °K
R = gas constant (8.314 J/mol K)
T = temperature
n = electrons transferred
F = Faraday constant (96500 C/mol)
a_{Cl^-} = chloride ion activity

It is generally more convenient to consider concentrations rather than activities ($a_{Cl} = \gamma_{Cl}\ [Cl\ \ ]$), then the Nernst equation can be rewritten as follows:

$$E_{AgCl}(T) = E^{o'}_{AgCl}(T) \quad \frac{RT}{nF}\ln[Cl \quad] \tag{2.2}$$

where $$E^{o'}_{AgCl}(T) = E^{o}_{AgCl} \quad \frac{RT}{nF}\ln\gamma_{Cl}$$

Equation 2.2 shows that variations in the chloride ion concentration in the filling solution change the redox potential. Along with the metal electrode, it controls the value of potential by maintaining the reference electrode (RE) at equilibrium (see values in Table 3.1). Since there is generally a large chloride concentration gradient across the reference electrode frit, a slow diffusion of chloride ions from the filling solution into the test solution occurs; such that the reference potential will gradually change when used.

The filling solution not only has major effects on the reference electrode potential in an electrochemical measurement but it also can act as a source for ionic contamination of the test solution because the filling solution of an Ag/AgCl electode contains chloride ion, a know aggressive species. Thus, the leak rate must be considered carefully. The general leak rate is designed to be about 1 μ L/h (Kelly *et al*,. 2003).

2.2.2 Temperature Effects

The second parameter in the Nernst equation is temperature. In Table 2.1 the change of the reference electrode potential with the temperature, $\frac{dE^o}{dT}$, are tabulated relative to the standard hydrogen electrode at 25 °C.

In order to calculate the electrode potential as a function of temperature, the activity coefficients at each temperature must be known. Available activity coefficients for a KCl solution at elevated temperatures have been summarized by Bogaerts and Van Haute, 1984. It was shown that the activity coefficient decreases with increasing temperature (Figure 2.2).

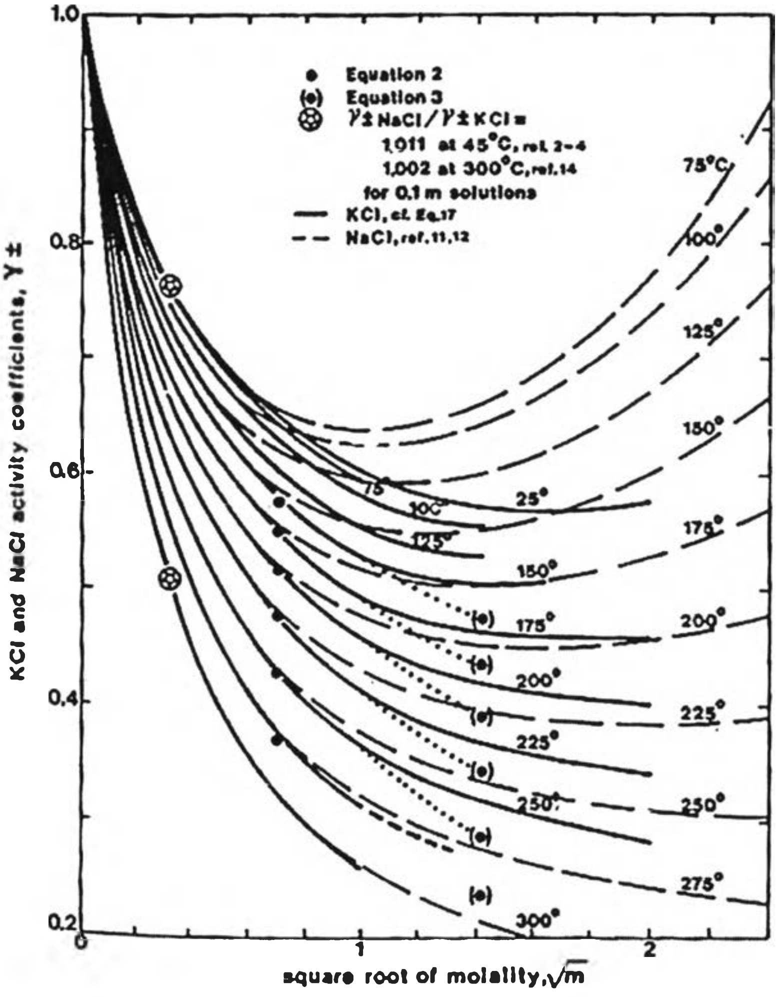

Figure 2.2 Estimated mean ionic activity coefficients for KCl solutions at elevated temperatures (Broken lines indicate NaCl activity coefficients for comparison).

2.2.3 Liquid Junction Potential

The liquid junction potential is a potential difference that arises between two different ionic solutions in contact because of the differential mobility of the ions across the junction. These potentials are difficult to reproduce, tend to be unstable, and are seldom known with any accuracy. Steps must be taken to minimize them or to make them predicable (Senanayake and Muir, 1988, Susuki *et al.*, 1998; Bagg, 1990, 1992, 1993; Oh *et al.*, 2003).

The simplest example is the case of two solutions containing the same salt in different concentrations. The salt will diffuse from the higher concentration side to the lower concentration side. However, the diffusion rate of the cation and the anion of the salt will not be the same (see mobility in Table 2.2). For the case that anions move faster; consequently, an excess negative charge will accumulate on the low concentration side, while an excess positive charge will accumulate on the high concentration side of the junction due to the slow moving cations. This sets up a potential difference that will start an electromigration of the ions that increases the net flux of the cations and decrease the net flux of the anions. In steady state conditions, the two ions move at the same speed and a potential difference will be created between the two solutions.

Table 2.2 Ions relative mobility (Barry and Lynch, 1991)

Symbolic ion name	Full ion name	Valency	Relative mobility
Li^+	Lithium	+1	0.525
Na^+	Sodium	+1	0.682
K^+	Potassium	+1	1.000
Ca^{2+}	Calcium	+2	0.409
Zn^{2+}	Zinc	+2	0.359
Br^-	Bromide	-1	1.063
Cl^-	Chloride	-1	1.039
F^-	Fluoride	-1	0.753
I^-	Iodide	-1	1.045
SO_4^{2-}	Sulphate	-2	0.544

The basic equation for the junction potential is:

$$LJP = \frac{RT}{F}\int_1^2 \sum_n \frac{t_i}{z_i} d\ln a_i \tag{2.3}$$

where LJP = liquid junction potential

t_i = transport number (related to the mobility of the ion) of the i th ion

z_i = algebraic value of the charge on the ion

a_i = activity of the ion

n = Implies that the summation is carried out over the n kinds of ions present

Barry and Lynch, (1991) simplified Equation 2.4 for the generalized Handerson Equation of N polyvalent ions by making the following assumptions.

1) Diffusion takes place in one dimention
2) A linear concentration gradient across the boundary $C_1//C_2$
3) Activity coefficient gradients are constant throughout the junction.
4) Concentration independent values of ionic mobility and conductance

Equation 2.3 can be rewritten as:

$$LJP = \frac{RT}{F} S_F \ln\left\{\frac{\sum_{i=1}^{N} z_1^2 u_i a_i^L}{\sum_{i=1}^{N} z_1^2 u_i a_i^R}\right\} \tag{2.4}$$

$$S_F = \frac{\sum_{i=1}^{N} (z_i u_i)(a_i^L \quad a_i^R)}{\sum_{i=1}^{N} (z_i^2 u_i)(a_i^L \quad a_i^R)} \tag{2.5}$$

where a_i^L = activity of species on the left hand side of the boundary region

a_i^R = activity of species on the right hand side of the boundary region

u_i = mobility of each ionic species

Liquid junction potential between KCl (4M) and water at temperatures of 0, 25 and 100 °C are shown in Table 2.3. The calculated liquid junction potential using the Handerson equation is in satisfactory agreement with experimentally observed values obtained by Bagg, 1992. It should be pointed out that liquid junction potential can significantly increase with temperature.

Table 2.3 Liquid junction potential (mV) for KCl(4M)‖water at 0, 25 and 100°C.

	Temperature (°C)		
	0	25	100
LJP	2.7	-4.8	-20.2
LJP*	-1.5	-8.0	-19.3

* Calculated using the Handerson equation.

2.2.4 Thermal Liquid Junction Potential

A temperature difference between the RE and a test solution at high temperature results in a thermal potential drop across the salt bridge, the so called thermal liquid junction potential. When an electrolyte solution is placed in a temperature gradient, an internal electric field develops instantaneously due to the migration of ions. After a time, concentration gradients arise in the solution, leading to a diffusion potential. The thermal liquid junction potential can be calculated from Equation 2.6 (Oh *et al.*, 2003).

$$TLJP = \frac{1}{F}\int_{T_2}^{T}\sum_{N}\frac{t_i S_i^*}{z_i}\, d\ln T \qquad (2.6)$$

where $TLJP$ = thermal liquid junction potential

S_i^* = entropy of transport of each species

There have been many attempts to determine the thermal liquid junction potential. The evaluation of the initial state TLJP has been permitted by thermodynamic analysis of the cell Ag-AgCl/KCl/AgCl-Ag(T) (Macdonald *et al*,. 1979). The experimental setup is depicted in Figure 2.3. The potential differences were recorded between the two Ag/AgCl electrodes as a function of time. It was found that the TLJP increased in an approximately parabolic manner with Δ T (=T -298.5 °K) for KCl concentration ranging from 0.005 to 0.505 mol/kg and temperatures as high as 548.15 °K.

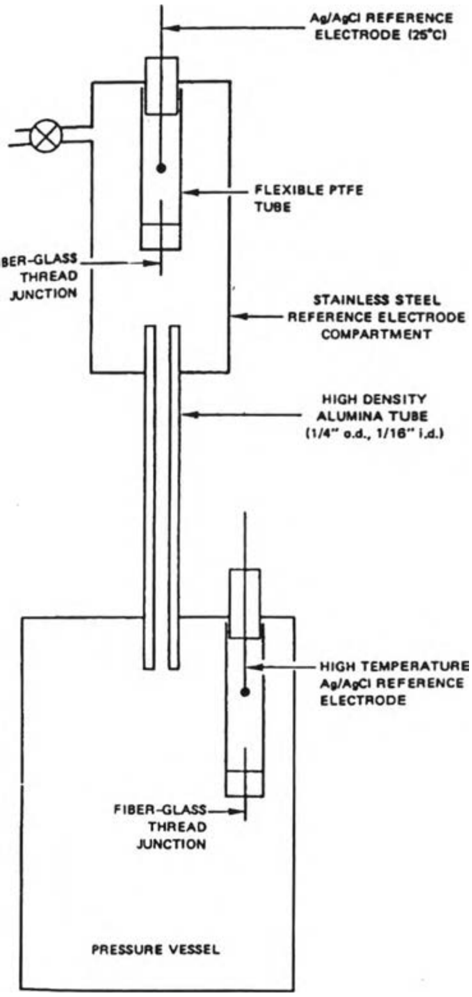

Figure 2.3 Experimental setup for the determination of the TLJP (Macdonald *et al.*, 1979).

TLJP are derived from the observed thermal cell potential and calculated Nernstian contributions and are represented as cubic equations, the regression coefficients for seven KCl concentrations are summarized in Table 2.4,

$$TLJP = A_0 + A_1 + A_2 \Delta T^2 + A_3 \Delta T^3 \tag{2.7}$$

Table 2.4 Regression coefficient for TLJP as a function of KCl concentration

mol/kg	10^5A_0	10^3A_1	10^5A_2	10^8A3
0.005	-0.183823	0.240195	0.028139	0.717903
0.010	0.364229	0.100502	0.155944	0.386629
0.025	0.510975	0.050871	0.223140	0.190336
0.051	0.571523	0.082103	0.200802	0.236327
0.102	0.964776	0.105669	0.175339	0.265190
0.252	0.951401	0.072907	0.223231	0.173853
0.505	0.478089	0.084250	0.214629	0.180993

TLJP data are plotted in Figure 2.4 as a function of mol/kg and Δ T. As the temperature difference becomes greater, the TLJP increases rapidly in the positive direction. The other important feature of the data plotted in Figure 2.3 is that TLJP apparently exhibits a very weak dependence on concentration between 298.15 and 523.15 °K.

2.3 High Temperature Reference Electrode Development

Much research has been done with the objective of developing high temperature reference electrodes with the following requirements: 1) the electrode needs to be sufficiently rugged to withstand the transient high temperature and pressure system; 2) the electrode element must be thermally and chemically stable at the prevailing temperature and must not exhibit a mixed potential; 3) the internal solution should be well-defined thermodynamically; 4) the liquid junction potential

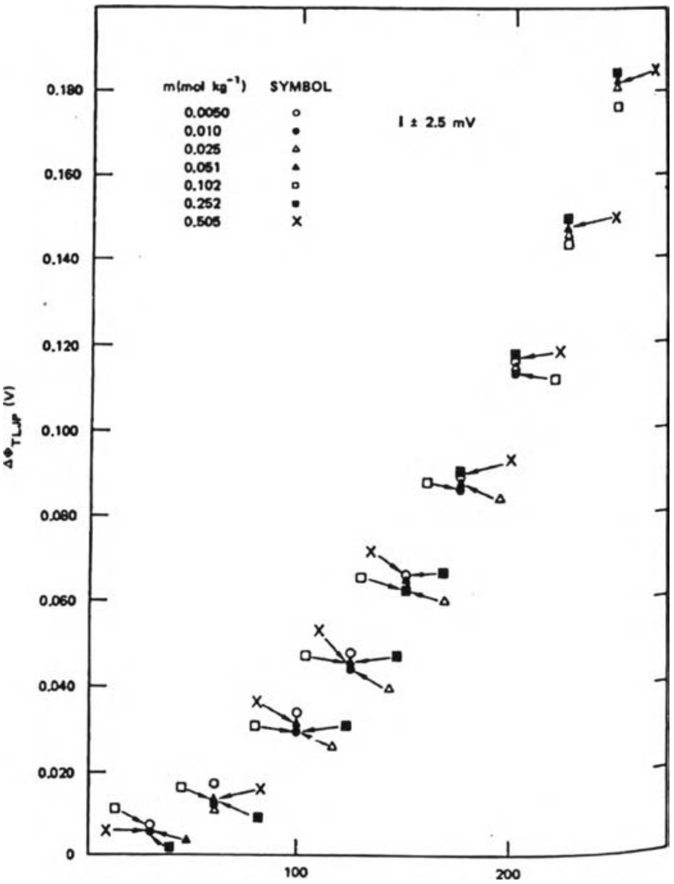

Figure 2.4 Thermal liquid junction potentials as a function of Δ T (= T-298.15 K) for various KCl concentrations (M).

should be reduced to as low a value as possible so it may be neglected or can be estimated reliably, 5) the electrode potential must be related to a well defined thermodynamic scale (eg., the SHE scale). Reference electrodes used in high temperature systems can be divided into two classes, internal reference electrodes (IRE) and external reference electrodes of which the external pressure balanced reference electrode (EPBRE) is the most prominent member. The internal reference electrode such as SHE is impractical to use in high pressure and temperature systems since it is difficult to control hydrogen pressure and ion activity in solution. Therefore, most reference electrodes developed are of the external type. However, the external pressure balanced reference electrode is less accurate compared to the internal type (Greely et al., 1960). This is due to the uncertainty in thermal liquid junction potential (TLJP). Thus, the development of methods for calculating TLJP are required to obtain accurate potential measurements.

It was shown by Lvov and Macdonald (1996) that the induced thermal diffusion along an isothermal salt bride can make a very significant contribution to the measured potential, it maybe be as much as ±150 mV. Therefore the key to improve the accuracy of the electrode is to devise a way of maintaining a uniform concentration or maintaining a well-defined concentration gradient along the electrolyte bridge. Lvov and Macdonald (1997) solved the problem by developing a flow through external pressure balanced reference electrode (FTEPBRE) for potentiometric and pH measurements in high temperature aqueous solutions, which can be accurately used over wide ranges of pressure and temperature. The unique feature of the advanced FTEPBRE is that the reference solution flows through the electrode so that the concentration of solution across the thermal liquid junction is well-defined. Since the electrolyte concentration profile is maintained constant, uncertainty in the TLJP can be eliminated at a given temperature and pressure.

Reference electrodes are necessary for online corrosion measurements so there have been many attempts to design and construct appropriate reference electrodes for use in given environments. Much experience has been gained on applying several types of reference electrodes to monitor corrosion potential at high temperature. Navas and Gomez Briceno (1997) fabricated and modified three types of high temperature reference electrodes, which are copper/copper(I) oxide with a yttrium-stabilized zirconia (YSZ) membrane, silver/silver-chloride couple and a platinum electrode. Results showed the reliability and chemical stability under BWR operating conditions. Success was also achieved from a platinum electrode by Sampedro *et al.*, 1999. It performed well in a geothermal brine solution at high pressure and temperatures about 250 oC

High temperature electrodes for the nuclear industry have been specially designed to operate in high radiation environments and are capable of withstanding rapid pressure and temperature gradients (Manahan and Cetin 2000). Even though the silver/silver-chloride external pressured balanced reference electrodes showed the reliability in continuous hot operation for two years fuel cycles, TLJP was a significant problem. The TLJP must be accounted for in the conversion of the measured potential to the standard hydrogen electrode (SHE) scale. Correction factors for the TLJP to the measured potential were given by Bosch *et al.*, 2003 by taking into account all the thermal diffusion phenomena. A simple correction algorithm proved to be adequate for pressure drop calculation as a function of temperature difference across the salt bridge.

Recently, LIRES, a European sponsored research project with the objective to develop high temperature reference electrodes succeeded in developing reference electrodes for electrochemical measurements inside the core of a Light Water Reactor (LWR). The reference electrodes were a yttrium-zirconium electrode, an external silver/silver-chloride electrode, a rhodium electrode, and a palladium electrode. The test results, in the laboratory, have shown that the four in-core high temperature reference electrodes work properly at the representative LWR water chemistries at the required operating pressures and temperatures.