CHAPTER II

PRELIMINARY WORK

The oxidising power of ions is known to the users usually by two different ways, one is to try in the actual experiment and the other, which is more practical, to study from the tabulated redox potentials of a series of ions. A few group of scientists have made contribution to these tabulated values through their work.

The redox potentials of the polyoxidation states elements were obtained mostly by the direct measurement of their potentials including are Fe(III) / Fe(II), Co(III) / Co(II) and Tl(III) / Tl(I). Although redox potential of the last name pair in aqueous solution was well established, generally known as 1.25 volts, scarcely any data on its potential in nonaqueous solvent exist. Study of previous work can yield informations concerning techniques used and problems encountered in such measurements. The literature survey revealed that most of the work on redox potentials of polyoxidation states ions has been done during the period of 1905-1940 afterwhich the interest seemed to be died out.

The previous investigators used hydrogen electrode or calomel electrode as a reference electrode. Some chose to measure the potential of cells with liquid junction whereas some groups tried to eliminate the junction. As it should be expected, Nernst equation has employed in the computation of the redox potential. It should be noted that those investigators used concentration ratio in their calculations instead of ion activities.

One of the early work of this line seems to be that of Spencer and Abegg (2). They studied the oxidation potential of thallous-thallic ions in nitric, hydrochloric and sulphuric acids, and in the presence of various salts using cell I.

$$\mathrm{Pt/Tl(III),\ Tl(I),\ acid\ anion,\ free\ acid}/\tfrac{\mathrm{N}}{10}\ \mathrm{KCl/Hg_2Cl_2/Hg} \quad \ldots\ldots\ldots\ldots \mathrm{I}$$

The measurements were made at 25°C, liquid junction potentials were neglected in the calculation of the e.m.f. The 0.1 N calomel potential was taken as equal to -0.336 volt . The standard potential (E°) at various acid concentrations calculated from Nernst equation are given in Table 2.1 .

In 1920 Grubb and Hermann (3) measured the oxidation potentials at 18° ± 0.5°C of the following cells.

$$\mathrm{Pt}\left|\begin{matrix}\mathrm{Tl_2SO_4}\\ \\ \mathrm{Tl_2(SO_4)_3}\end{matrix}\right., \mathrm{H_2SO_4(c)}\,\Big|\,\mathrm{H_2SO_4(c)}\,\Big|\,\mathrm{N\ KCl,\ Hg_2Cl_2}\,\Big|\,\mathrm{Hg} \quad \ldots\ldots \mathrm{II}$$

Table 2.1

Concentrations ratio of Tl(III) : Tl(I)	Anion	Acid surplus	$E^{\bullet}_{\mathrm{Tl(III)/Tl(I)}}$ (volts)	
1 : 1	Nitrate	0.3 mol. HNO_3	1.199	
1 : 1	"	0.413 mol. HNO_3	1.193	
1 : 1	"	1.0 mol. HNO_3	1.173	
1 : 1	Sulphate	0.0903 mol. H_2SO_4	1.163	
1 : 1	"	0.226 mol. H_2SO_4	1.156	
1.18 : 1	Chloride	0.0235 mol. HCl	0.934	
1 : 1	"	0.105 mol. HCl	0.859	
1 : 1	"	0.190 mol. HCl	0.828	
1 : 3	"	0.00217 mol. HCl	0.958 1.010	Saturated $\frac{1}{100}$ Saturated
1 : 3	"	0.00069 mol. HCl	0.963 1.041	Saturated $\frac{1}{100}$ Saturated
5.4 : 1	"	0.042 mol. HCl	0.928	

Table 2.1 Continued

Concentrations ratio of Tl(III) : Tl(I)	Anion	Acid surplus	$E^{\bullet}_{\mathrm{Tl(III)/Tl(I)}}$ (volts)
5.4 : 1	Tartrate	0.042 mol. HCl	0.897
5.4 : 1	Acetate	0.042 mol. HCl	0.860
5.4 : 1	Cyanate	0.042 mol. HCl	0.844
5.4 : 1	Oxalate	0.042 mol. HCl	0.765
5.4 : 1	Bromide	0.042 mol. HCl	0.751
5.4 : 1	Nitrite	0.042 mol. HCl	0.676
5.4 : 1	Iodide	0.042 mol. HCl	0.664
5.4 : 1	Thiocyanate	0.042 mol. HCl	0.603
5.4 : 1	Sulphite	0.042 mol. HCl	0.341
5.4 : 1	Cyanide	0.042 mol. HCl	0.308
5.4 : 1	Thiosulphate	0.042 mol. HCl	0.126

$$\mathrm{Pt}\left|\begin{matrix}\mathrm{Tl_2SO_4}\\ \mathrm{Tl_2(SO_4)_3}\end{matrix}\right.,\ \mathrm{H_2SO_4(c)}\ \Big|\ \mathrm{H_2SO_4(c = 2\ N),\ Hg_2SO_4}\ \Big|\ \mathrm{Hg}\ldots\mathrm{III}$$

$$\mathrm{Pt}\left|\begin{matrix}\mathrm{Tl_2SO_4}\\ \mathrm{Tl_2(SO_4)_3}\end{matrix}\right.,\ \mathrm{H_2SO_4(c)}\ \Big|\ \mathrm{H_2SO_4(c)}\ \Big|\ \begin{matrix}\mathrm{sat.NH_4NO_3}\\ \mathrm{or\ sat.KCl}\end{matrix}\ \Big|\ \mathrm{N\ KCl,\ Hg_2Cl_2}\ \Big|\ \mathrm{Hg}\ \ldots\ldots\ldots\mathrm{IV}$$

The values assumed for the standard electrode potential of the reference electrodes on the hydrogen electrode standard scale are as follows:

N calomel = -0.286 volt

2 N mercury-mercurous sulphate = -0.676 volt

The value of the e.m.f. obtained with cell IV was the same as that of cell III. The difference in e.m.f. between cell II and IV was obviously due to the liquid junction potential which was found to be 0.0295 volt when the sulphuric acid concentration in the Tl(III)/Tl(I) compartment was 1.964 N.

They reported that the standard oxidation potential as calculated by Nernst equation was -1.211 volts.

These workers had also made a re-calculation using a different value of E° of N calomel electrode which has been proposed by Glasstone (4) i.e., -0.2792 volt and a new standard Tl(III)/Tl(I) electrode potential became -1.204 volts.

Grubbe and Hermann had compared their results with that of Abegg and Spencer by making allowance for the concentration difference. The discrepancy is noticeable (-1.2045 volts for the former and -1.153 volts for the latter) and this might be due to the fact that the liquid junction potentials were neglected in Abegg and Spencer's work.

Later, Partington and Stonhill (5) investigated the oxidation potential of Tl(III)/Tl(I) electrode in the presence of sulphate ions using the following cells.

$$\mathrm{Pt}\left|\begin{matrix}\mathrm{Tl_2SO_4}\\ \mathrm{Tl_2(SO_4)_3}\end{matrix}\right.,\ \mathrm{H_2SO_4(c)}\,\big|\,\mathrm{H_2SO_4(c)}\,\big|\,\mathrm{H_2},\ \mathrm{Pt} \qquad \ldots\ldots\ldots\mathrm{V}$$

$$\mathrm{Pt}\left|\begin{matrix}\mathrm{Tl_2SO_4}\\ \mathrm{Tl_2(SO_4)_3}\end{matrix}\right.,\ \mathrm{H_2SO_4(c)},\ \mathrm{Hg_2SO_4(sat.)}\,\big|\,\mathrm{Hg}\,\big|\,\mathrm{Hg_2SO_4(sat.)},\ \mathrm{H_2SO_4(c)}\,\big|\,\mathrm{H_2},\ \mathrm{Pt}\ldots\mathrm{VI}$$

The concentration of the sulphuric acid was the same throughout each cell, and the concentration ratio of Tl(III)/Tl(I) was made equal to unity. For each concentration of sulphuric acid (ranging from 1 to 0.0125 formal), the actual thallium salt concentrations were progressively decreased by a suitable dilution, and the value approached by the electromotive force as these salt concentrations approached zero was obtained. Hence the liquid potentials were eliminated and the standard electrode potential of 1.2207 volts were resulted.

The effects of other anions, for example perchlorate ion on the potential of Tl(III)/Tl(I) electrode were studied by Sherril and Hass (6). They measured the e.m.f. of cells VII and VIII

$$\begin{array}{l|l|c|l} \mathrm{Pt},\ \mathrm{H_2(g)} & \mathrm{HClO_4}(c_1) & \begin{array}{c}\mathrm{TlClO_4}(c_3)\\ \mathrm{HClO_4}(c_1)\\ \mathrm{Tl(ClO_4)_3}(c_3)\end{array} & \mathrm{Pt} \quad \text{.......VII}\end{array}$$

$$\begin{array}{l|l|c|l} \mathrm{Pt},\ \mathrm{H_2(g)} & \mathrm{H_2SO_4}(c_1) & \begin{array}{c}\mathrm{Tl_2SO_4}(c_3)\\ \mathrm{H_2SO_4}(c_2)\\ \mathrm{Tl_2(SO_4)_3}(c_2)\end{array} & \mathrm{Pt} \quad \text{......VIII}\end{array}$$

For cell VII with the acid-thallic-thallous perchlorate mixtures, covering an acid concentration range of 0.5-1.22 formal, the oxidation potential was determined not only by Nenst equation, but also by the empirical relationship of E° and ionic strength, I, of the solution namely

$$E^{\circ} = 1.2466 + 0.0076\, I + 0.00482\, I^2$$

They got the value of E° equal to 1.260 volts in 1.0 formal $HClO_4$ and 1.247 volts for the extrapolated molal potential of thallous-thallic ion.

For cell VIII with the acid-thallic-thallous sulphate mixtures, covering an acid concentration range of 0.16 to 0.30 formal, the formal electrode potential computed by Nernst equation was found to vary appreciably at the lower concentration ratios of Tl(III)/Tl(I), but to remain nearly constant when the concentration ratio exceeded unity.

The E° value varied slightly with the acid concentration from 1.205 volts at 0.16 formal sulphuric acid solution to 1.207 volts at 0.30 formal sulphuric acid solution.

Noyes and Garner (7) measured the e.m.f. of the cell:

$$\mathrm{Pt, H_2(1\ atm.)} \left| \mathrm{HClO_4(c')} \right| \mathrm{HNO_3(c)} + \begin{matrix} \mathrm{Tl(III)(c_2)} \\ \mathrm{Tl(I)(c_1)} \end{matrix} \Big| \quad \mathrm{Pt} \ldots \mathrm{IX}$$

The formal oxidation potential (E°) of Tl(III)/Tl(I) electrode had been computed in the usual way and reported the value of 1.2303 ± 0.0007 volts at 25°C and 1.193 ± 0.001 volts at 0°C in nitric solution.

This value remained constant when the ratio of Tl(III)/Tl(I) was varied one hundred-fold and nitric acid concentration was varied from 0.5 to 2 formal.