PART-2

AMPEROMETRIC DETERMINATIONS INVOLVING

REDUCTION WITH THIOMALIC ACID
SECTION 1
AMPEROMETRIC DETERMINATION OF OSMIUM

Amperometric Determination of Osmium (VIII)

Amperometric determination of Os(VIII) was carried out with the help of TSH in the following supporting electrolytes:

i. 0.5M NaOH
ii. 0.5M NH₃ + 0.5M NH₄Cl

The metal species - TSH titrimetric molar ratio of 5:1 was obtained in both these media.

Amperometric determination of Os(VIII) in 0.5M NaOH medium

Amperometric determination of this species was successfully carried out in this medium. Cathodic waves of the metal species as well as the anodic wave of TSH were exploited for the purpose. In the former case (cathodic titrations), TSH was used as titrant while in the latter case (anodic titrations), metal species was the titrant. Metal species - thiomalic acid titrimetric molar ratio obtained was 5:1 in both cases.

Polarographic characteristics of the metal species

Os(VIII) gave three well defined, diffusion controlled waves in this medium as reported by Meites. The diffusion region of the first wave stretched from -0.20V through -0.60V, that of the second wave from -0.85V through -1.40V and that
of the third wave from -1.60V. Meites (loc.cit.) has concluded that the first wave is due to the reduction of Os(VIII) to Os(VI), second wave, due to the reduction of Os(VI) to Os(IV) and the third wave due to the reduction of Os(IV) to Os(III).

Polarographic characteristics of TSH

TSH was found to give its characteristic reversible, one electron, anodic wave in 0.5M NaOH, similar to one reported by Agrawal et al. in 0.1M NaOH. The diffusion region spread over the potential range of -0.30V through -0.50V (fig. 2.1.1).

Amperometric Studies

(a) Amperometric determination of Os(VIII) using TSH as titrant (cathodic titration)

Both 1st and 2nd cathodic waves of Os(VIII) were exploited for the amperometric determination of Os(VIII). Titrations were carried out at -0.40V and -1.00V. The first titration voltage thus fell in the diffusion regions of the first wave of Os(VIII) and TSH both while the second one fell in the diffusion region of the second wave of Os(VIII) alone. Titrations resulted in L-shaped amperometric curves of the types (a) and (b) respectively shown in fig. 2.1.2. Metal species - TSH titrimetric molar ratio was found to be 5:1 at both voltages. During titrations, colour of the osmium solution changed to pink. Results are included in table 2.1.1.
**Fig. 2.1.1**: Polarogram of 5x10^-4 M TSH in 0.5 M NaOH medium (residual current excluded).

**Fig. 2.1.2**: Amperometric titration curves of Os(VIII)-TSH system in 0.5 M NaOH medium:

- Titration voltages: (a) -0.40V (b) -1.00V
- Conc. of Os(VIII): 5x10^-4 M
- Conc. of TSH: 5x10^-3 M (titrant)

- **Os(VIII):TSH = 5:1**

\[ \text{x = Residual current line at: } -0.40V \]

\[ \text{y = Residual current line at: } -1.00V \]
Table 2.1.1

Amperometric determination of Os(VIII) in 0.5M NaOH medium

<table>
<thead>
<tr>
<th>Titrant</th>
<th>TSH solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titration voltages</td>
<td>-0.40V and -1.00V</td>
</tr>
<tr>
<td>Range of concn. of TSH used</td>
<td>5x10^{-2}M - 2.5x10^{-4}M</td>
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</table>

<table>
<thead>
<tr>
<th>Conc. of Os(VIII) taken</th>
<th>Conc. of Os(VIII) obtained (Mean)</th>
<th>% error (Mean)</th>
<th>Standard deviation Sx10^{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mx10^{3}</td>
<td>Mx10^{3}</td>
<td></td>
<td>Sx10^{3}</td>
</tr>
<tr>
<td>5.0000</td>
<td>5.0000</td>
<td>0.000</td>
<td>0.0000</td>
</tr>
<tr>
<td>1.0000</td>
<td>1.0000</td>
<td>0.000</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.5000</td>
<td>0.5000</td>
<td>0.000</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.1000</td>
<td>0.1000</td>
<td>0.000</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.0500</td>
<td>0.0500</td>
<td>0.000</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.0400</td>
<td>0.0399</td>
<td>0.250</td>
<td>0.0002</td>
</tr>
<tr>
<td>0.0350</td>
<td>0.0342</td>
<td>2.286</td>
<td>0.0005</td>
</tr>
<tr>
<td>0.0250</td>
<td>0.0235</td>
<td>6.000</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

It is noteworthy that titrations at -0.40V always yielded nearly zero diffusion current at the null point. On the other hand, in case of titrations at -1.00V, the diffusion current remaining unneutralized at the null point was always almost equal to that of the 2nd wave (table 2.1.2).
Table 2.1.2

Study of amperometric curves (cathodic titrations) obtained at -1.00V in 0.5M NaOH medium

<table>
<thead>
<tr>
<th>Concns. of Os(VIII) taken (Mx10^3)</th>
<th>i_d of II wave alone measured before starting titration (μA)</th>
<th>i_d obtained at the null point (μA)</th>
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<td>5.000</td>
<td>15.600</td>
<td>15.948</td>
</tr>
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<td>1.000</td>
<td>3.120</td>
<td>3.240</td>
</tr>
<tr>
<td>0.500</td>
<td>1.520</td>
<td>1.580</td>
</tr>
<tr>
<td>0.100</td>
<td>0.312</td>
<td>0.346</td>
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<tr>
<td>0.040</td>
<td>0.122</td>
<td>0.136</td>
</tr>
<tr>
<td>0.035</td>
<td>0.105</td>
<td>0.118</td>
</tr>
<tr>
<td>0.025</td>
<td>0.074</td>
<td>0.076</td>
</tr>
</tbody>
</table>

Checking of interference and specificity

Interference of various cations and anions in the above titrations was checked. Three concentrations of Os(VIII), viz. 5x10^-3 M, 1x10^-3 M and 5x10^-4 M were chosen for such studies. Mg(II), Al(III), V(V), Zn(II), WO_4^{2-}, CH_3COO^-, Ox^{2-}, NO_3^-, SO_4^{2-} and Cl^- did not interfere in the estimation of Os(VIII) even when present in the cell-solution to the extent of twenty times in excess of the concentration of Os(VIII) solution.
Presence of Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Ru(III), Rh(III), Pd(II), Cd(II), Ir(III), Pt(IV) and \( S_2O_3^{2-} \) in the cell-solution was tolerated in varying degrees.

Ir(III) did not interfere when the maximum concentration was double the concentration of Os(VIII) in the solution.

Ni(II), Ru(III) and Rh(III) did not interfere when the maximum concentration was equal to the concentration of Os(VIII) in the solution.

Cd(II) did not interfere when the maximum concentration was 1/5 of the concentration of Os(VIII) in the solution.

Co(II) and Pd(II) did not interfere when the maximum concentration was 1/10 of the concentration of Os(VIII) in the solution.

Mn(II) did not interfere when the maximum concentration was 1/15 of the concentration of Os(VIII) in the solution.

Cr(III), Fe(II), Pt(IV) and \( S_2O_3^{2-} \) did not interfere when the maximum concentration was 1/20 of the concentration of Os(VIII) in the solution.

Cu(II), Hg(II), Mo(VI) and Mn(VII) interfered seriously at all concentrations.

The non-interfering species did not interfere even when added to Os(VIII) solution simultaneously. Equal concentration of all non-interfering species was maintained in the cell for these specificity tests, the maximum being \( 2.5 \times 10^{-4} \) M. Higher
concentrations were not attempted in order to avoid the super-saturation of the solution in the cell. Os(VIII) concentrations selected for this study were the same as mentioned above in case of interference studies.

**Amperometric determination of Os(VIII) using it as titrant (anodic titration)**

Anodic titrations were also carried out in this medium at -0.40V and -1.00V. The first titration voltage thus fell in the diffusion regions of the first wave of Os(VIII) and TSH both, while the second one fell in the diffusion region of the second wave of Os(VIII) alone. Amperometric curves of the types (a) and (b) shown in fig. 2.1.3 were obtained at the two respective titration voltages. Metal species - TSH titrimetric molar ratio was found to be 5:1 at both voltages. A light pink colour appeared in the cell in the course of titrations. Results of titrations are included in table 2.1.3.

Concentrations of Os(VIII) lower than $1\times10^{-4}$ M could not be estimated as the gradual addition of the metal species into TSH produced only a linear rise in cathodic current and no amperometric curves could be constructed.
Fig. 2.1.3: Amperometric titration curves of Os(VIII)-TSH system in 0.5M NaOH medium:

Titration voltages: (a) -0.40V (b) -1.00V
Concn. of TSH = 2.5x10^{-4} M
Concn. of Os(VIII) = 5x10^{-3} M
in the titrant: 5x10^{-3} M
solution

x = Residual current line at: -0.40V
y = Residual current line at: -1.00V

Volume (ml) of Os(VIII) added
Table 2.1.3
Amperometric determination of Os(VIII) in 0.5M NaOH medium

Titrant : Os(VIII) solution
Titration voltages : -0.40V and -1.00V
Range of concn. of TSH used : 2.5x10^{-4} - 5x10^{-6} M

<table>
<thead>
<tr>
<th>Concн.of Os(VIII) taken (Mx10^{-3})</th>
<th>Concн.of Os(VIII) obtained (Mean) Mx10^{-3}</th>
<th>%age error (Mean)</th>
<th>Standard deviation Sx10^{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0000</td>
<td>5.0000</td>
<td>0.000</td>
<td>0.0000</td>
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<tr>
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<td>0.5000</td>
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<td>0.000</td>
<td>0.0000</td>
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<tr>
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<tr>
<td>0.1000</td>
<td>0.0980</td>
<td>2.000</td>
<td>0.0010</td>
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</table>

Checking of interference and specificity

Interference of various cations and anions in the above titrations was checked. Three concentrations of Os(VIII), viz. 5x10^{-3} M, 1x10^{-3} M and 5x10^{-4} M were selected for such studies. Mg(II), Al(III), V(V), Zn(II), WO_4^{2-}, CH_3COO^-, O_2^-, NO_3^-, SO_4^{2-} and Cl^- did not interfere in the estimation of Os(VIII) even when present in the cell-solution to the extent of twenty times in excess of the concentration of Os(VIII) in the titrant solution.
Presence of Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Ru(III), Rh(III), Cd(II), Ir(III) and S$\textsubscript{2}O$\textsubscript{3}$^{2-}$ in the cell-solution was tolerated in varying degrees.

Ni(II) and Rh(III) did not interfere when the maximum concentration was equal to the concentration of Os(VIII) in the titrant solution.

Cd(II) and Ir(III) did not interfere when the maximum concentration was 1/5 of the concentration of Os(VIII) in the titrant solution.

Co(II) and Ru(III) did not interfere when the maximum concentrations was 1/10 of the concentration of Os(VIII) in the titrant solution.

Mn(II) did not interfere when the maximum concentration was 1/15 of the concentration of Os(VIII) in the titrant solution.

Cr(III), Fe(II) and S$\textsubscript{2}O$\textsubscript{3}$^{2-}$ did not interfere when the maximum concentration was 1/20 of the concentration of Os(VIII) in the titrant solution.

Cu(II), Pd(II), Hg(II), Pt(IV), Mo(VI) and Mn(VII) interfered seriously at all concentrations.

The non-interfering species did not interfere even when added to the cell-solution simultaneously. Equal concentration of all non-interfering species was maintained in the cell for these specificity tests, the maximum being
2.5 \times 10^{-4} \text{ M. Higher concentrations were not attempted in order to avoid the super-saturation of the solution in the cell. Os(VIII) concentrations selected for this study were the same as mentioned above in case of interference study.}

**Amperometric determination of Os(VIII) in 0.5M NH}_3 + 0.5M NH}_4 Cl medium**

Amperometric determination of Os(VIII) species was successfully carried out in 0.5M NH}_3 + 0.5M NH}_4 Cl medium as well. Cathodic waves of metal species were exploited for the purpose. Metal species-TsH molar titrimetric ratio obtained was 5:1.

**Polarographic characteristics of the metal species**

Os(VIII) gave three well defined waves in this medium as reported by Meites. The limiting region of the first wave stretched from -0.10V through -0.20V and that of the second wave from -0.30V through -1.25V. The third wave started after -1.25V. Meites (loc.cit.) concluded that the first wave is due to the reduction of Os(VIII) to Os(VI) and the second wave, due to the reduction of Os(VI) to Os(IV); the third wave, according to him, is a catalytic hydrogen wave.

**Polarographic characteristics of TsH**

Polarographic characteristics of TsH in this medium have already been discussed in section 4 of part 1. It may
be recalled that the wave is fully diffusion controlled and the wave height, proportional to the concentration of TSH. Diffusion region stretches over the potential range of -0.20V through -0.40V.

**Amperometric Studies**

Both 1st and 2nd waves of Os(VIII) were exploited for the amperometric determination of this metal species. Titrations were carried out at -0.15V, -0.35V and -1.00V. The titration voltage, -0.15V fell in the diffusion region of Os(VIII) alone (first wave), -0.35V in the diffusion regions of Os(VIII) (second wave) as well as TSH and -1.00V in the diffusion region of the second wave of Os(VIII) alone. Titrations curves of types shown in fig.2.1.4., were obtained at different voltages mentioned therein. Metal species -TSH titrimetric molar ratio of 5:1 was deduced from these curves. During the course of titrations, colour of the osmium solution changed to pink. The results are included in table 2.1.4.

It is noteworthy that titrations at -0.15V always yielded nearly zero diffusion current at the null point. On the other hand, in case of titrations at -0.35V and -1.00V, the diffusion current remaining unneutralized at the null point was always almost equal to that of the second wave (table 2.1.5).
Fig. 2.1.4: Amperometric titration curves of Os(VIII)-TSH system in 0.5M NH₃+0.5M NH₄Cl medium:

Titration voltages: (a) -0.15V (b) -0.35V (c) -1.00V

Concn. of Os(VIII): 5x10⁻⁴ M
Concn. of TSH (titrant): 5x10⁻³ M

x = Residual current line at: -0.15V
y = Residual current line at: -0.35V
z = Residual current line at: -1.00V

Os(VIII)-TSH = 5:1
Table 2.1.4
Amperometric determination of Os(VIII) in 0.5M NH₃ + 0.5M NH₄Cl medium

<table>
<thead>
<tr>
<th>Titration voltages</th>
<th>Range of concn. of TSH used</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSH solution</td>
<td>5x10⁻²M - 2.5x10⁻⁴M</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concns. of Os(VIII) taken (Mx10⁻³)</th>
<th>Concns. of Os(VIII) obtained (Mx10⁻³)</th>
<th>%age error (Mean)</th>
<th>Standard deviation (Sx10⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0000</td>
<td>5.0000</td>
<td>0.000</td>
<td>0.0000</td>
</tr>
<tr>
<td>1.0000</td>
<td>1.0000</td>
<td>0.000</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.5000</td>
<td>0.5000</td>
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<td>0.0000</td>
</tr>
<tr>
<td>0.1000</td>
<td>0.1000</td>
<td>0.000</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.0500</td>
<td>0.0500</td>
<td>0.000</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.0400</td>
<td>0.0399</td>
<td>0.250</td>
<td>0.0002</td>
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<td>0.0350</td>
<td>0.0348</td>
<td>0.571</td>
<td>0.0004</td>
</tr>
<tr>
<td>0.0250</td>
<td>0.0232</td>
<td>7.200</td>
<td>0.0014</td>
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</tbody>
</table>

Attempts were also made to estimate Os(VIII) in this medium using the metal species itself as titrant (anodic titrations). However, no fixed stoichiometric ratio could be obtained.
Table 2.1.5

Study of amperometric curves (cathodic titrations) obtained at -0.35V and -1.00V in 0.5M NH$_3$ + 0.5M NH$_4$ Cl medium

<table>
<thead>
<tr>
<th>Conc'n of Os(VIII) taken</th>
<th>$i_d$ of II wave alone measured before starting point at -0.35V</th>
<th>$i_d$ obtained at the null point at -0.35V</th>
<th>$i_d$ of II wave alone measured before starting titration at -1.00V</th>
<th>$i_d$ obtained at the null point at -1.00V</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M \times 10^3$</td>
<td>($\mu$A)</td>
<td>($\mu$A)</td>
<td>($\mu$A)</td>
<td>($\mu$A)</td>
</tr>
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<td>25.040</td>
<td>23.740</td>
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<td>4.276</td>
<td>4.280</td>
<td>5.040</td>
<td>5.380</td>
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<td>0.550</td>
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<td>0.182</td>
<td>0.142</td>
<td>0.158</td>
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</table>

Checking of interference and specificity

Interference of various cations and anions in the above titrations was checked. Three concentrations of Os(VIII), viz. $5 \times 10^{-3}$ M, $1 \times 10^{-3}$ M and $5 \times 10^{-4}$ M were selected for such studies. Na(I), Mg(II), Al(III), Zn(II), WO$_4^{2-}$, CH$_3$COO$^-$, Ox$^{2-}$, NO$_3^-$ and SO$_4^{2-}$ did not interfere in the estimation of Os(VIII) even when present in the cell-solution to the extent of twenty times in excess of the concentration of Os(VIII).
Presence of V(V), Cr(III), Mn(II), Co(II), Ni(II), Ru(III), Rh(III), Cd(II), Pd(II), Ir(III), and Pt(IV) in the cell-solution was tolerated in varying degrees.

V(V), Ru(III) and Ir(III) did not interfere when the maximum concentration was equal to the concentration of Os(VIII) in the solution.

Rh(III) and Pt(IV) did not interfere when the maximum concentration was 1/5 of the concentration of Os(VIII) in the solution.

Cr(III), Co(II) and Pd(II) did not interfere when the maximum concentration was 1/10 of the concentration of Os(VIII) in the solution.

Mn(II), Ni(II) and Cd(II) did not interfere when the maximum concentration was 1/20 of the concentration of Os(VIII) in the solution.

Fe(II), Cu(II), Hg(II), Mo(VI), Mn(VII) and $S_2O_3^{2-}$ interfered seriously at all concentrations.

The non-interfering species did not interfere even when added to Os(VIII) solution simultaneously. Equal concentration of all non-interfering species was maintained in the cell for these specificity tests, the maximum being $2.5 \times 10^{-4}$ M. Higher concentrations were not attempted in order to avoid the supersaturation of the solution in the cell. Os(VIII) concentrations selected for this study were the same as mentioned above in case of interference studies.
Amperometric determination of Os(VIII) with the help of TSH was successfully carried out in two media:

i. 0.5M NaOH

ii. 0.5M NH₃ + 0.5M NH₄Cl

Both the species were found to be polarographically active in both these media. Estimation of Os(VIII) could be accomplished in medium (i) by exploiting the cathodic waves of the metal species (cathodic titrations) or the anodic wave of TSH (anodic titrations) using thiomalic acid or Os(VIII) respectively as titrant. Estimation in medium(ii) involved the suppression of the cathodic current of Os(VIII) by TSH titrant. In all cases, Os(VIII):TSH titrimetric molar ratio was found to be 5:1.

TSH gave its usual one electron anodic wave in the two media with the diffusion region stretching from -0.30V through -0.50V in 0.5M NaOH and from -0.20V through -0.40V in the 0.5M NH₃ + 0.5M NH₄Cl medium. The wave characteristics in the former medium were similar to those reported by Agrawal et al in 0.1M NaOH while in case of the latter medium, they were similar to those reported by Tiwari and Kapoor in ammonia – ammonium chloride buffer medium of pH = 9.

Os(VIII) was observed to give a three wave polarogram in each of these media as reported by Meites. In medium(i) the diffusion region of 1st wave stretched from -0.20V through
That of the 2nd wave from -0.85V through -1.40V and that of the 3rd wave from -1.60V onwards. According to Meites (loc.cit.), the waves corresponded to the reduction scheme:

\[
\begin{align*}
\text{Os(VIII)} & \xrightarrow{1\text{st wave}} \text{Os(VI)} \xrightarrow{2\text{nd wave}} \text{Os(IV)} \xrightarrow{3\text{rd wave}} \text{Os(III)}.
\end{align*}
\]

The heights of the successive cathodic waves were in the ratio of 2:2:1.

Diffusion regions of the first two waves in medium(ii) were -0.10V through -0.20V and -0.30V through -1.25V respectively and in all probability, they were due to successive reduction of Os(VIII) to Os(VI) and Os(IV) as concluded by Meites (loc.cit.). The third wave, which started after -1.25V in this medium, did not represent any further reduction of Os(VIII) and was only a catalytic hydrogen wave.

Titrations in any of the two media (whether cathodic or anodic) gave strong indications of the reduction of Os(VIII) by TSH. This is not surprising in view of the fact that Os(VIII) is a very hard species and TSH seems to have a marked tendency to undergo oxidation by such species. Otherwise also, OsO_4 is a known powerful oxidizing agent.

Amperometric titrations (cathodic as well as anodic) in medium(i) were performed at -0.40V and -1.00V. The first titration voltage fell in the diffusion regions of TSH as well as first wave of Os(VIII), while the second one fell
in the diffusion region of the second wave of Os(VII) alone. Amperometric curves of the types (a) and (b) of fig. 2.1.2 were obtained when TSH was used as titrant (fig. 2.1.2 clearly shows the second arm of the curve at -0.40V passing on to the anodic side with the addition of excess TSH) while those of types (a) and (b) of fig. 2.1.3 were obtained when the metal species was used as titrant (again it is clear from the figure that the first arm of the curve at -0.40V starts on the anodic side). The high unneutralized current at the null point in titrations at -1.00V (fig. 2.1.2) always corresponded to the $i_d$ of 2nd wave of Os(V VIII) (table 2.1.2).

Cathodic titrations in medium (ii) carried out at -0.15V, -0.35V and -1.00V yielded curves of the types (a), (b) and (c) respectively of fig. 2.1.4. TSH was used as titrant. Obviously -0.15V fell in the diffusion regions of TSH and the 1st wave of osmium, -0.35V in the diffusion regions of the 2nd wave of the metal species and TSH while -1.00V fell in the diffusion region of Os(V II) alone. It is because of -0.15V falling in the diffusion regions of both species (1st wave in case of Os VIII) that the second arm of the curve at this voltage passes on to anodic side with the addition of excess TSH. Curves (b) and (c) of the fig. 2.1.4 show very high current at the null point; unneutralized current always was almost equal to the $i_d$ of 2nd wave of Os(VII) (table 2.1.5). Curve (b) of fig. 2.1.4 obtained through titration at -0.35V shows
appreciable current remaining on the cathodic side even after null point was exceeded substantially, although this voltage lies in the anodic diffusion region of TSH. This is due to the fact that much higher current of the second wave of osmium more than compensates the anodic current resulting from increasing concentration of TSH. However, it is noteworthy that the second arm consistently moves towards the anodic side as the titration advances.

Following reaction can be proposed to explain the titrimetric molar ratio of 5:1:

\[
5\text{SO}_4^- + \text{HS-CH(COOH)-CH}_2\text{-COOH} \rightarrow 5\text{SO}_3^- + \text{HCOOH} + 3\text{CO}_2 + \text{H}_2\text{S} + \text{H}_2\text{O} \quad \ldots \quad (i)
\]

Reduction of Os(VIII) to Os(VI) was established from the fact that whenever cathodic titrations were performed at -1.00V in medium(i) or -0.35V or -1.00V in medium(ii), the diffusion current remaining unneutralized at the null point was almost always equal to that of the second wave of osmium (table 2.1.2 and 2.1.5), which is known to appear as a result of electro-reduction of Os(VI) species. On the other hand, titrations (cathodic or anodic) at -0.40V in medium(i) and -0.15V in medium(ii) always yielded only near zero diffusion current (fig. 2.1.2 and 2.1.4) at the null point, obviously due to the total reduction of Os(VIII) by TSH. It may be mentioned again that the cathodic current of osmium at these voltages in the respective media appears due to the electro-reduction of Os(VIII) to Os(VI).
Reduction of Os(VIII) to Os(VI) was indicated by change of colour also. It was observed that the colour of the osmium solution changed from yellow to pink in the course of titration. Pink is the colour of the osmate ion $\left[\text{OsO}_2(\text{OH})_4\right]^{2-}$, and $\text{OsO}_3$, appearing in equation (i), presumably exists in this form in the basic media employed.

Other products of the reaction embodied in equation (i) were also identified in the 5:1 solution. They can be expected to be arrested in the NaOH medium in the form of HCOONa, $\text{Na}_2\text{CO}_3$ and $\text{Na}_2\text{S}$. Presence of formate was confirmed by silver mirror test with Tollen's reagent and that of $\text{CO}_3^{2-}$ by lime water test. $\text{S}^{2-}$ was tested by reacting the solution with HCl and exposing the lead acetate paper to the $\text{H}_2\text{S}$ vapour thus evolved; the lead acetate paper turned black.

The methods evolved are quite efficient and very dilute solutions of Os(VIII) can be estimated with a high degree of accuracy in any of the media employed. A number of foreign cations and anions do not interfere and specificity is also good. Tolerance for other platinum metal ions was, however, low in both media. It is noteworthy that to the best of the knowledge of the author, no direct amperometric method of determining Os(VIII) at d.m.e. has been reported before.