CONCLUSIONS

As a result of the investigations, described in the previous sections, it is considered that the whole question of the usage of metal indicator and reference electrodes in polarography and potentiometry has been clarified from many points of view, and many of the discrepancies, apparent or real, in the literature have been resolved. The overall performance of the bimetallic electrode system is recounted here.

The bimetallic electrode system Ag-Mo was studied thoroughly using polarographic and potentiometric techniques. It proved useful, where the conventional electrode system failed.

PART I - CATHODE RAY POLAROGRAPHIC WORK

Polarography of silver is rather difficult, because of the interference of mercury reduction, which occurs at the same potential at which silver is also reduced. An alternate electrode system to DME-Hg pool has to be found.

Reproducible curves are not obtained on d.c. polarograph when metal indicator electrodes are used. Silver indicator electrode was used successfully on the cathode ray polarograph which has got much faster voltage scanning facility. Molybdenum wire was employed as a reference electrode. Silver and mercury reduction peaks were well separated, occurring at -0.57 and -0.43 V respectively in 0.1M sulpho-
salicylic acid medium. In other supporting electrolytes current concentration linearity for silver was not obtained and hence all the work was done using 0.1M sulfosalicylic acid. Silver electrode gave reduction wave for silver and mercury. Other cations such as Cu$^{+2}$, Zn$^{+2}$, Cr$^{+6}$, Fe$^{+3}$ etc and anions such as Cl$, Br$, I$^-$ etc were not reduced on silver electrode.

Silver amalgam wire electrode was also used as an indicator electrode in order to understand fully the electrode mechanism of silver reduction on dropping mercury and silver electrodes. On this electrode, the mercury and silver reductions are very much separated, occurring at -0.28 and +0.13 V(vs Mo electrode) respectively. The primary purpose of choosing an alternate electrode system is thus fulfilled. Reduction peaks for amalgam forming cations, such as copper, zinc and non amalgam forming cations such as ferric, chromate were obtained on silver amalgam electrode, just as in the case of DME. It thus behaves as a mercury electrode for these cations including silver. But for mercury reduction, it behaves more like silver electrode.

Replacement of molybdenum reference electrode by tungsten produced silver peaks which were not proportional to the silver concentrations, in spite of the close similarities between the chemical and pH properties of the two.
Potentiometrically also, it was proved that molybdenum was far superior reference electrode compared to tungsten. The difference of behaviour between these two electrodes in the case of silver response, may be ascribed to the adherent silver deposit on the tungsten surface in concentrated silver solution.

It was not possible to eliminate oxygen reduction wave completely in most of the solutions. Only in the alkaline solution, the wave almost disappeared. In presence of gelatin, the wave was reduced, but was enhanced in the presence of thymol. Further purification of nitrogen, as well as the rate and time of bubbling did not significantly reduce the oxygen wave. The effect of employing different supporting electrolytes as well as different temperatures was studied. From this study it was inferred that the reduction wave is due to the surface adsorbed oxygen. However, the interference due to oxygen is not serious. For amalgam electrode, the silver peak comes before the oxygen wave and for the silver electrode, oxygen wave is S-shape and silver reduction is obtained in the form of peak and no interference results. Moreover, the oxygen reduction occurs at -0.2 V and the silver reduction at -0.6 V.

Various factors affecting silver reduction were studied. Silver peaks vanished on addition of maxima
suppressors, therefore in the voltammetry of silver ion, maxima suppressors should be avoided. Temperature had no effect on silver reduction, the peak current remaining practically constant from 0 to 42°C for both the electrodes. Silver reduction peaks were obtained only on the fresh amalgam electrode and aged electrode, even 24 hours old, failed to function as an indicator electrode. Silver electrode tolerated up to 0.04% acidity, and the amalgam electrode up to 0.24% acidity. For both the electrodes, the current decreased on the addition of sulphuric acid. In acid solutions, the current concentration linearity is obtained over a wide range for the amalgam electrode, compared to the silver electrode. But in 0.1M sodium hydroxide solution, the peak current remains constant for the amalgam electrode, but varies linearly with silver concentration for silver electrode. Amalgam electrode should be used in acidic solutions and silver electrode is to be preferred in the alkaline solution.

Current concentration linearity curves were obtained for different lengths of silver and amalgam electrodes. The linearity is obtained up to 1.4 cm long silver electrode and 0.8 cm long amalgam electrode. For 1.0 mM silver concentration, the graph of peak current vs silver electrode length shows a rising curve which can be divided into two straight lines, intersecting at about 1.0 cm. For amalgam electrode,
however, a single straight line is obtained. In polarography, the indicator electrode should be a micro electrode. These results show that the conditions for being a micro electrode are not very critical.

Being used in the wire form, these electrodes are cylindrical in nature. Moreover, silver ion, after reduction deposits on the electrode surface. One is therefore, compelled to take into account Nicholson's equation for cylindrical diffusion as well as Berzins and Delahay's equation. Sevick's or Randles equations also are applicable to the wire electrode with certain limitations. All these equations were therefore tried for these two electrodes. The observed current was found to be 10-15 times smaller in the case of silver electrode and 5-10 times smaller for the amalgam electrode. This was considered to be due to the large capacity currents, the increasing irreversibility of the longer electrodes and decreasing polarisibility. In the case of metal electrodes, the roughness factor has to be taken into account to calculate the actual area which may be 2 to 10 times the apparent area. The capacity current is proportional to the actual area, but the diffusion current is proportional to the apparent area only. The surface of the amalgam electrode being smoother than the silver electrode, the extent of deviation of the observed
and the calculated currents is smaller than that obtained for silver electrode. The net result amounts to as if a much smaller area is available. Randle's equation is therefore modified so that the peak current instead of being directly proportional to the area of the electrode \( A \), is proportional to the power of the area \( A^x \), \( x \) varying from 1.5 to becoming constant at 2.5 at longer lengths of silver electrodes. In the case of amalgam electrode, \( x \) tends to be constant at about the value of 2.0. Randles equation, without modification is obeyed for micro electrodes (length less than 0.1 cm).

The use of silver indicator electrode for silver reduction lays the foundation of a technique that may be called 'Selective Polarography'. The metal indicator electrode will respond to it's own ions preferentially, as in the case of potentiometry. They can therefore be used in the analysis of that particular metal ion. The study is in progress for zinc electrode and a fuller evaluation of the technique will be possible after the completion of study for several metal indicator electrodes.

PART II - POTENTIOMETRIC STUDIES

Potential - pH diagram for molybdenum-SCE system gave an unbroken straight line over the entire pH range of \(<2\) to \(>11\), contrary to some earlier reports, with a slope of
53 mV/pH, compared to the slope of 41 mV/pH for W-SCE. In buffer solutions, however, both molybdenum and tungsten electrodes gave smaller slopes of 40 mV/pH. Salting out effect does not occur for Mo and W electrodes. Molybdenum potential does not change for a fixed pH value, containing different anions. Contrary to the behaviour of glass and antimony electrodes, molybdenum and tungsten electrode potentials were not affected by different rate of stirring. Length of the electrode had no effect, but a 19 s.w.g. Mo electrode gave a higher potential compared to the 25 s.w.g. electrode.

In the strong acid - strong base titrations, three systems were used and compared, Glass-SCE, Mo-SCE and Mo/MoO$_3$-SCE. Upto 0.01N concentration, the first two systems gave comparable results, while low inflections were obtained for the last system. For 0.001N concentration, only Mo-SCE system enabled the end point to be determined, while the two other systems failed completely. Though, it is quite clear that glass can not be replaced by molybdenum for estimating pH of a solution, it can very well replace it in the potentiometric titrations.

Silver electrode may behave as a pH electrode, as indicated by the theory of metal/metal oxide electrodes. But silver electrode cleaned with 1:4 nitric acid failed
to give any response to various buffered and unbuffered solutions. It was therefore thought that it might be feasible to use it as a reference electrode in acid-base titrations with molybdenum as a pH electrode. Potential pH response curves in unbuffered solutions for Mo-Ag system taken over the range of 4-11 pH show that this system is even better than Mo-SCE, as the slope obtained here is 55 mV/pH. However W-Ag system response is not as good as Mo-Ag but better than W-SCE system. But in the buffered solutions the response deteriorates compared to Mo-SCE system.

For strong acid – strong base titrations for 0.1 and 0.01N good curves were obtained for Mo-Ag, end points comparing well with true visual end points. But the curve height, the inflection acround end point is less for Mo-Ag compared to Mo-SCE. No end point could be detected at 0.001N. Reverse titration, alkali in the beaker and acid in the burette did not give good results. The length of molybdenum as well as silver electrode had no effect on the titration performance. The titration curve flattens out rather suddenly, after the end point. Unlike many bimetallic electrode systems, where both the electrodes respond to the same ion with time difference giving rise to a peak, this system gives rise to the usual S shape potentiometric curve,
confirming that the silver electrode does behave as a reference electrode. During the start of the titration, on the acidic side, the silver surface is covered with a layer of Ag₂O, which is not very passivating. After the end point on the alkaline side, the oxide present is Ag₂O₂. The change over from Ag₂O to Ag₂O₂ may not be quick and hence the curve flattens out rather abruptly. Nonetheless, it must be borne in mind that Mo-Ag system functions well up to 0.01N concentration.

Mo-Ag system was then tried for weak acid (e.g., acetic acid and chromotropic acid) - strong base titrations. As noted earlier for strong acid titrations, the end points obtained with glass - SCE and Mo-Ag are identical, and the inflections for the latter are smaller compared to the former system.

These acids were titrated against sodium hydroxide in mixed solvents, up to 90% methanol and acetone. Mo-Ag system gave results comparable to the glass-SCE system. The adsorption of the organic solvent on these electrodes was negligible, when the percent mixture of the solvent was less. Benzilic acid, which is very much soluble in ethanol or methanol and only slightly in water, was also titrated against the alkali. In ethanol, the curve heights for glass-calomel and Mo-Ag are nearly the same, but when the titration
was performed in methanol, though the end points are identical, the curve height for Mo-Ag is much smaller compared to Glass-calomel. Mo-Ag system, therefore, can substitute the glass-calomel system in mixed titrations, as the end points obtained are identical.

It is reported that silver may behave as a red-ox indicator electrode. In view of the resisting power of molybdenum to various chemical solution, from strongly acidic to strongly alkaline solutions, molybdenum may also behave as a red-ox electrode. But both did not behave as red-ox electrodes. Molybdenum electrode also did not respond to the concentration changes of the molybdate ion. In the bimetallic system of Pt-Mo and Pt-Ag, where molybdenum and silver function as reference electrodes, the end points obtained were the correct end points and the curve heights were comparable to the Pt-SCE system. In the ferrous-dichromate titrations, the curve heights for Pt-Ag and Pt-Mo are much higher in that order compared to Pt-SCE.

Ag-Mo system can very well be used in argentimetric halide titrations, obtaining true end points and getting higher wave heights for chloride and iodide compared to Ag-calomel (sulphate) system. Unlike the previous bimetallic curves, a peak was obtained here. A loose deposit
of silver is formed on the molybdenum surface and therefore it may give a pseudo response to the silver ion. In the titrations of mixtures of halides also, the curve heights for chloride and iodide are higher compared to Ag-calomel (sulphate) system.

**PART III - SEMI MICRO CELL WORK**

It is clear from the above discussion that Ag-Mo system can be used in polarography for the silver ion reduction in the presence of mixture of other cations. The same system can also be used in potentiometry for strong acid - strong base, weak acid - strong base titrations in aqueous and mixed solvents as well as for argentimetric halide titrations. This electrode system is therefore, very suitable for the fabrication of a semi-micro cell (0.2 - 0.5 ml) which can be used both in polarography and potentiometry.

Silver peaks were taken in the mixture of acetone or methanol, in which silver was highly soluble, and sulfo-salicylic acid. Silver content was estimated in these organic solvents and alkalies by evaporating the solvent or alkali and taking the residue in supporting electrolyte. 10 p.p.m. of silver could be estimated by this method.