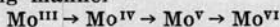


## A STUDY OF THE OXIDATION OF TRIVALENT MOLYBDENUM

SISTER MARY MARTINETTE, B.V.M., *Mundelein College, Chicago*  
L. F. YNTEMA, *Saint Louis University, Saint Louis, Missouri*

That the oxidation of trivalent molybdenum may be carried out with considerable ease is evidenced by the fact that certain trivalent molybdenum compounds in solution are readily oxidized by atmospheric oxygen. Since trivalent molybdenum is oxidized from a valence of positive 3 to a valence of positive 6 and  $\text{Mo}^{\text{IV}}$  and  $\text{Mo}^{\text{V}}$  are known, it is to be expected that the oxidation proceeds in the following manner—



In this work, the oxidation of molybdenum was followed very closely by means of potentiometric titrations, with bimetallic electrode pairs and an electron tube used in the circuit. Various oxidizing agents, addition agents, and acid concentrations were employed. The resulting data were plotted to give the titration curves for the oxidation of molybdenum.

The results, while not so complete and satisfactory as we had hoped they would be, have opened a field for further research. The work is being continued at Saint Louis University, where this project was begun. In the past, several articles on the oxidation of trivalent molybdenum have appeared. In most cases there was question of the oxidation  $\text{Mo}^{\text{IV}} \rightarrow \text{Mo}^{\text{V}}$ . However, Jakob and Michalewicz<sup>1</sup> concluded from their experiments that the potential of a  $\text{Mo}^{\text{V}}$  solution was not nearly so great as that of a  $\text{Mo}^{\text{IV}}$  solution and consequently when the  $\text{Mo}^{\text{III}} \rightarrow \text{Mo}^{\text{IV}}$  oxidation appeared the  $\text{Mo}^{\text{IV}} \rightarrow \text{Mo}^{\text{V}}$  oxidation would not appear, and when the  $\text{Mo}^{\text{IV}} \rightarrow \text{Mo}^{\text{V}}$  oxidation appeared the  $\text{Mo}^{\text{III}} \rightarrow \text{Mo}^{\text{IV}}$  oxidation would not.

These investigations led us to carry out oxidation experiments on reduced potassium molybdate solutions and on potassium chloromolybdate solutions under varying conditions, in an effort to explain further the oxidation steps. The measurement of amplified potential differences between bimetallic electrodes ap-

peared to offer good results so we assembled the apparatus shown in fig. 1. This set-up was a modification of that of Goode<sup>2</sup>. Since it is not possible to obtain accurate results by means of potentiometric measurements when an extremely small amount of current is being drawn from the cell under investigation or when the cell resistance is abnormally high, a five-electrode tube was introduced into the ordinary potentiometric circuit. Our particular tube was an RCA 6K7.

Among the electrode pairs used were:

- Platinum-Chromel
- Platinum-Nickel
- Platinum-Polarized platinum
- Nickel-Chromel

The platinum-chromel pair gave by far the best results in the preliminary titrations and consequently was used throughout. Both the oxidizing and the reduced solutions were approximately  $N/10$  but the strength of the acid mediums was much greater. The  $\text{K}_2\text{MoO}_4$  solution was standardized by the accepted method<sup>3</sup>. This same technique was used throughout to reduce the molybdenum, but the  $\text{Mo}^{\text{III}}$  was run from the Jones reductor into a reaction vessel filled with  $\text{CO}_2$ . The  $\text{CO}_2$  atmosphere was necessary to prevent oxidation by the air.

The oxidizing agents used were:

1. Ceric sulfate,
2. Potassium permanganate,
3. Ferric salts,
4. Potassium dichromate.

The various reaction mediums were:

1.  $\text{H}_2\text{SO}_4$  (N, 0.4N, 0.6N)
2. HCl (2N, N, 0.4N)
3. Zimmermann-Reinhardt solution (20-25°C. and 60-70°C.)
4.  $\text{H}_3\text{PO}_4$  (1.5 N.)

The addition reagents were:

1.  $\text{MnSO}_4$ ,
2.  $\text{NH}_4\text{F}$
3.  $\text{MnSO}_4$  and  $\text{NH}_4\text{F}$
4.  $\text{Ce}(\text{SO}_4)_2$ .

<sup>1</sup> Jakob and Michalewicz, *Rozeniki Chem.*, **12**, 576-588 (1932).

<sup>2</sup> Goode, *J. Am. Chem. Soc.*, **44**, 26 (1922).

<sup>3</sup> Willard and Fenwick, *J. Am. Chem. Soc.*, **44**, 2516-2529 (1922).

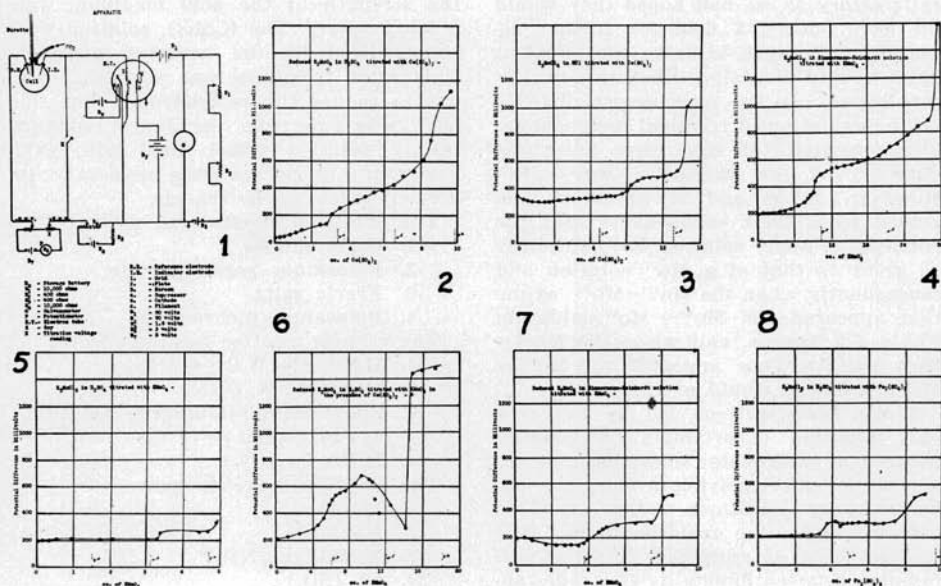
Ceric sulfate has advantages over potassium permanganate as an oxidizing agent because it may be used in chloride solutions, is stable over long periods of time and has a potential close to that of the permanganate.

The curve shown in fig. 2 is that of  $\text{Mo}^{\text{III}}$  in  $\text{H}_2\text{SO}_4$ , titrated with  $\text{Ce}(\text{SO}_4)_2$ . The theoretical and actual end-points do not coincide, and there is no evidence of the oxidation  $\text{Mo}^{\text{IV}} \rightarrow \text{Mo}^{\text{V}}$ . Using  $\text{Mo}^{\text{III}}$  in  $\text{HCl}$ , we obtained a curve in which the end-points again fell short of the theoretical end-point, and there was a break which corresponded to the  $\text{Mo}^{\text{IV}} \rightarrow \text{Mo}^{\text{V}}$  end-point, fig. 3. Addition agents did not improve these results. In general, the ceric sulfate titrations proved unsatisfactory. If a  $\text{Mo}^{\text{III}} \rightarrow \text{Mo}^{\text{IV}}$  oxidation occurred, there was no evidence of a  $\text{Mo}^{\text{IV}} \rightarrow \text{Mo}^{\text{V}}$  oxidation, and vice versa. An important contributing factor might be the inability to regulate the pH of the molybdenum solution when the oxidizing agent was added. The ceric sulfate itself is strongly acid, and the potentials of oxidants will vary with pH.

Titration of the  $\text{Mo}^{\text{III}}$  with  $\text{KMnO}_4$  in  $\text{H}_2\text{SO}_4$  solution did not produce the desired curve, so the potassium chloromolybdate solution was used in a Zim-

mermann-Reinhardt solution, fig. 4. While this titration proceeded rather smoothly, the  $\text{Mo}^{\text{IV}} \rightarrow \text{Mo}^{\text{V}}$  reaction was not indicated. When the titration of  $\text{K}_2\text{MoCl}_6$  was repeated, this time in a sulfuric acid solution, a curve, fig. 5, was obtained, in which the break  $\text{Mo}^{\text{IV}} \rightarrow \text{Mo}^{\text{V}}$  was evident but not the  $\text{Mo}^{\text{III}} \rightarrow \text{Mo}^{\text{IV}}$  end-point. The titration of  $\text{Mo}^{\text{III}}$  in  $\text{H}_2\text{SO}_4$  with  $\text{KMnO}_4$  in the presence of  $\text{Ce}(\text{SO}_4)_2$  gave a very strange curve, fig. 6. The drop in potential difference might indicate that the potential for  $\text{Mo}^{\text{IV}} \rightarrow \text{Mo}^{\text{V}}$  is lower than that for  $\text{Mo}^{\text{III}} \rightarrow \text{Mo}^{\text{IV}}$ , as suggested by Jakob and Michalewicz. The titration of reduced  $\text{K}_2\text{MoO}_4$  in Zimmermann-Reinhardt solution with  $\text{KMnO}_4$  gave a very nice break in the curve for the oxidation  $\text{Mo}^{\text{IV}} \rightarrow \text{Mo}^{\text{V}}$ , fig. 7.

Since at no time did we obtain a curve in which three steps in the oxidation were clearly indicated, it seemed advisable at this point to try oxidizing agents which would carry the oxidation only from  $\text{Mo}^{\text{III}}$  to  $\text{Mo}^{\text{V}}$ , as there was no question of the possibility of oxidation to  $\text{Mo}^{\text{VI}}$ . Ferric salts were chosen for this purpose. In the case of  $\text{Mo}^{\text{III}}$  in  $\text{H}_2\text{SO}_4$ , titrated with ferric sulfate, the oxidation proceeded nicely, giving us both the  $\text{Mo}^{\text{III}} \rightarrow \text{Mo}^{\text{IV}}$  and the  $\text{Mo}^{\text{IV}} \rightarrow \text{Mo}^{\text{V}}$  breaks in



the curve, fig. 8, though, again, the theoretical and actual end-points were not the same.

In conclusion, it is evident from these data that the oxidation of molybdenum is not so simple as one might expect. It presents several complications which are not readily explainable. Why the oxidation from  $\text{Mo}^{\text{III}}$  to  $\text{Mo}^{\text{IV}}$  takes place in  $\text{H}_3\text{PO}_4$  and not in  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$  solutions when titrated with  $\text{KMnO}_4$ , in the absence of addition reagents, is a matter for further investigation. One possible explanation is based on the assumption of the formation of stable complexes which are not readily attacked by  $\text{KMnO}_4$ .

Careful experiments have shown that the possibility of air oxidation in these titrations did not exist. However, in any one of the titrations when the total time of titration was longer than two hours, the amount of oxidizing agent required

fell far below the theoretical amount.

The appearance of the  $\text{Mo}^{\text{IV}} \rightarrow \text{Mo}^{\text{V}}$  end-point too early in the oxidation and the subsequent oxidation of  $\text{Mo}^{\text{VI}}$ , giving a complete oxidation long before it is to be expected, is not to be explained by any ordinary chemical means. There appears to be an oxidant other than  $\text{KMnO}_4$  present, yet what it might be is not known. Spectrographic examination of the solution as the oxidation is being carried out might lead to a solution of the problem. Such analysis might show the presence of the complex ions which we feel may be present in the solutions.

#### REFERENCES

1. Jakob and Michalewicz, *Roczniki, Chemj.* **12**, 576-588 (1932).
2. Goode, K. H., *J. Am. Chem. Soc.*, **44**, 26-29 (1922).
3. Willard, H. H. and Fenwick, F., *J. Am. Chem. Soc.*, **44**, 2516-2529 (1922).
4. Hillebrand, W. F. and Lundell, G. E. F., *Applied Inorganic Analysis*, John Wiley and Sons, N. Y., (1929).