Amperometric Studies on Chromium(III) and Iron(III) Hydroxocyanotungstates(IV)

The formation and composition of Cr^{III} and Fe^{III} hydroxocyanotungstates(IV) have been investigated amperometrically by titrating $CrCl_3$/ferric alum and potassium hydroxocyanotungstate (IV). On reviewing the literature it has been found that no attempt has yet been made to study the composition of the precipitates formed by the above interactions.

Experimental. Potassium hydroxotetracyanotungstate (IV) tetrahydrate, $K_4[W(CN)_4(OH)_4]\cdot 4H_2O$ was prepared following the directions of MIKHALEVICH and LITVINCHUK[1]. Its solution was kept stored in an amber-coloured bottle wrapped in black paper. The strength was determined potentiometrically by titrating with $K_3[Fe(CN)_6]$[1].

Chromic chloride, ferric ammonium sulphate and other materials used were of Anala^R (B.D.H.) grade-reagents. Their solutions were made in triply distilled water and strengths determined by usual methods.

A Fischer Elecdropode (sensitivity $\times$ 10) was used for performing amperometric titrations. A dropping mercury electrode having $t = 4.5$ sec at Ed. e. $= 0.0$ V (v. S.C.E.) in conjunction with a saturated calomel electrode was used for current measurements. KCl (0.1 M) was used as the base electrolyte and gelatin (0.01% for Cr^{3+} and 0.02% for Fe^{3+} reaction) as the maximum suppressor.

The titrations were carried out at applied potentials, -1.3 V and 0.45 V (lying on the plateaux of the polarograms of chromic chloride and ferric alum, respectively, both in 0.1 M KCl). Purified nitrogen was bubbled through the cell after each addition of the titrant, this ensured a thorough mixing of the reactants and made the mixture oxygen free. All the titrations were performed at $30 \pm 0.1°C$.

Both direct (metal ion solution in the cell) and reverse (hydroxocyanide solution in the cell) titrations were performed with varying concentrations. The results are summarized in the Table and representative curves are shown in the Figure.

Discussion. Both the direct and reverse amperometric titrations between chromic chloride/ferric alum and potassium hydroxocyanotungstate (IV) give a combining ratio of 1:1 pointing towards the formation of KM^{III} $[W^{IV}(CN)_4(OH)_4]$ (M being Cr/Fe).

In direct amperometric titration of chromic chloride, the current at first increases and then decreases (Figure, curve I). This behaviour may be explained on the basis of solubility of the complex formed whose concentration is very low at first. When the solution becomes saturated with the complex, precipitation occurs and the current begins to decrease. This decrease in current continues until the end point is reached and then the current remains constant in view of non-reducibility of the hydroxocyanotungstate(IV) at d.m.e. In reverse titrations, the observed current remains almost unchanged on the addition of chromic chloride solution until the end point is reached, after which the diffusion current due to Cr^{3+} ions increases linearly, with the addition of the latter (Figure, curve II).

With ferric alum, the shapes of the titration curves are typical, both in the direct as well as reverse titrations (Figure, curves III and IV).

The titration graphs are so well defined that potassium hydroxotetracyanotungstate (IV) can be suitably employed for the estimation of Cr^{3+} and Fe^{3+} ions amperometrically.
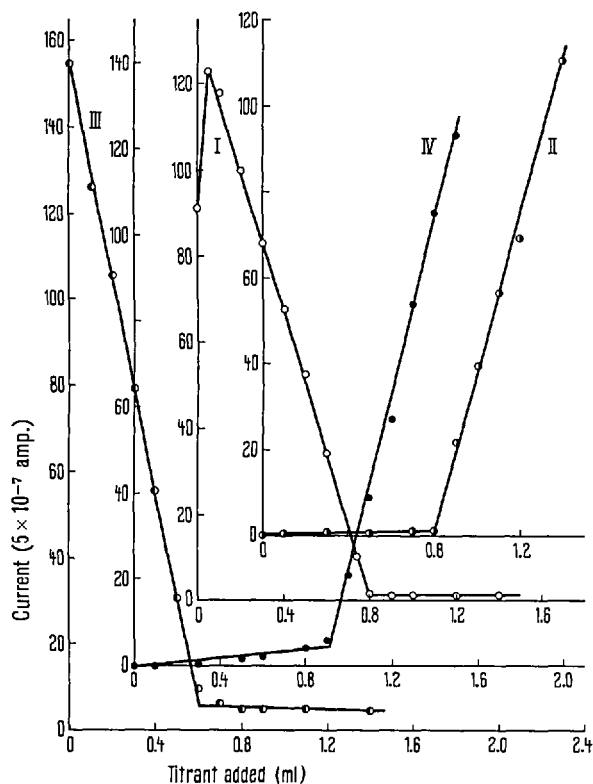
Amperometric titration curves. Direct: (I) 0.1 M $K_4[W(CN)_4(OH)_4]$ added to 10 ml of 0.008 M $CrCl_3$; (III) 0.1 M $K_4[W(CN)_4(OH)_4]$ added to 10 ml of 0.006 M ferric alum; reverse: (II) 0.1 M $CrCl_3$ added to 10 ml of 0.008 M $K_4[W(CN)_4(OH)_4]$; (IV) 0.1 M ferric alum added to 10 ml of 0.009 M $K_4[W(CN)_4(OH)_4]$.

Zusammenfassung. Die Zusammensetzung von in wässeriger Lösung gebildeten Ionenpaaren des Anions $[W(CN)_4(OH)_4]^{4-}$ mit Cr^{3+} bzw. Fe^{3+} wird amperometrisch ermittelt.

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[1] K. N. MIKHALEVICH and V. M. LITVINCHUK, Zh. Neorg. Khim. *4*, 1775 (1959); *9*, 2391 (1964).

Summary of the results of amperometric titrations

Molarity of the solutions (M)		Equivalence point (ml)	
Metal ion	Hydroxocyanide	Calculated	Observed
Direct titrations			
Cr^{III} 0.008	0.1	0.8	0.8
0.006	0.1	0.6	0.6
0.004	0.1	0.4	0.4
Fe^{III} 0.010	0.1	1.0	1.0
0.008	0.1	0.8	0.8
0.006	0.1	0.6	0.605
Reverse titrations:			
Cr^{III} 0.1	0.008	0.8	0.8
0.1	0.006	0.6	0.59
0.1	0.004	0.4	0.40
Fe^{III} 0.1	0.012	1.2	1.2
0.1	0.009	0.9	0.91
0.1	0.006	0.6	0.61