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NOTE

A Novel Electrolytic Technique for Oxidation-Reduction

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Electrolysis in a specially designed W-shaped cell offers isolation of desired oxidation-reduction products after electrolysis of certain solutions of electrolytes. Oxidation and reduction of Ce, Co, Mn, Cr, V and other industrially important metal ion solutions has been successfully obtained and compared with the products obtained by conventional chemical methods. This method does not require elaborate and tedious chemical operations as encountered with conventional methods. It thus offers a simple and easy alternative for oxidation-reduction.

Formation of boundaries corresponding to acidic, neutral and basic zones during electrolysis of electrolytic solution in a W-tube-cell has been reported by some workers.[1–4] Cr(III)-EDTA complexes by this method have also been reported. Oxidation of Co^{2+}, Ce^{3+} and similar metal ions needs elaborate chemical treatment with meticulous experimentation. It is felt that electrolytic technique may provide easy and simple alternative for obtaining oxidation-reduction products and collect them separately for desired utility. With this end in view, the report of the work undertaken is presented in this paper.

Solutions of $Ce_2(SO_4)_3$, $CoSO_4$, NH_4VO_3, $K_2Cr_2O_7$ in sulphuric acid medium of suitable normality were subjected to electrolysis in a specially designed W-shaped Cell for appropriate times and with suitably applied D.C. voltages. The cell has been fabricated from Corning glass tubing of internal diameter 1.2 cm. Platium wires (dia. 1.5 mm, length 1.5 cm) fused in glass tubes have been used as electrodes. Power for electrolysis has been derived from a suitable variable DC power supply unit (0–250 V). The duration of electrolysis has been adjusted according to the oxidation state of the desired end-product, which is indicated by change in colour in the anode/cathode compartments as well as from other standard chemical methods. Thus oxidation products from Ce(III) to Ce(IV), Co(III), Cr(III) to Cr(VI) have been successfully obtained and verified. Similarly, reduction of V(V), Cr(VI), Ce(IV) has also been achieved. These oxidation states have been obtained without any other chemical treatment within 15–20 minutes. Absorption spectra of the reaction products from anode/cathode compartments as well as other chemical tests have confirmed these results.

It is well known in volumetric analysis that H_2S, SO_2 and $SnCl_2$ and several

other reagents are used as reducing agents. However, passage of H_2S through water bubbler and removal of excess H_2S which necessitates an addition of mercuric chloride is a cumbersome process. Sulphur dioxide needs critical adjustments of acidity. At higher concentration it acts as an oxidising agent instead of a reducing agent. The amount of stannous chloride is also critical in volumetric analysis. The effectiveness of reductor columns depends upon the degree of amalgamation of the basic metal, particle size, acidity of the solution, the length of the reductor columns, and the speed of flow of effluent. Reduction with amalgams in titrimetric analysis also suffers from similar limitations. The redox or ion exchange resins have recently attracted wide publicity; however in this process sometimes the activity of the resin itself depletes during continuous usage in reduction or oxidation process.

It has to be noted that electrolysis of solutions of electrolytes in a W-shaped cell at higher voltages is a non-Faradic process which involves generation of heat. The process of diffusion controlled migration of ions is also hindered and an ion-free zone intervening the acidic and basic zones could be established. The nature of the end-products obtained in the anode/cathode compartment is governed by the concentration of electrolyte and the amount of the current passed. Thus without using any resins or sintered glass or porous isolator, a simple W-shaped cell facilitates isolation of reaction products in the anode/cathode compartment. The oxidation states of the metal ions can be conveniently controlled by the passage of current and time duration.

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