# 77. *The Electrolytic Production of Quadrivalent Uranium.*

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The conditions for the complete electrolytic reduction of acid uranyl chloride solutions to quadrivalent uranium have been studied, especially the factors affecting the limiting current density and hence the efficiency of the main cathodic process. The reduction was followed quantitatively through time–potential curves under various conditions.

Apart from the polarograms obtained by Harris and Kolthoff (*J. Amer. Chem. Soc.*, 1945, **67**, 1884; 1946, **68**, 1175; 1947, **69**, 446) little work has been reported on the electrolytic reduction of uranyl solutions to quadrivalent uranium, and most of it was directed to the determination of uranium as electrolytically deposited hydrated yellow or black oxides; the electro-reduction of uranyl salts at a mercury cathode was also made the basis of a process for the determination of uranium (Sutton, *J. Nat. Res. Council,* Canadian Atomic Energy Project, N.R.C. No. 1591, 1945). For these reasons and also because of the possible use of quadrivalent uranium for determining the standard redox potential of the uranium system, interest has been focused particularly on the production of uranous solutions in a high state of purity.

The work now reported clarifies the optimum conditions for the complete electrolytic reduction of uranyl chloride to the quadrivalent state in solutions containing hydrochloric acid. Different experimental conditions were tried in order to study the cathodic process and particularly the factors affecting the limiting current density and hence the efficiency of the main reduction process : these factors were the concentration of uranyl ions, acidity of solutions, temperature, rate of stirring of catholyte, and nature of electrode.

## EXPERIMENTAL

*Materials.*—The reagents used were of high grade (B.D.H.), and the uranyl solutions were analysed for uranium gravimetrically as $U_3O_8$. The bright electrode was a cylindrical platinum wire gauze of 12·56 cm. circumference and 4 cm. high. A similar electrode was coated with spongy platinum-black, and a third was gold-plated. Each experiment was carried out with a freshly prepared electrode, washed thoroughly with distilled water and then with the solution to be used for electrolysis.

*Electrolytic Reduction Cell.*—The reaction vessel was a 400-ml. Pyrex beaker fitted with a rubber stopper provided with six openings for the following parts : (1) The stirrer, which consisted mainly of the two glass parts of a syringe, was moved by a D.C. motor that allowed regular and easily controlled stirring. (2) The anode element, which was enclosed in a thin porous clay compartment, consisted of a platinum wire 20 cm. long sealed into a glass tube fitted with an outer jacket and a gas inlet and exit for carbon dioxide; this served, when necessary, to sweep any accumulated chlorine away from the anode compartment and prevent possible diffusion to the catholyte. (3) The cathode element. (4) The salt-bridge was provided with a reservoir at the upper end of the limb dipping into the catholyte to eliminate gas bubbles when experiments were carried out at high temperatures; it was refilled before each experiment to minimise diffusion of foreign ions into the potassium chloride solution. (5) The indicator electrode was made of a platinised platinum sheet 1 × 2 cm. (6) The gas inlet and exit for carbon dioxide were fitted with mercury traps. These different parts were inserted through ground joints to allow their removal when required. A layer of mercury was spread over the rubber stopper to prevent ingress of atmospheric oxygen. The cell was then kept in an adjustable constant-temperature bath. The carbon dioxide used was purified by passage through leuco-indigo-carmine and chromous sulphate solutions.

*Determination of the Cathode Potential.*—Direct measurements of the different potentials maintained at the cathode under examination while current strength was varied were made by connecting the cathode through a salt-bridge, to a saturated calomel reference electrode and measuring the e.m.f. thus formed by means of a sensitive potentiometer, sufficient time being allowed for constant conditions to be attained. The error due to any ohmic fall of potential across the solution was minimised by drawing out the end of the salt-bridge to a moderate capillary and placing it close to the surface of the cathode. Before an electrolysis was started, purified carbon dioxide gas was bubbled through the solution.

*Results.*—*Effect of concentration of uranyl ions.* Solutions were 1·4M in hydrochloric acid and 0·0461, 0·0692, or 0·0922M in uranyl chloride. The limiting current density was found to vary almost in proportion to the concentration of uranyl ions. The effective thickness of the diffusion layer remained, however, constant in all cases. These investigations were made at room temperature without stirring of the catholyte, but results on stirred solutions were similar.

*Effect of acidity.* Solutions were stirred at 550 r.p.m. and were 0·0461M with respect to uranyl-ion concentration. Experiments were carried out both at room temperature and at 80° while the concentration of the free hydrochloric acid was varied between 0·1 and 7·5M. The limiting current density was found to increase with acid concentration up to 6M and then decreased at higher acidities owing probably to some sort of concentration polarisation and the deposition of thin grey films on the cathode.

*Effect of temperature.* Solutions were equally stirred and the acidity was kept at 2M and the uranyl concentration at 0·0461M while the temperature was altered from 30° to 80°. The limiting current density was found to increase with rise of temperature, the value at 80° being about 1·5 times that at 30°.

*Effect of stirring.* Solutions were 0·0922M with respect to uranyl-ion concentration and 1·4M in hydrochloric acid. The rate of stirring of the catholyte varied between 350 and 1600 r.p.m. The limiting current density was found to rise with increase in rate of stirring, and the thickness of the diffusion layer decreased but was never eliminated. It was also found that stirring had a greater effect on the limiting current density than rise of temperature.

*Type of electrode.* The limiting current density was comparatively high with platinised platinum and low with bright electrodes. The bubble hydrogen over-voltage potential, beyond which hydrogen was freely evolved, was lowest with platinised electrodes. Since high over-voltage cathodes allow the possibility of greater degree of reduction, lead and mercury cathodes were tried. The former were unsuitable, as they reacted with the acid present, turning uranyl solutions green before the current was applied. The mercury cathodes gave better results, and the values obtained for the limiting current density were the lowest of those for inert electrodes, the bubble hydrogen over-voltage being comparatively high. In all cases, the results indicated only one stage in the reduction to quadrivalent uranium.

In the reduction process, acid uranyl chloride solutions were used as catholytes, and hydrochloric acid solutions of the same concentration as anolytes. The reduction was followed quantitatively, under various conditions, through time-potential curves. The prevailing redox potentials during reduction were measured by the aid of a single electrode (preferably platinised platinum electrode, 2 cm.$^2$) against a saturated calomel reference electrode. Quick equilibria were obtained only when working at 80°. After each process of reduction, samples were taken for analysis for both quadri- and sexa-valent uranium, by means of potassium iodate titration and gravimetric determination of total uranium as $U_3O_8$. The results showed clearly that reduction to the quadrivalent state proceeded almost to completion as shown by the one inflection in each of the time-potential curves and also by the amount of potassium iodate required for the back titration to the sexavalent state. The reduction proceeded with slight polarisation, the extent of which decreased with increasing acidity up to 4M-HCl. At higher acidity (6·5—7·5M-HCl), the process proceeded with somewhat greater polarisation, accompanied by the deposition of thin grey films on the cathode, especially at high current density. Owing to the formation of these diaphragms, the yield was only about 98% of the theoretical value. However, the reduced solutions were found by analysis to contain mainly quadrivalent uranium. Solutions investigated were always made of 173 ml. of uranyl solution containing 10·9800 g. of $U_3O_8$ per litre. The acidity varied between 2 and 7·5M-HCl. The applied current density varied between about 2 and 20 milliamp./cm.$^2$ of the cathode. In all cases, experiments were carried out at 80° and catholytes were stirred equally.

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