

concentration of indicator—5λ of a 0.4 per cent methanol solution, or about 40 times the concentration used by Hildebrand and Reilly with 'Calcon'.² In this respect I find Eriochrome Black *T* to be superior to the latter indicator at such micro-levels. With the very small volumes involved, the coloration of 'Calcon' is undetectable at the recommended concentration: and using this indicator sufficiently concentrated to produce a visible coloration leads to gross inaccuracies which the use of blank determinations cannot correct at the calcium-levels it is desired to estimate. On the other hand, the high concentration of Eriochrome Black *T* required to give a detectable colour apparently does not affect the accuracy of the results.

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Lowest Oxidation States of Technetium and Rhenium

THE polarographic reduction of perhenate ion, ReO_4^- , to rhenide ion has been studied in some detail^{1,2}; although the possibility of a $-I$ state for technetium has been mentioned³, no experimental evidence for such a state appears in the literature.

The polarographic reductions of potassium perhenate and pertechnetate in 2 *N* potassium chloride have been compared. For perhenate, Lingane¹ found that the reduction wave was considerably larger than that expected for an eight-electron reduction to $\text{Re}(-I)$, although he found that the *n* values tended towards this value with increasing concentration. Our results agree with Lingane's in dilute solutions, but at concentrations greater than 0.5 mM the reduction wave corresponds exactly to an 8-electron reduction.

For potassium pertechnetate in 2 *N* potassium chloride, an 8-electron, irreversible, diffusion-controlled reduction very much the same as for perhenate is observed, clearly showing that reduction to a $-I$ oxidation state occurs. In dilute solutions, technetium shows a similar effect to rhenium in that the *n* values become greater than 8, although this does not occur until concentrations in the range of about 0.025 mM are reached. The half-wave potential of the single wave varies slightly with concentration, being -1.15 V. at 0.1 mM and -1.12 V. at 0.01 mM. The wave is well defined and would be suitable for the determination of technetium in concentrations down to 1 p.p.m.

The nature of the reduced rhenium species has generally been considered to be Re^- or $[\text{Re}(\text{H}_2\text{O})_4]^-$, and solid rhenides have been isolated^{4,5}. However, we have found that aqueous solutions of perhenate reduced by sodium amalgam show a well-defined proton resonance in the high-field region characteristic⁶ of transition metal to hydrogen bonds at ~ 850 cycles/sec. vs. water at 56.45 Mc./sec.; aqueous solutions of a solid rhenide after passing through a cation resin column have also been found (Ginsberg, A. P., and Miller, J. M., Columbia University, New York, personal communication) to give a similar resonance line.

In alkaline solution, therefore, the reduced 'rhenide' species contains an $\text{Re}-\text{H}$ bond; this finding also

shows that the presence of strong field ligands such as carbon monoxide, substituted phosphines, or cyanide, which are also bound to the metal atom in all previously known transition-metal complex hydrides, is not a pre-requisite for the formation of a transition metal-hydrogen bond in a complex compound.

While the precise nature of the anionic species is not known, if we accept the analytical data of Floss and Grosse⁵ for the solid rhenides, namely, $\text{Li}[\text{Re}(\text{H}_2\text{O})_4]$, then it seems reasonable to assume that the species are of the type $[\text{HRe}(\text{OH})(\text{H}_2\text{O})_3]^-$, $[\text{H}_3\text{Re}(\text{OH})_3(\text{H}_2\text{O})]^-$, etc.

Technetium may prove to form similar species. Details of this work will be published elsewhere.

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Effects of Electron Bombardment upon Bromides of Cadmium and Silver

SOME interesting effects of electron bombardment upon certain inorganic substances were reported by de Souza Santos¹. I have also observed rather similar phenomena with silver bromide and cadmium bromide under the electron microscope, although the type of reaction is not the same as that in de Souza Santos's experiments.

Electron bombardment of silver bromide causes local reduction to metallic silver and the reduced silver tends to gather locally².

In addition, cadmium bromide is photosensitive³. Electron bombardment reduced it to metallic cadmium⁴; the reduced metal consists of very minute crystals and keeps closely to the original form of the cadmium bromide⁵. In my experiments special care was taken that the specimen of cadmium bromide was not in contact with the film supporter in the electron-microscope or diffraction apparatus, but was held in space by a wire mesh.

Thus different metals reduced by electron bombardment behave differently, an effect that I am inclined to attribute to differences of crystal structure. Silver bromide crystallizes in the rock-salt structure, whereas cadmium bromide possesses a hexagonal layer structure which is anisotropic⁶. Fig. 1 shows the reductive process due to electron bombardment in the (001)-plane of cadmium bromide, where the formation of triangular and hexagonal holes occurs. These suggest the existence of an effect of crystal structure on the morphological changes produced by electron bombardment. The anisotropy of the crystal