

and the dibenzoate, m.p. 97.5°, and active work on the constitution of this anhydride is also in progress. The normal action of sodium amalgam on 1:6-dichloro 1:6-dideoxymannitol would be the exchange of the two chlorine for hydrogen atoms in (I), and this has, indeed, taken place, since the isolation from the reaction mixture of crystalline 1:6-dideoxymannitol (II), m.p. 147–148°, has also been accomplished.

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¹ Montgomery, R., and Wiggins, L. F., *J. Chem. Soc.*, 2204 (1948).

² Siwoloff, A., *Annalen*, 233, 372 (1886).

Increase of Oxygen Overpotential at a Platinum Anode by Reducing Agents

DURING a study of electrolytic oxidation processes, the surprising observation has been made that the presence of low concentrations of certain reducing agents, which normally function as depolarizers, will bring about very substantial *increases* in the potential at which oxygen is evolved at a platinum anode. The effect was first noted with dilute solutions of sodium thiosulphate in phosphate buffer electrolysed at high current densities, but it has since been found to occur to varying extents with a large number of oxidizable substances containing sulphur and/or nitrogen. The phenomenon has been studied by polarizing a clean platinum wire anode in an inert electrolyte until the potential became substantially steady; a quantity of the oxidizable substance was then added and the anode potential observed over a further period of electrolysis. In general, where the added substance was active in giving the effect, an almost immediate rise of potential occurred which reached a maximum value within a few minutes. Below are shown the elevations of anode potential observed after two minutes with a variety of addition agents, each at a concentration of 0.01 *M*, in the electrolysis of a phosphate buffer (0.2 *M* KH_2PO_4 + 0.2 *M* Na_2HPO_4 , pH 6.8) at 20°C. with an anodic current density of 0.15 amp./sq. cm.

Substance added	Rise of potential
Thiourea	0.63 volt
Ammonium thiocyanate	0.59
Sodium tetrathionate	0.45
Sodium sulphide	0.44
Urea	0.41
Sodium thiosulphate	0.37
Thioglycollic acid	0.34
Hydroxylamine sulphate	0.22
Sodium azide	0.20
Biuret	0.20
Sodium sulphite	0.18
Sodium nitrite	0.17
Metol	0.16

No comparable effects were observed with other oxidizable substances not containing sulphur or nitrogen.

The phenomenon now reported is not specific to any one electrolyte, but has been observed in acid and alkaline electrolytes of different types, and the magnitude of the effect seems to increase with increasing acidity. Thus, under the same conditions as before, thiourea produced an elevation of 0.84 volt in *N* sulphuric acid, 0.63 volt in phosphate buffer, and 0.43 volt in *N* potassium hydroxide. A limited investigation (using sodium thiosulphate and tetrathionate) of the influence of concentration of the

oxidizable substance showed that, even at a concentration of 0.0001 *M*, a small but appreciable rise of potential was produced; this increased rapidly with rise of concentration to a very flat maximum between 0.005 and 0.01 *M*, and thereafter decreased. Provided the working current-density was above the limiting value for diffusion of the added substance to the anode, so that oxygen was always evolved, variation of current density appeared to have little influence on the magnitude of the elevation, and substantially the same results were obtained over the range 0.05–0.3 amp./sq. cm.

The effect appears to be specific to platinum as anode material, since no elevation of potential has been observed with gold, palladium, graphite and nickel anodes, and the phenomenon thus appears to have some features in common with the influence of fluoride, the presence of which has long been known¹ to raise the oxygen overpotential at platinum, but which has little influence at other electrode materials². The present effects, however, are much greater than those observed with fluoride under comparable conditions.

It might at first sight be thought that the substances which produce the potential elevations act by poisoning the electrode surface; but this does not appear to be so, since an anode at which the potential has been raised undergoes no permanent change, and on rinsing with water and inserting in fresh electrolyte gives its normal (low) potential. The effect appears to be bound up with the oxidation of the added substance, and in prolonged electrolyses the potential decreases as the addition agent is used up. Any suggestion as to the cause of the phenomenon must at present be entirely speculative, but it appears possible that the effect may be brought about by the added substance removing some essential intermediate involved in the evolution of oxygen at a platinum anode, and so retarding the rate of the electrode reaction.

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¹ Müller, *Z. Elektrochem.*, 10, 776 (1904). Müller and Scheller, *Z. anorg. Chem.*, 48, 112 (1906).

² Hickling and Hill (unpublished work).

Chromatography on Alumina-impregnated Filter Paper

SINCE the technique of paper partition chromatography is generally inapplicable to fat-soluble substances, we have investigated the use of alumina-impregnated filter paper for this purpose. We have found that such paper run in simple organic solvents forms, in effect, an adsorption chromatogram on a micro scale, and combines the advantages of alumina chromatography with the elegance of paper chromatography.

Flood¹ has shown that filter paper when impregnated with alumina exhibits selective adsorption of inorganic ions. He confined his attention to the chromatography of inorganic cations by a method which seems to depend on ion exchange with cations present in the alumina. Hopf² further developed the method and has employed papers containing other adsorbents; for example, blotting paper containing fullers' earth, and starch paper. He also incorporated in the paper reagents forming coloured complexes