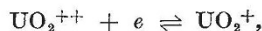


## LETTERS TO THE EDITORS

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## Electrochemistry of Uranium

An account of the polarographic reactions of the uranium ions has just been published<sup>1</sup>. During 1944, experiments on this subject were made at this Laboratory, the publication of which has been delayed by war conditions. In general, our results confirm those of Kolthoff and Harris. The first wave in the uranyl polarogram is due to the reaction

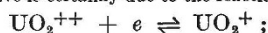


and the second 'wave' to a two-stage reduction from U V to U III. The American authors do not mention the fact that this second wave always shows a perceptible kink at half its height: the kink is more easily observed in sulphuric acid solutions, in which the first part of the wave has an irregular non-logarithmic form, and the second part something close to the logarithmic form of a reversible wave.

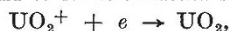
We have studied the oxidation waves of U III solutions in normal sulphuric and normal hydrochloric acids, as well as the reduction waves of U IV solutions described by Kolthoff and Harris, and find that the oxidation waves have nearly the same half-wave potentials as the reduction waves (-0.94 v. in normal hydrochloric acid, and -1.10 v. in normal sulphuric acid, both vs. the N.C.E.). Our values

for the gradients of the  $\log \frac{i}{i_d - i}$  plots for these waves are nearer the theoretical value for one-electron transfer than theirs, but are nevertheless somewhat high, indicating that the reaction is not perfectly reversible.

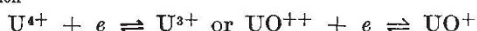
Since, in agreement with the American workers, we find that none of the half-wave potentials of the uranyl polarogram varies systematically with the hydrogen-ion concentration, it is clear that none of the three successive reductions involves hydrogen ions, and therefore that a chemical step or steps of inverse hydrolysis must occur somewhere between the starting substance,  $\text{UO}_2^{++}$ , and the end product,  $\text{U}^{3+}$ . The first wave is certainly due to the reaction



the second wave could be due to a reaction such as



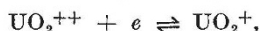
resulting in the formation of solid oxide or hydroxide at the electrode surface, at any rate in sulphuric acid solutions, where the wave is obviously caused by an irreversible reaction. This would be followed by the chemical step, giving rise to  $\text{U}^{4+}$  or  $\text{UO}^{++}$ , and finally the reaction



(we consider the latter less likely) would be responsible for the third wave.

Reducing the free acid concentration of a hydrochloric acid solution of  $\text{UO}_2^{++}$  progressively at constant total chloride concentration causes the second uranyl wave to flatten and disappear, followed by the first. When the acidity becomes too low, the chemical reaction mentioned above would not take place fast enough, and the second part of the second wave would be eliminated; at still lower acidities, solid hydroxides would begin to be deposited on the dropping electrode in the first reduction.

Kolthoff and Harris suggest that, since the half-wave potential of the first uranyl wave (which is independent of acidity) is different from the redox potential of  $\text{UO}_2^{++}/\text{U}^{4+}$  mixtures as given by a platinum electrode (which varies with the acidity), the reactions at the platinum and mercury electrodes are probably different. This assumption does not seem necessary. We have established by experiments with a platinum micro-electrode that  $\text{U}^{4+}$  cannot be reversibly oxidized at such an electrode at any potential within the range that can be studied, so that the potential of a platinum electrode in uranyl-uranous mixtures is not the true reversible potential of a U VI/U IV equilibrium (as it was apparently taken to be by earlier workers). However, if the potential-determining reaction at a platinum electrode is the same as that at a mercury electrode, namely,



the observed Nernst equation dependence of the potential upon the various concentrations can be explained. We suppose that a mixed solution of  $\text{UO}_2^{++}$  and  $\text{U}^{4+}$  contains a small concentration of  $\text{UO}_2^+$ , maintained by the equilibrium



(representing the total of several reactions).

In a solution, 1 mole in each of  $\text{UO}_2^{++}$  and  $\text{U}^{4+}$ , and 1 N in  $\text{H}^+$ , the concentration of  $\text{UO}_2^+$  would be about  $10^{-8}$  mole, calculated from the potentials. This concentration would vary in such a way with the concentrations of the other ions that the equation, established experimentally by Titestad<sup>2</sup>,

$$E = E_0 + \frac{RT}{2F} \ln \frac{(\text{UO}_2^{++})(\text{H}^+)^4}{(\text{U}^{4+})}$$

is obeyed. However,  $E_0$  here is not the true standard potential of the electrode reaction.

Our results agree with those of Kolthoff and Harris in showing that the first uranyl wave is due to a one-electron transfer. We have

studied in more detail the interesting question of the ion of pentavalent uranium, probably  $\text{UO}_2^+$ , formed in this reduction. No solid salts of this ion are known, so it must be unstable. According to the idea stated above, the concentration of this ion can be determined approximately from the equation

$$E = E_0' + \frac{RT}{F} \ln \frac{(\text{UO}_2^{++})}{(\text{UO}_2^+)},$$

where  $E$  is the potential of a platinum electrode in the solution, and  $E_0'$  the half-wave potential of the first uranyl wave: and changes in the  $\text{UO}_2^+$  concentration cause corresponding changes in the platinum electrode potential. In this way we have been able to follow the decomposition of  $\text{UO}_2^+$  formed in uranyl solutions by electrolytic reduction; we find that this reaction is of the second order in  $(\text{UO}_2^+)$ , as expected, and that the rate varies with the acidity. In addition, we have shown that the concentration of this ion is increased above the equilibrium value by illuminating the solution, and that this fact is responsible for the potential-shift which a platinum electrode undergoes in the light in such solutions ('Becquerel Effect'; see Titestad, *loc. cit.*). From studies of the activation energy of the disproportionation, however, we conclude that the potential-determining ion is probably not identical with the disproportionating ion, but that the concentrations of the two are in constant ratio to each other in a given solution, this ratio being a function of the acidity and temperature. For example, the ions might be  $\text{UO}_2^+$  (determining the potential) and  $\text{UO}(\text{OH})^{++}$  (disproportionating); these are interconvertible by hydrolysis or inverse hydrolysis.

It is not unlikely that unstable ions might be detected electrochemically in systems of the salts of other transition elements.

We hope to publish details of this work in the near future.

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Oct. 2.

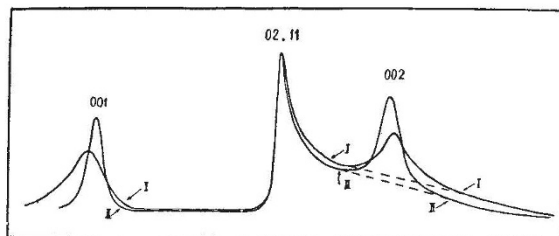
<sup>1</sup> Kolthoff and Harris, *J. Amer. Chem. Soc.*, **67**, 1484 (1945).

<sup>2</sup> *Z. phys. Chem.*, **63**, 689 (1908).

## The Clay Minerals Halloysite and Meta-halloysite

X-RAY studies of these minerals in relation to (a) their reactions with organic liquids (MacEwan), (b) the effect of heat treatment (G. W. B. and K. R.) have led us to certain conclusions which can best be expressed in a joint communication. Meta-halloysite has the same formula as kaolinite,  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ , and from the work of Hendricks and others<sup>1</sup> is generally considered to have a closely similar structure, consisting of layers of Si-O tetrahedra and Al-O(OH) octahedra which in kaolinite<sup>2</sup> are arranged regularly above each other, but which in meta-halloysite are stacked with "considerable disorder" or even, as we believe, with almost complete disorder as regards the orientation of the layers. In what follows we set out briefly the evidence for this view of the meta-halloysite structure.

In the first place, such a structure would be expected to give two types of line in an X-ray powder photograph: (i) 'crystalline' reflexions with indices (00l) having the usual symmetrical distribution of intensity, and (ii) lines from the two-dimensional layers with characteristic asymmetric intensity distribution with indices (hk). No reflexions should occur with indices (hkl). We find that all the reflexions from meta-halloysite, with the possible exception of a broad band between  $d = 2.56$  and  $2.33$  Å., can be satisfactorily indexed as (00l) or (hk) with the following lattice parameters:  $a_0 = 5.14$  Å.,  $b_0 = 8.90$  Å.,  $c_0 = 7.2$  Å. The reflexions to which (hk) indices are assigned all have the asymmetrical shape characteristic of those from a two-dimensional lattice (see figure). The band between  $2.56$  and  $2.33$  Å., for certain meta-halloysites, appears to break up into four diffuse lines, two of which cannot be reconciled with this indexing and may therefore provide evidence for some degree of ordering in the orientation of the layers. We consider therefore that the essential character of the meta-halloysite structure is that it consists of randomly oriented sheets. Similar structures have been suggested for carbon black<sup>3</sup> and montmorillonite<sup>4</sup>.



MICROPHOTOMETER RECORDS OF LOW-ORDER REFLEXIONS FROM NATURAL AND HEAT-TREATED META-HALLOYSITE, CURVES I AND II RESPECTIVELY.

Halloysite differs from meta-halloysite in having an additional  $2\text{H}_2\text{O}$  per 'molecule' and consists, according to Hendricks<sup>1</sup>, of the same layers which occur in kaolinite and meta-halloysite, with intervening layers of  $\text{H}_2\text{O}$  molecules. MacEwan<sup>5</sup> has shown that halloysite-organic complexes can be formed in which the  $\text{H}_2\text{O}$  layers are replaced by organic layers. Both halloysite and its organic compounds give X-ray photographs similar to those of meta-halloysite, with only the basal reflexions changed, corresponding to an expanded  $c_0$  parameter. The character of the (hk) reflexions and the absence of (hkl)