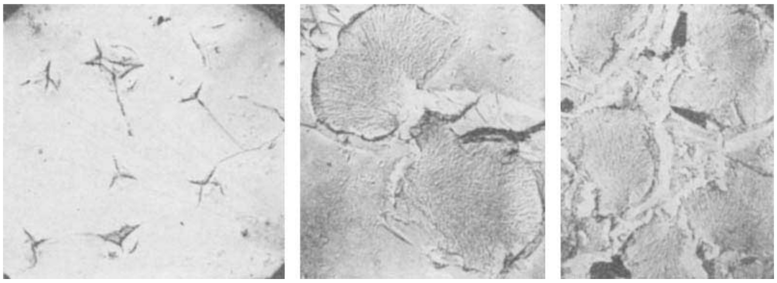

(a) (b) (c)

Fig. 4. Electron micrographs a, b and c correspond to points A, B and C (Fig. 1) and show the initial cracking of the film and subsequent appearance at the surface of the crystalline oxide. Magnification, a and c × 4,250, b × 6,500

Electron diffraction studies of films formed at various voltages at 25° C. and 90° C. have shown that at the lower temperature the oxide surface remains amorphous, but at 90° C., although the oxide gives diffuse haloes of Nb_2O_5 below the plateau, at and above the plateau the structure corresponds to crystalline Nb_2O_5.

Figs. 4*a*, *b* and *c* show electron micrographs obtained at points *A*, *B* and *C* (Fig. 1) and reveal the initiation of cracks in the surface at the plateau and the subsequent projection of crystals of Nb_2O_5 through the overlying amorphous surface layer. At 25° C., although similar cracks (similar to Fig. 4*a*) appeared at the surface at ~190 V., there was no visible evidence of crystallization even after prolonged passage of charge.

From the present work it is evident that initially the oxide surface is continuous and amorphous and that the arrest in the rise in voltage, that is, the plateau, is associated with the formation of discontinuities in the oxide which are caused by crystallization of the amorphous oxide.

Cathcart *et al.*[1] have found that during the high-temperature oxidation of niobium at 350–500° C. the growth law is initially parabolic, but, at a critical thickness which depends on temperature and time, becomes linear owing to cracking of the oxide. From marker experiments they conclude that film growth is due to anion migration through the oxide and that cracking results from the stresses which arise from the formation of the oxide at the metal/metal oxide interface.

Vermilyea[2] has described the phenomenon of field crystallization where anodically formed amorphous Ta_2O_5 has been shown to crystallize in the presence of a strong electric field and considers that rupture of the amorphous oxide is due to this crystallization which occurs within the amorphous oxide. The similarity of the photomicrographs (Fig. 4) to those obtained by Vermilyea for tantalum indicates that the phenomenon observed in the present work is due to field crystallization and that a similar mechanism is applicable.

Recent electron diffraction studies of thermal oxide films on niobium[3] have shown that the oxide is amorphous when protective but is crystalline when non-protective, indicating that film rupture is due to crystallization.

It is apparent from the present work that there are many similarities in the behaviour of niobium during anodic and thermal oxidation, as in both cases film thickening results in discontinuities in the oxide so that oxidation continues linearly. It should be observed that a protective oxide from the point of view of anodic oxidation is one where film growth proceeds to only a limiting thickness and then practically ceases owing to an alternative electrode process, that is, gas evolution. Fig. 2 shows that film growth of the anodic oxide continues owing to crystallization and consequent film rupture so that the oxide cannot be regarded as truly protective.

It is possible, therefore, that a similar mechanism occurs during the thermal oxidation of niobium and that crystallization of the amorphous oxide, rather than oxide formation at the metal/metal oxide interface as postulated by Cathcart *et al.*, is the main cause of the stresses which result in discontinuities in the oxide and a linear growth law.

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RADIATION CHEMISTRY

Role of Ferrous Hydride in the Oxidation of Ferrous Ion by Hydrogen Atoms

The oxidation of ferrous ion by atomic hydrogen was recently postulated to proceed by hydride ion formation[1]:

$$Fe^{2+} + H \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} FeH^{2+} \qquad (1)$$

$$FeH^{2+} + H^+ \xrightarrow{k_2} Fe^{3+} + H_2 \qquad (2)$$

Recently the work of Dainton and Peterson[2] demonstrated the use of nitrous oxide for discrimination between various forms of hydrogen atoms (or their analogues) in γ-irradiated aqueous solutions. This technique may be applied in the establishment of the oxidation mechanism of ferrous ion by hydrogen atoms.

In the *p*H region up to 2 the radiation-chemical oxidation of ferrous ion solutions containing nitrous oxide by H atoms will proceed by (1) and (2) or alternatively by:

$$H + N_2O \xrightarrow{k_3} N_2 + OH \text{ (or } N_2OH) \qquad (3)$$

$$OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- \qquad (4)$$

This scheme leads to the following results:

$$\text{(I)} \qquad G(N_2) = \frac{G_H}{1 + \dfrac{k_1\beta[Fe^{2+}]}{k_3[N_2O]}}$$

$$\text{(II)}\quad G(H_2) = G_{H_2} + \frac{G_H}{1 + \dfrac{k_3[N_2O]}{k_1\beta[Fe^{2+}]}}$$

where :

$$\beta = \frac{[H^+]}{(k_{-1}/k_2) + [H^+]}$$

and hence :

$$\text{(III)}\quad \frac{G(N_2)}{G(H_2) - G_{H_2}} = \frac{k_3[N_2O]}{k_1[Fe^{2+}]}\left(\frac{k_{-1}}{k_2}\right)\frac{1}{[H^+]} + \frac{k_3[N_2O]}{k_1[Fe^{2+}]}$$

The linear plot (Fig. 1) is obtained in good agreement with equation III. From the ratio of the slope to intercept we obtain $(k_{-1}/k_2) = 0{\cdot}05$ mole litre^{-1}. These results cannot be readily reconciled with any alternative mechanism previously proposed for this reaction :

$$\begin{array}{ll}(1{\cdot}1) & Fe^{2+}H_2O + H \rightarrow Fe^{3+}OH^- + H_2\\ (1{\cdot}2) & Fe^{2+} + H + H^+ \rightarrow Fe^{3+} + H_2\\ (1{\cdot}3) & H + H^+ \rightleftarrows H_2^+\\ (2{\cdot}3) & Fe^{2+} + H_2^+ \rightarrow Fe^{3+} + H_2\end{array}$$

Mechanism (1·1) is not consistent with the dependence on pH of the Gs ratio, while according to the triple collision or the oxidation mechanism involving H_2^+ the intercept in Fig. 1 should be zero.

The oxidation of the ferrous ion by hydrogen atoms externally generated in an electrode-less discharge was recently re-investigated in our laboratory[3] over a wide region of H^+ and Fe^{2+} ions concentration. These results yield the value of k_{-1}/k_2 in the region of 0·05–0·02 mole litre^{-1}, in good agreement with the radiation-chemical results.

This ratio of rate constants is consistent with the pH independence of the relative rates of competing reactions of Fe^{2+} and methanol for hydrogen atoms[4]. However, the investigation of the competition between Fe^{2+} and oxygen[5] requires that k_{-1}/k_2 should be of the order of 0·01.

These results indicate the identity of hydrogen atoms produced by ionizing radiation at low pH and atomic hydrogen externally generated. From Fig. 1 we obtain $k_1/k_3 = 60$ and the application of the value of k_1 independently obtained[1,3] leads to $k_3 \sim 10^3 - 10^4$ litre mole^{-1} sec.$^{-1}$. Thus the interaction of hydrogen atoms as such with nitrous oxide is a relatively slow process, while at pH above 3, efficient decomposition occurs[2]. This behaviour is analogous to that of hydrogen peroxide in neutral[6] and acid[7] solutions. It appears that the hydrogen atom precursor in neutral solutions is the solvated electron, while the 'acid form' is the genuine hydrogen atom. The assumption that the acid form of atomic hydrogen involves only H_2^+ is in disagreement with the slowness of its formation[8]. This species is of importance only in acid solutions where no alternative efficient scavenging of hydrogen atoms occurs, as in the oxidation of I^- by hydrogen atoms[1,8].

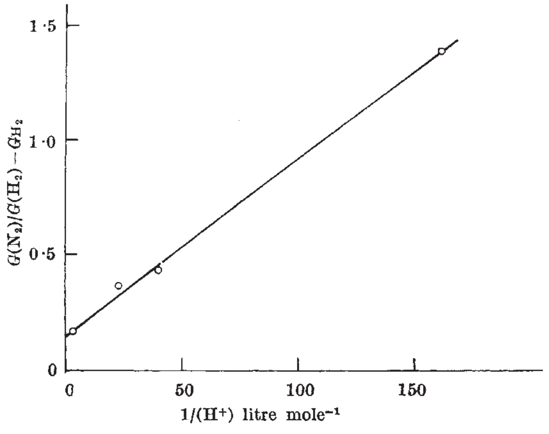

Fig. 1. Plot of the experimental results (ref. 2) for the radiation-chemical oxidation of 10^{-3} *M* ferrous sulphate solutions containing 0·01 *M* nitrous oxide

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Detection of Photochemical Oxidation of Sulphur Dioxide by Condensation Nuclei Techniques

THE purpose of the tests reported in this communication was to prove that condensation nuclei techniques could be used in a qualitative way in the determination of the predominating reaction. Since quantitative performance depends on controlling several variables, proof that qualitative determinations were possible was needed to justify further work. Since sulphuric acid particles have been found to act readily as condensation nuclei, the manner of their formation from sulphur dioxide in the atmosphere was chosen as the subject of the investigation.

Several investigations have been made of the conversion of sulphur dioxide in the air to form sulphuric acid ; for example, those of Blacet[1] and of Gerhard and Johnstone[2]. They indicate that oxidation of the sulphur dioxide by ozone is insignificant compared to the action initiated by the absorption of the radiation by the sulphur dioxide molecule. The molecule then becomes activated. The series consists of the following reactions :

$$SO_2 \rightarrow SO^*_2 \qquad (1)$$

$$SO^*_2 + O_2 \rightarrow SO_4 \qquad (2)$$

$$SO_4 + O_2 \rightarrow SO_3 + O_3 \qquad (3)$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \qquad (4)$$

They showed that reaction (5) is of minor importance.

$$SO_2 + O_3 \rightarrow SO_3 + O_2 \qquad (5)$$

As an example they pointed out that the addition of nitrogen dioxide, which produces ozone catalytically, did not measurably change the rate of production of sulphuric acid, whereas the rate at which sulphuric acid was produced was directly proportional to the amount of sulphur dioxide present.

The tests made here confirm their results. The production of sulphuric acid was detected by a condensation nucleus detector[3]. It has been found that the condensation nucleus detector is highly sensitive to the presence of sulphuric acid particles in