The Oxidation of Copper and Zinc.

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It is found that the reaction $^{18}O_2 + {}^{16}O_2 \rightleftharpoons 2{}^{16}O^{18}O$ does not occur on the growing oxide film during the oxidation of copper at 50—110°, or zinc at 370—400°: initial oxygen pressures in both cases were *ca.* 3 cm. No exchange of oxygen with the films was observed. The observations are briefly discussed with reference to current theories regarding the mechanism of oxidation of these metals.

MUCH work has been devoted to the study of oxidation and tarnishing reactions on metals, and the results have been very valuable in developing the theory of the defect solid state. The general nature of the oxidation mechanism in terms of defect structures is believed to be understood in a number of cases, but little is known about details of the reaction.

The process being written very crudely as:

$$O_{2(g)} \rightleftharpoons O_{2(ads)} \quad \dots\dots\dots\dots \quad (1)$$

$$O_{2(ads)} + 2M \longrightarrow 2MO \quad \dots\dots\dots\dots \quad (2)$$

and the nature of $O_{2(ads)}$ not being discussed for the moment, it is the second stage about which most is known. Some information about the first stage can be obtained by a detailed examination of the effect of oxygen pressure upon the overall rate of oxidation and upon the apparent activation energy. Such a study has been recently carried out on the oxidation of zinc by Moore and Lee (*Trans. Faraday Soc.*, 1951, **47**, 501). In order to explain their results they postulated, among other things, a reversible adsorption of oxygen as atoms on the zinc oxide surface; apart from this, their kinetic analysis contains an inconsistency which will be discussed elsewhere.

With a view to determine the nature of the adsorption step we have studied the oxidation of zinc foil (Johnson Matthey Spec. Pure) using Moore's technique of pre-oxidation with isotopically normal oxygen: the oxidation proper was followed by using a 1 : 1 mixture of normal oxygen and oxygen containing *ca.* 30% of ^{18}O so that the proportion of $^{18}O_2$ molecules in the gas was markedly greater than for a fully equilibrated gas containing *ca.* 15% of ^{18}O. During the oxidation a representative small quantity of the oxygen in contact with the zinc oxide surface was bled off continuously into a mass-spectrometer and analysed at frequent intervals for masses 32, 34, and 36. This is essentially the technique we have used to study the oxygen exchange and equilibration reactions on solid oxide surfaces (*J.*, 1950, 1170, 1175; *J.*, 1954, 1509, 1517, 1522). At temperatures of 370° and 400° C and initial oxygen pressures of 2—5 cm. falling to zero, there was no equilibration of the oxygen; *i.e.*, the reaction

$$^{16}O_2 + {}^{18}O_2 \rightleftharpoons 2\,{}^{16}O^{18}O \quad \ldots\ldots\ldots \quad (3)$$

did not occur to a detectable extent although the rates of oxidation were appreciable. No isotopic exchange with the surface was detected. Using finely powdered zinc oxide containing interstitial zinc and prepared by burning pure zinc metal in air, we have shown (*J.*, 1954, 1522) that under similar conditions of temperature and pressure reaction (3) is catalysed by zinc oxide, with an apparent activation energy of 22 kcal. mole^{-1}, and proceeds more rapidly than the exchange of oxygen with the surface. The surface coverage with oxygen during these reactions is at most some 0·1%.

The conclusion seems clear that reversible adsorption/desorption of oxygen, ***involving dissociation***, while possible on the powder, does not take place on the surface of zinc oxide in contact with the bulk metal. The temperatures involved are much less than $0{\cdot}5T_m$ (° K), where T_m is the melting point of zinc oxide (~2370° K), so that there should be no appreciable mobility of sub-surface ions (cf. Anderson *et al.*, *J.*, 1948, 1729; *Discuss. Faraday Soc.*, 1950, **8**, 238; Huttig, *Angew. Chem.*, 1936, **49**, 882); this we have confirmed in that the oxygen exchange reaction involves only the surface layer of oxygen ions (*J.*, 1954, 1517).

We suggest that the dissociative adsorption of oxygen is promoted by sub-surface interstitial zinc atoms, Zn_i, which at our temperatures are virtually immobile in the powdered zinc oxide: *e.g.*, by a reaction such as:

$$Zn_i + O_{2(g)} \rightleftharpoons 2O_{(ads)}^- + Zn_i^{2+} \quad \ldots\ldots\ldots \quad (4)$$

When the Zn_i atoms are immobilized in sub-surface layers this reaction will be reversible, and the $O_{(ads)}^-$, having some mobility over the surface (*J.*, 1954, 1522), will tend to desorb in partnership with ad-ions from other molecules, thus leading to equilibration. If the life on the surface is long enough there will also be a tendency for surface exchange to occur. [Incidentally, the presence on the surface of $O_{(ads)}^-$ of limited mobility may well cause the low-temperature semiconductivity, of small activation energy, often found with oxides in contact with air (cf. Schwarz, *Proc. Phys. Soc.*, 1949, **62**, *A*, 530).] The powdered zinc oxide, being formed at a high temperature, is in a well-defined crystalline state and may be expected to be relatively free from strains, defects, and lattice vacancies, but the zinc oxide film growing on the oxidising metal will have a less perfect structure and will moreover have a high concentration of Zn_i diffusing out from the metal–oxide interface. In the latter case we suggest that (4) is followed at once by:

$$Zn_i^{2+} \longrightarrow Zn_l^{2+} \quad \ldots\ldots\ldots\ldots \quad (5)$$

an $O_{(ads)}^-$ also picking up a second electron, either from the conduction band of the oxide or from a second Zn_i, and moving into place as O_l^{2-} where the suffix l refers to an ion in its proper lattice position.

We have made similar observations upon the oxidation of copper to cuprous oxide at relatively low temperatures. Copper was prepared by reducing "AnalaR" copper sulphate solution with hot ammoniacal hydrazine, followed by filtration and thorough washing. The metal was subjected to four cycles of alternate oxidation and reduction as described by Garner, Stone, and Tiley (*Proc. Roy. Soc.*, 1952, *A*, **211**, 472) and finally oxidised to a thickness of *ca.* 150 Å by means of normal oxygen. The oxidation process was then followed at temperatures from 50° to 110° C and initial oxygen pressures of 1—3 cm., the non-equilibrated enriched oxygen being used, in a constant-volume apparatus. In no case was either equilibration or exchange observed. The oxidation followed the law

$$p_t/p_0 = \exp(-kt) \text{ or } -dp_t/dt = kp_t \quad \ldots\ldots\ldots \quad (6)$$

as found by Wilkins and Rideal (*Proc. Roy. Soc.*, 1930, *A*, **128**, 394, 407) under similar conditions at temperatures from 142° to 242°, using copper strip, but our apparent activation energy was 15·5 kcal. mole^{-1}, in contrast to their value of 9·5 kcal. mole^{-1}; Garner, Stone and Tiley (*loc. cit.*) quote a value of possibly 7 kcal. mole^{-1} for the activation energy for adsorption of oxygen upon cuprous oxide films at about room temperature. Castellan and Moore (*J. Chem. Phys.*, 1949, **17**, 41) found a value of 38 kcal. mole^{-1} for the diffusion of vacancies through the bulk oxide lattice at temperatures around 900° C. Other literature values (in kcal. mole^{-1}) for the oxidation of copper include: Krup and Jasczcz (*Mét. Z.*, 1935, **2**, 329) 20·3, from 750° to 1070°; Gulbransen (*Trans. Electrochem. Soc.*, 1943, **83**, preprint, from *Chem. Abs.*, 1943, **37**, 2251) 24·9; Dravnieks (*J. Amer. Chem. Soc.*, 1950, **72**, 3761) ~35, from observations at 600° and 690°.

We conclude that, at least under our conditions, the dissociative adsorption of oxygen upon cuprous oxide is irreversible and is brought about by a mechanism such as that suggested by Garner, Stone, and Tiley (*loc. cit.*), *viz.*,

$$O_{2(g)} + 2Cu_{l}^{+} \longrightarrow 2O_{(ads)}^{-} + 2Cu^{2+} \quad . \ . \ . \ . \ . \ . \ . \quad (7)$$

Reaction (7) is then followed rapidly by the other changes necessary to incorporate $O_{(ads)}^{-}$ into the lattice—the movement of Cu^{+} ions from surface or sub-surface layers into place in proper lattice positions around the $O_{(ads)}^{-}$, the loss of one positive charge by the Cu^{2+}, the gain of an electron by $O_{(ads)}^{-}$, and the formation of two positive holes per O atom, which diffuse to the metal–oxide interface, where they are destroyed. It is possible that in our experiments (7) is the rate-determining step in the oxidation; an apparent activation energy of 15·5 kcal. mole^{-1} may not be unreasonable in view of the figure of 22 kcal. mole^{-1} found by us for the analogous reaction (4) on zinc oxide. The different activation energies recorded by various workers, mentioned above, for what may be the same process, may reflect differences in preparation of the oxide or in experimental conditions (cf. Gwathmey and Benton, *J. Chem. Phys.*, 1940, **8**, 431; *J. Phys. Chem.*, 1942, **46**, 969; Bénard and Talbot, *Compt. rend.*, 1946, **222**, 796): in addition, at low temperatures the reaction may be complicated by formation of nuclei of cupric oxide.

A more detailed study of the above and allied matters is in progress and will be reported elsewhere.

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