Chemisorption of Oxygen on Gold

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GOLD is reported[1] to be exceptional among clean metals in its failure to chemisorb molecular oxygen at room temperature, but there is conflicting evidence about its inertness at higher temperatures.[2] Exposure of gold to an electric discharge in air or oxygen has been reported[3] to give an increase of over one volt in the work function, probably because of oxidation. Since gold is often regarded as an inert reference surface in contact-potential measurements[4] it is of interest to establish the conditions under which gold is genuinely unaffected by oxygen.

A similar inactivity towards molecular hydrogen is shown by many metals in addition to gold.

Atomic hydrogen may be readily adsorbed by these metals, and the rates of subsequent recombination and desorption can provide further information about the energetics of chemisorption.[5] We have found that atomic oxygen is rapidly adsorbed on gold films at 77° K and at room temperature, giving work function changes of the order of one volt. Desorption does not occur below 400° K. The experiments were carried out with evaporated gold films (600 Å thick) deposited on glass under ultra-high vacuum conditions in a cell designed for surface-potential measurements by the diode method. A rhenium filament was used as the cathode and also to dissociate the oxygen, which was dosed in keeping the pressure below 10^{-5} torr.[6] Surface areas were determined by the physical adsorption of xenon[7] prior to the admission of oxygen. The films were completely sintered and non-porous.

At 77° K atomic oxygen was readily adsorbed until the number of oxygen ad-atoms was equal to the number of xenon atoms which were adsorbed at monolayer coverage on the same film. At this point the oxygen surface potential was $-0{\cdot}9$ v, and the ratio of oxygen atoms to surface gold atoms was probably about 1 : 4. Further adsorption took place but with a marked decrease in the slope of the surface potential isotherm and with a slow positive drift[6,8] after the initial negative increment of surface potential given by each dose of oxygen. Some incorporation of oxygen may have taken place.

In a separate experiment the oxygen adsorption at 77° K was interrupted when the surface potential had reached $-0{\cdot}5$ v and the cell was allowed to warm to room temperature. No desorption took place, but the surface potential was reduced to about $-0{\cdot}3$ v. On cooling to 77° K and admitting oxygen, a further negative surface potential change occurred which was again reduced by warming to room temperature. The effect of repeating this operation several times is shown by (b) in the Figure. This behaviour resembles that observed during the oxidation of more active metals,[6,8,9] and may be attributed to incorporation of chemisorbed oxygen. The same final result was achieved by adsorption of atomic oxygen at room temperature. Incorporation at room temperature seems probable because the adsorbed oxygen atoms can considerably exceed the number of surface metal atoms.

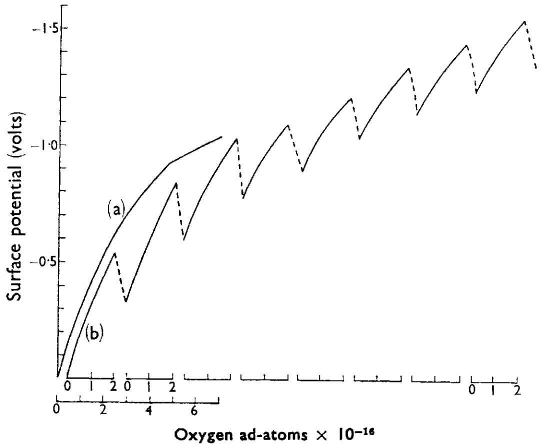

FIGURE. *Surface potential of oxygen on gold film as a function of number of ad-atoms, (a) at 77° K only, and (b) at 77° K but with warming to room temperature (– – –) at intervals.*

Desorption, measured with the filament cold, did not commence below 400° K, and was not complete at 520° K. However, reaction with atomic hydrogen appeared to remove the adsorbed oxygen completely, and to restore the original gold surface. The adsorption sequences already described could then be repeated. These results suggest that there is an appreciable activation energy for desorption. We cannot rule out the possibilities that dissociative adsorption may be exothermic, particularly at low coverage, and that it may be an activated process affected by trace impurities or defects which may account for the discrepant reports cited.

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[1] M. W. Roberts, *Quart. Rev.*, 1962, **16**, 71; B. J. Hopkins, C. H. B. Mee, and D. Parker, *Brit. J. Appl. Phys.*, 1964, **15**, 865.

[2] L. G. Carpenter and W. N. Mair, *Trans. Faraday Soc.*, 1959, **55**, 1924; N. V. Kul'kova and L. L. Levchenko, *Kinetics and Catalysis* (*U.S.S.R.*), 1965, **6**, 688.

[3] C. Ouellet and E. K. Rideal, *J. Chem. Phys.*, 1935, **3**, 150.

[4] L. A. Rudnitskii, N. V. Kul'kova, and M. I. Temkin, *Kinetics and Catalysis* (*U.S.S.R.*), 1964, **5**, 154.

[5] J. Pritchard and F. C. Tompkins, *Trans. Faraday Soc.*, 1960, **56**, 540; J. Pritchard, *ibid.*, 1963, **59**, 437.

[6] W. A. Crossland, C. A. Marr, and H. T. Roettgers, S.T.L. Report TM952, 1967.

[7] J. Pritchard, *Nature*, 1962, **194**, 38.

[8] T. Delchar and F. C. Tompkins, *Proc. Roy. Soc.*, 1967, *A*, **300**, 141.

[9] C. M. Quinn and M. W. Roberts, *Trans. Faraday Soc.*, 1964, **60**, 899.