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A Study of the Effect of Surfaces on Oxygen Atom Recombination at Low Pressures

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ABSTRACT

The study of O-atom recombination on various metal surfaces as applied to satellite mass spectrometer measurements has continued. Results at this time are in the 10^{-6} - 10^{-5} torr pressure range and lower, mainly with gas mixtures of O_2, O-atoms, Ar and small amounts of NO. The results indicated that no metal studied was totally inert to atom recombination. A recombination coefficient, γ, of somewhat less than 10^{-4} was obtained for the glass reaction vessel after conditioning the surface. Particular attention has been given to gold and a recombination coefficient of 3×10^{-3} was found. Titanium was found to be very catalytic ($\gamma > 0.05$); and aluminum relatively passive, although the activity for each metal depended on a number of variables.

INTRODUCTION

Three different types of experimental techniques were devised as previously discussed in our interim report of 7 August 1968. Although similar results were obtained from each experimental arrangement, only one method readily lead to expressing the recombination coefficient as a number.

Hydrogen atoms and other gaseous impurities, temperature variation and surface preparation all appear to effect the interaction of oxygen atoms with the surface.

No attempt was made to distinguish between "recombination" of atoms on the surface to oxygen molecules and "combination" to an oxide layer.

EXPERIMENTAL

Oxygen atoms and NO are added to a reaction vessel in a steady system at a low pressure using liquid helium for cryogenic pumping. The electric discharge which produces the oxygen atom supply is shut-off causing a decrease in the concentration of O-atoms. The decrease in the NO + O chemiluminescence observed is first order and varies from 3 seconds in an empty system to very fast decay rates with reactive samples from which the recombination coefficients, γ, are calculated. It should be noted that the decay rate is independent over a large pressure range. The chemiluminescence was observed by means of a selected low noise EMI photomultiplier (9502 SA) with a continuous output displayed as a function of time.

RESULTS

Recombination efficiencies for oxygen atoms on various metal surfaces are listed in Table 1. The gold supplied to us by NASA had a surface area of 5 cm^2 per side and its recombination efficiency was twice that obtained for gold sheet. The gold sheet sample showed a temperature dependence for efficiency with γ=0.0033 at 20°C, 0.0086 at 160°C; and increased to 0.029 in the presence of H-atoms (see interim report of 7 August 1968).

The test sample of titanium was an alloy #367 consisting of 6% Al, 4% V and the balance titanium. The results showed a very rapid catalysis similar to silver. A series of reactions may be postulated to explain these results:

$$Ti + O \rightarrow TiO \text{ (evaporates)} \quad (1)$$

$$TiO + O \rightarrow Ti + O_2 \quad (2)$$

$$TiO + O \rightarrow TiO_2 \quad (3)$$

It is not certain at present if reaction 2 is possible thermodynamically. The TiO_2 is apparently inert, but the TiO may volatilize and cause O-atom consumption for an extended period. When the sample was removed and the O-atom pressure increased for a period of time, reaction (3) oxidized all the invisible traces of Ti (and TiO) completely to TiO_2 or $(TiO_2)_n$ and the O-atoms then survived for many collisions; i.e., the walls were "conditioned" for low pressures again. In an analogous way vanadium may also go through the same type reactions as 1-3.

The aluminum foil sample used had the same geometry as the gold sheet. Initally, it gave a recombination efficiency similar to the gold sheet and also exhibited temperature effects, but after passing O-atoms at a higher pressure over its surface for a short time an efficiency of 0.005 was obtained and show little change with the addition of H-atoms.

SUMMARY AND FUTURE WORK

Results have been obtained on a variety of metals. Briefly it can be said that:

Gold is frequently inert initially to O-atoms, cleaning-up with time and actively combining O-atoms especially at higher temperatures or when hydrogen atoms are present. The gold sample, similar to that used in the spectrometer and supplied by NASA-GSFC, was reasonably rapid in recombination but initialy

experiments on the one sample indicated greater stability with increased temperature.

Titanium was actively recombining O-atoms over a series of reactions discussed under results. Unless a satisfactory procedure can be found for accommodating the surface, which would apparently consist of formation of a stable inert TiO_2 layer, the use of titanium in probably inadvisable.

Aluminum when machined and polished appears relatively inert and stable and is still one of the more promising metals for satisfactory operation over a long period.

See also Table I for additional results.

Continued effort will be made along these lines with improvement on the physical measurements and extension of the data. The evaluation of non-metals will be pursued in future work.

An abstract of the technique and results has been submitted for presentation at the Minneapolis meeting of the ACS, April 1969. A copy of the abstract is appended.

TABLE I

TYPICAL RECOMBINATION EFFICIENCIES FOR OXYGEN ATOMS ON VARIOUS SURFACES AT ROOM TEMPERATURE

Metals	γ	Remarks
Gold plate	0.0060	Supplied by NASA
Gold sheet	0.0033	Increasing with temperature
Al	0.0032	foil
Al accommodated	0.0056	Passed O-atoms at high pressure over surface
Ta	0.0058	
Stainless Steel	0.036	
Ni	0.040	
Al 1100	0.050	Very rough surface
Ag	>0.05	
Ti	>0.05	

CATALYTIC RECOMBINATION OF OXYGEN ATOMS ON METAL SURFACES in the 10^{-4} to 10^{-6} torr PRESSURE REGION

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ABSTRACT

The recombination efficiency of oxygen atoms impinging on various surfaces has been studied. A pyrex reaction vessel was used with O-atoms concentrations in the order of 10% and total pressures of 10^{-4} to 10^{-6} torr. The gas phase oxygen atom concentration was monitored by using the chemiluminescent reaction of NO with O-atoms. A stream of oxygen atoms was supplied to a stirred-flow reactor system which was cryogenicly pumped with liquid helium. The afterglow intensity was proportional to the oxygen atoms, and the decay rate of the oxygen atoms was a function of the pumping speed and the surface recombination. First order decay of the intensity was obtained when the oxygen atom discharge was turned off. They decay rate was then used to calculate the recombination coefficient, γ, for these operating conditions. The recombination rates at these very low pressures are found in general to be somewhat less than those reported in the literature for much higher O-atom concentrations, possibly because catalytic heating effects do not occur over the entire surface (surface area ~ $10cm^2$) which would tend to increase the recombination rate. Localized heating and surface conditioning effects will be discussed and recombination coefficients reported.