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EFFECT OF SURFACE PREPARATION AND GAS FLOW ON
NITROGEN ATOM SURFACE RECOMBINATION

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SUMMARY

The effects of surface preparation and gas flow on the recombination of nitrogen atoms at copper and platinum surfaces were determined. Atoms were generated by an electrodeless 2450-megacycle-per-second discharge, and their concentration was measured by gas-phase titration with nitric oxide. Test surfaces were either vacuum-evaporated films or spheres machined from bulk metal and cemented around small glass-bead thermistors. Heat released by recombination was measured as the difference in electrical energy required to maintain a given thermistor temperature with and without a catalytic surface exposed.

Recombination coefficients measured at flow velocities of 1120, 1790, 2250, and 3460 centimeters per second and at pressures of 0.42 and 0.59 millimeter of mercury showed that flow conditions had no effect. The results were also independent of atom concentration. A rough indication of the temperature dependence was obtained; it was greater for copper than for platinum.

Platinum films deposited on platinum or on glass had the same activity—about 3 percent of the atoms impinging recombined. With copper, however, the glass substrate greatly reduced the percent of atoms recombining over that of a bulk copper substrate where 4 percent of the impinging atoms recombined. This effect could be overcome by depositing a second film on top of the first.

Bulk metal samples were subjected to various surface treatments including polishing, degreasing with a chlorinated hydrocarbon, washing with nitric acid, and rinsing with water. Polished, degreased platinum had low activity compared to an evaporated film, but nitric acid treatment made it equivalent. Polished, degreased copper was only slightly less active than a copper film; nitric acid etching decreased the activity still further, probably by preferentially exposing facets of low catalytic efficiency.
INTRODUCTION

The recombination of atoms on surfaces has been a subject of interest for many years, because it represents a relatively simple type of catalytic reaction. Most of the early work dealt with hydrogen atoms. Recently, there has been a rapid increase in the level of effort in this field, and more attention has been given to the surface recombination of oxygen and nitrogen atoms. The present interest can be attributed, at least in part, to the need for such information in space exploration (refs. 1 and 2) and in connection with the passage of satellites through dissociated atmospheric gases (ref. 3). It is to be hoped, of course, that the accumulation of reliable data will also lead to general insight about the mechanism of surface recombination.

The present report describes some observations on the recombination of nitrogen atoms. The work was planned to answer several questions about the effects of surface preparation and about the comparability of measurements made in various ways.

Several experimental approaches have been used by various investigators; the aim in all of them is to determine either what fraction of the atoms striking a surface recombine on it or the relative recombination efficiencies of various surfaces. The experiments comprised measuring a thermal effect due to the release of heat of recombination. The different experimental arrangements are as follows: (1) Atoms from a partly dissociated stream of gas diffuse along a side tube to the test surface (refs. 2 and 4); (2) the test surface is placed directly in the main stream (refs. 5 and 6); or (3) the test surface is put in a chamber, into which the gas enters by effusion through a small hole (ref. 7). If data obtained by the different techniques are to be compared, it is important to know whether flow conditions affect the results. One of the objectives of the present work was to answer this question with arrangement (2) used over a range of Reynolds numbers.

The catalytic effectiveness of a surface is affected by its structure and cleanliness, both of which may vary with the method of preparation. The major part of the work described in this report deals with measurements of nitrogen atom recombination on platinum and copper prepared in various ways. Both vacuum-evaporated and bulk metal specimens were used. The latter were subjected to various cleaning routines, including treatment with nitric acid, which etches copper but merely cleans platinum. The effect of the substrate on the effectiveness of vacuum-evaporated surfaces was also studied.
APPARATUS

The apparatus used was essentially the same as that described in reference 6 and is shown schematically in figure 1. Dissociation was produced and maintained in the discharge tube with a 2450-megacycle-per-second, 125-watt, variable-power microwave generator. A more accurate rotameter than was used in reference 6 metered the working gas, which for the present study was water-pumped nitrogen. The discharge tube was evacuated by a 300-cubic-foot-per-minute rotary-piston vacuum pump, and the discharge tube pressure was measured with a Pirani vacuum gage. There was a controlled leak of nitrogen directly into the vacuum pump inlet so that nitrogen flow through the discharge tube and the pressure in the discharge tube could be controlled independently.

The percent nitrogen atoms in the gas stream was determined by a gas titration using nitric oxide (ref. 8). The titration probe was made from a hypodermic needle positioned at the axis of the discharge tube, and the flow of nitric oxide was directed opposite that of the main gas stream (fig. 1). The flow of nitric oxide from a gas cylinder was controlled by a custom-built, stainless-steel, capillary-type valve, and the nitric oxide flow rate at the titration end point was metered by a small rotameter that was more precise than the one used in the earlier work.

Recombination heat was measured with two glass-bead thermistors about 0.09 inch in diameter. One was bare and served as a reference; the other was the test thermistor and carried either a catalytic or noncatalytic surface. These thermistors replaced the titration probe after the completion of the gas titration (fig. 1). Proper positioning of the thermistors was accomplished by rotating the probe holder; that is, every measurement, including titration, was made at the same point in the gas stream. The power through and the resistance of the thermistors were determined from measurements made with a modified Wheatstone bridge circuit, which was similar to the one reported in reference 6 except that it was automatically balanced. Balancing of the bridge was accomplished by automatically varying the voltage across the bridge which, in turn, changed the thermistor resistance by electrical heating.

PROCEDURE

The experimental procedure involved two steps: (1) gas titration to determine nitrogen atom concentration, and (2) recombination heat measurements. The various test conditions used are listed in table I.

Titration of Nitrogen Atoms

The concentration of nitrogen atoms in the stream at the test position was measured by a gas titration with nitric oxide (ref. 8). Since
nitric oxide and nitrogen atoms react very rapidly and in equimolar proportions, the mole flow rate of nitric oxide is equal to the local mole flow rate of atoms at the titration end point. The end point is determined by the appearance of the greenish-white light emitted by the reaction

\[ \text{NO} + \text{O} \rightarrow \text{NO}_2 + h_v \]

which occurs whenever NO is added in excess of the stoichiometric amount for the reaction

\[ \text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O} \]

Reproducibility of the end point was better than 5 percent.

The titration was carried out over a range of microwave generator output powers for each of the four nitrogen flow rates used, and the results are shown in figure 2. These results must be converted into mass fraction of nitrogen atoms in the stream for subsequent reduction of the data and are presented in that form in table II.

Recombination Heat Measurements

The number of atoms recombining on a surface per unit time was measured electrically. The power required to maintain a thermistor at some temperature in the stream of partially dissociated gas was first measured with a noncatalytic surface exposed and then with the test surface exposed. The difference in electrical power required to maintain a given temperature under the two conditions is equal to the heat released by recombination.

Since it was impossible to obtain two thermistors perfectly matched in size and electrical characteristics, the same one was employed for both measurements. This meant that considerable time elapsed between the two measurements, during which the test surface was prepared. Consequently, the room temperature could not be expected to remain constant, and, since the apparatus was not adiabatic, changes in ambient temperature affected the heat loss. Small corrections to the measured recombination heat were therefore required and were supplied by the second thermistor (fig. 1), which served as a reference.

Test Surface Preparation

As mentioned previously, it was necessary to measure the power required to maintain a thermistor at a given temperature when its surface was noncatalytic. The noncatalytic surface used in tests of metal
vacuum-evaporated onto glass was simply the uncoated glass bead of the
thermistor. This procedure was acceptable because, although glass does
catalyze atom recombination, it is orders of magnitude less effective than
metals (refs. 4, 9, and 10). For tests of bulk metal samples a thin non-
catalytic coating to cover the metal surface was required. Acrylic lac-
quered proved to be as noncatalytic toward nitrogen atom recombination as
glass; this is shown in table III, where the voltage across the bridge
circuit for glass and acrylic lacquer surfaces is compared under the same
experimental conditions.

Vacuum evaporations were carried out at pressures below 1 micron of
mercury. Thermocouple grade platinum and copper were used. There was
no cold trap between the bell jar and the oil diffusion pump; therefore,
some preliminary tests were made with evaporated platinum surfaces to see
whether back-diffusion of pump oil was affecting the results. These
tests consisted of recombination measurements before and after degreasing
with a chlorinated hydrocarbon solvent. Since no difference was found in
the results, there was evidently no interfering oil film, and vacuum-
evaporated surfaces were considered ready for testing without further
treatment.

The bulk metal surfaces were made by cementing small, hollow, ma-
chined spheres around thermistor beads. Platinum spheres were formed
from swaged and fused thermocouple wire and copper spheres from commer-
cial rod that was better than 99.9 percent pure. The surfaces were al-
ways mechanically polished prior to any special treatment. The polish-
ing process for both platinum and copper spheres consisted of rubbing
first with diamond dust and then with commercial metal polish until a
mirror finish was obtained. In addition, the copper spheres were given
a final polish with commercial copper cleaner.

The special surface treatments that were tested for effects on re-
combination comprised two or more of the following steps: (i) degreas-
ing with a chlorinated hydrocarbon, (2) cleaning or etching with dilute
nitric acid, (3) cleaning or etching with concentrated nitric acid, and
(4) flushing with distilled water. Any course of treatment always began
with degreasing and ended with a water rinse. Specific treatments are
listed in tables IV and V.

It was reported in reference 6 that platinum surfaces must be bom-
barded by nitrogen atoms for about 3 hours before a constant recombi-
ation coefficient is obtained. This result was observed, and the same
procedure was also followed in the present work. No such effect was
noted for copper in the present experiments, although it was expected
because the samples gradually became discolored upon exposure to nitro-
gen atoms. Nevertheless, extended exposure of the copper surfaces to the
partly dissociated stream was permitted before final data were taken.
CALCULATIONS

The recombination coefficient $\gamma$ is defined as:

$$\gamma = \frac{\dot{g}_i - \dot{g}_r}{\dot{g}_i}$$  \hspace{1cm} (1)

where $\dot{g}_i$ is the number of moles of atoms that strike a unit surface per second, $\dot{g}_r$ is the number reflected, and

$$\dot{g}_i = \frac{1}{4} n \bar{c} x'$$

where

- $n$ number of moles per cubic centimeter, $P/\sqrt{T}$
- $\bar{c}$ mean molecular velocity, $(\sqrt{RT/nM})^{1/2}$
- $x'$ mole fraction of atoms about a mean free path from the surface which are about to strike the surface

$P$ pressure

$R$ gas constant

$T$ temperature

The net mass flux of atoms $G$ is

$$G = M(\dot{g}_i - \dot{g}_r) = \gamma \dot{g}_i$$

Therefore,

$$\frac{G}{M} = \gamma \left( \frac{1}{4} n \bar{c} x' \right)$$  \hspace{1cm} (2)

Consider the composition $x$ of the reacting gas right at the wall: Half of the molecules are about to strike the wall, and half of the molecules have just collided with the surface. Hence,

$$x = \frac{1}{2} x' + \frac{1}{2} (1 - \gamma)x' = \frac{1}{2} (2 - \gamma)x'$$  \hspace{1cm} (3)

Now, using equation (3) to eliminate $x'$ in equation (2) gives

$$x = \frac{1}{2} (2 - \gamma) \frac{G}{M} \frac{1}{\frac{1}{4} n \bar{c}}$$  \hspace{1cm} (4)
Solving equation (4) for $Y$ results in

$$Y = \frac{2G}{\frac{1}{\gamma} \cdot \text{Mn} \bar{\varepsilon}x + G}$$

(5)

However,

$$\text{Mn} \bar{\varepsilon}x = M \frac{P}{RT} \left( 3 \frac{RT}{\pi M} \right)^{1/2} \frac{2m_s}{l + m_s}$$

where $m_s$ is the mass fraction of atoms at the surface. Hence,

$$Y = \frac{G}{P \sqrt{\frac{M}{2\pi RT}} \frac{2m_s}{l + m_s}} \left( \frac{1}{1 + \frac{G}{2P \sqrt{\frac{M}{2\pi RT}} \frac{2m_s}{l + m_s}}} \right)$$

(6)

Equation (6) was used for calculating the value of $Y$. This equation for $Y$ differs from the equation used in reference 6 by a factor of

$$\frac{1}{1 + \frac{G}{2P \sqrt{\frac{M}{2\pi RT}} \frac{2m_s}{l + m_s}}}$$

which is close to unity for the present work.

The quantity $m_s$ is related to the mass fraction of atoms in the stream $m_{\infty}$ by the mass transfer Nusselt number correlation for spheres $Nu'$ (ref. 11):

$$Nu' = \frac{Gd}{\rho D_{12}(m_{\infty} - m_s)} = 2 + 0.6 \text{Re}^{1/2} \text{Sc}^{1/3}$$

(7)

where

d \quad \text{test thermistor diameter}

$\rho \quad \text{gas density}$

$D_{12} \quad \text{binary diffusion coefficient}$

$\text{Sc} \quad \text{Schmidt number}$

$\text{Re} \quad \text{Reynolds number}$
The density $\rho$ was calculated from the gas law; $D_{12}$ was calculated using the Lennard-Jones (6-12) potential according to reference 12, as was the viscosity used in calculating $Sc$ and $Re$. The value of $G$ was determined from the measured recombination energy and the test surface area of the thermistor; $m_\infty$ was determined from the gas titration and is shown in table II.

EXPERIMENTAL ACCURACY

The parameters that influence the accuracy of $\gamma$ are: (1) the recombination energy, (2) the surface temperature, (3) the mass fraction of nitrogen atoms in the stream, and (4) the flow rate of nitrogen. The accuracy of the recombination energy values and the surface temperature measurements was cause for concern because they were affected by changes in ambient temperature. The uncertainty in measuring the surface temperature, however, was at most $\pm 0.3$ C, which gives a maximum error in $\gamma$ of $\pm 0.3$ percent. Also, because of the reference thermistor correction, the uncertainty in the recombination energy affected the accuracy of $\gamma$ by less than $\pm 5$ percent.

The measured gas flow rates for nitric oxide in the gas titration and for the nitrogen through the discharge were both accurate to about $\pm 5$ percent. This uncertainty in the gas titration gives an accuracy of $\pm 5$ percent in the mass fraction of nitrogen atoms in the stream, which affects $\gamma$ by less than $\pm 7$ percent. Error in the flow rate of nitrogen into the discharge tube affects $\gamma$ more than any parameter; an uncertainty of $\pm 5$ percent gives an uncertainty in $\gamma$ of $\pm 3$ percent. Generally, the uncertainty in the various other parameters was less than the amounts just discussed, and the overall error in $\gamma$ was estimated to be about $\pm 10$ percent.

RESULTS AND DISCUSSION

Effect of Gas Flow

To determine whether flow conditions affect the measured recombination coefficients, Reynolds number was varied by changing the velocity, pressure, and thermistor diameter. The data for an evaporated platinum surface are shown in figure 3. It is seen that all the results are within a $\pm 10$ percent band of uncertainty over an approximately threefold variation of Reynolds number. It thus appears that the measurements and the method of reducing data yield coefficients that are unaffected by flow conditions. The present results should therefore be equivalent to those obtained by diffusion of atoms into a side arm.

The mass fraction of atoms in the gas stream varied, at a given Reynolds number, as microwave power output was changed (table II). It
can be seen from figure 3 that the recombination coefficient was unaffected. Therefore, it can be concluded that the recombination coefficient for nitrogen atoms on surfaces does not depend on atom concentration, a conclusion also reached by others for hydrogen and oxygen atoms (refs. 10, 13, and 14).

Reference 15 describes a phenomenon that caused some concern in this work. It was reported that nitrogen atoms combine on suitably prepared copper surfaces to form molecules in an excited state, which return to the ground state with emission of visible light at considerable distances from the surface. Recombination coefficients measured in the presence of such an effect would be falsely low if any appreciable part of the recombination energy were carried away in this manner. However, the experimental conditions used in the present studies were evidently not suitable for the production of excited molecules, because no such visible emission was ever observed.

Platinum Surfaces

Table VI presents a typical set of raw and reduced data. This particular series of tests was made with platinum vacuum-evaporated onto bulk platinum. Table IV summarizes all the results for platinum in various forms and subject to various surface treatments. Each recombination coefficient is the average of at least five determinations.

The value of $\gamma$ at 50$^\circ$C for a platinum film deposited directly on glass was 0.031. (Earlier results (ref. 6) were about 25 percent lower; however, in view of the improved apparatus, the present data are considered more reliable.) Chemical analysis showed that the amount of metal present corresponds to a spherical shell about 0.38 micron thick. In order to determine whether the substrate affected the results, the experiment was repeated with the film deposited on a platinum sphere; the $\gamma$ obtained was 0.029, essentially the same as before.

A bulk platinum specimen that had merely been degreased yielded a $\gamma$ of 0.016 and was thus only about half as effective a catalyst as the nominally clean vacuum-evaporated surfaces. The number was confirmed on three different occasions, with at least 10 measurements made each time. After the degreased surface was washed for 2 minutes in dilute nitric acid, $\gamma$ jumped to 0.026, and longer washes brought it to a value equivalent to that for vacuum-coated platinum. A comparable result was obtained by rinsing for a shorter time in concentrated nitric acid. It is thought that the acid may have acted as it did by its ability to remove iron contaminant, which undoubtedly was introduced in the machining process.

These data emphasized the care that must be used in preparing samples for recombination measurements. They also suggest that, in work with bulk
samples, it is advisable to measure $Y$ for the vacuum-coated form as a reference point. However, this must also be done cautiously, as will be pointed out in the discussion of results with copper.

A general increase of $Y$ with surface temperature was noted over the short range from $36^\circ$ to $61^\circ$ C covered in the experiments (fig. 4(a)). The solid line shown in figure 4(a) is a least-squares fit. The temperature dependence is about the same as that found for hydrogen atoms and indicated by the dashed line (ref. 2).

**Copper Surfaces**

The surface treatments and results for copper are summarized in table V. Each recombination coefficient is the average of at least 12 determinations.

An unexpected result was found when the recombination coefficients for single coatings of copper on glass and on copper spheres were compared. These films, which were prepared in an arbitrary but reproducible manner, were about 0.49 micron thick. Despite the fact that they were thicker than the platinum films, the glass substrate exerted a strong effect on recombination at the surface, whereas in the case of platinum it did not. This is shown in table V. The value of $Y$ at $50^\circ$ C for one coat of copper was 0.037 when it was deposited on bulk copper and only 0.012 on glass. A second coating applied on top of the first eliminated this difference.

It appears that the glass exerts an effect on the detailed structure of the surface. Visually, there was no obvious difference between single and double films: under high magnification, both were extremely smooth and homogeneous, with no sign of clumping or of uncoated glass.

The $Y$ for polished bulk copper that had been degreased and flushed with water was 0.034. When the sample was also etched briefly in dilute nitric acid, a slight but seemingly real decrease to 0.023 occurred. It is thought to be real because it is similar to the effect found by Nakada in his study of nitrogen recombination on single copper crystals (ref. 16). He observed that either the (100) or the (110) plane is more catalytic when mechanically polished than it is when polished and then etched with dilute nitric acid. In previous studies of hydrogen atom recombination, Nakada had found that the order of activity was $(110) > (100) > (111)$. He suggests that mechanical polishing exposes facets more active than the original surface, while nitric acid etching tends to bring out the (100) face with a resultant decrease in activity.

It is possible that the effect of metal contaminant introduced during machining is discernible in the data of table V, but, if so, it is smaller
than the analogous effect for platinum. The $\gamma$ for degreased bulk copper is somewhat smaller than the $\gamma$ for either vacuum-coated copper or doubly coated glass. Unlike platinum, however, copper cannot be freed of the presumed contaminant without bringing into play the effect of etching as just described.

The effect of temperature on recombination coefficient for copper is shown in figure 4(b). The line was determined by the method of least squares. Although a smaller temperature range was covered, it is clear that the temperature dependence is greater for copper than for platinum.

**SUMMARY OF RESULTS**

The fraction of nitrogen atoms that recombine upon striking copper and platinum surfaces in a partly dissociated stream was determined by subjecting vacuum-evaporated films and bulk metal samples to various surface treatments. The following results were obtained:

1. In the range studied, gas velocity, pressure, atom concentration, and Reynolds number do not affect the surface recombination coefficient for nitrogen atoms. Coefficients measured in a flowing gas stream can therefore be compared directly with those measured in static experiments.

2. The substrate may influence the surface activity of a vacuum-evaporated film. A large effect was found with copper deposited on glass, but no effect was observed with platinum.

3. Surface preparation affects the activity of bulk metal platinum and copper. Platinum can be cleaned with nitric acid so as to yield recombination coefficients equal to those for vacuum-evaporated material, but simple degreasing is not sufficient. On the other hand, the activity of degreased copper is only slightly less than that of evaporated films; nitric acid treatment etches the surface and lowers its activity, probably because facets of low catalytic efficiency are preferentially exposed.

4. Specially prepared platinum and copper surfaces recombine as much as 3 and 4 percent, respectively, of the nitrogen atoms that impinge. Without special treatment, the number of atoms recombining can be less than 1.5 percent.

5. The recombination coefficient for nitrogen atoms on platinum increases with temperature at about the same rate as for hydrogen atoms. Copper shows a considerably higher temperature dependence.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, June 20, 1961
REFERENCES


TABLE IV. COMPARISON OF RECOMBINATION COEFFICIENT FOR BULK PLATINUM AND VACUUM-COATED PLATINUM

[Nitrogen flow rate, 0.350 g/min; test pressure, 0.42 mm Hg;

Test surface area, 0.260 cm²; Reynolds number, 1.69.]

<table>
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<tr>
<th>Thermistor resistance, ohms</th>
<th>Voltage across bridge circuit with discharge on, V</th>
<th>Recombination energy, W</th>
<th>Mass fraction of N atoms in stream</th>
<th>Test surface temperature, °C</th>
<th>Recombination coefficient, γ</th>
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Figure 2: Titration results at various nitrogen flow rates.
Figure 3 - Effect of Reynolds number on recombination coefficient; platinum surface at 50°C.
Figure 4. - Surface activity for atom recombination as function of temperature.

Recombination coefficient, 1/x102

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