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TECHNICAL NOTE

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NITROGEN AND OXYGEN ATOM RECOMBINATION AT OXIDE SURFACES AND EFFECT OF A TESLA DISCHARGE ON RECOMBINATION HEAT TRANSFER

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SUMMARY

Recombination coefficients for nitrogen and oxygen atoms at metallic oxide surfaces were determined over a small temperature range. The effect of a Tesla discharge on the recombination heat transfer at some surfaces was also determined. The dissociated gases were generated by an 800-watt microwave generator, and the recombination heat-transfer measurements were made electrically with thermistors. The recombination coefficient measurements were made at oxide surfaces of calcium, copper, chromium, germanium, iron, and zinc. The Tesla discharge effect was determined at metallic surfaces of copper and iron and at oxide surfaces of calcium, copper, iron, and zinc.

On a relative basis, the recombination coefficients for oxygen atoms at these surfaces agreed with the results of other investigators. These oxygen atom results could be correlated on an acid oxide - basic oxide mechanism. The nitrogen atom results on these surfaces could not be explained by an acid oxide - basic oxide mechanism, as was possible for the oxygen atom results. The recombination coefficients were found to increase, decrease, or remain constant with increasing temperature, depending on the surface and the recombining atoms.

A Tesla coil discharge was found to have a large effect on the recombination heat transfer. This effect always caused an 8- to 16-percent decrease in the recombination heat transfer for oxygen atoms. For nitrogen atoms, the Tesla discharge sometimes caused an increase and sometimes a decrease in the recombination heat transfer. The largest increase was 6.4 percent, and the largest decrease was 43.7 percent. The results of the Tesla discharge indicate that recombination coefficient measurements may be affected by the discharge used to produce the atoms.

INTRODUCTION

Since the publication of the work by Linnett and Marsden in early 1956 on oxygen atom recombination at surfaces, numerous measurements have been made and the results published on the recombination of hydrogen, oxygen, and nitrogen atoms at surfaces (refs. 1 to 16). Some of these studies deal with the effect of single crystals and surface preparation (refs. 8 and 15). Other investigators have made measurements on a number of different surfaces and used the periodic table and the filling of the d-shell of the transition metals to help explain their results (refs. 4 and 11). In addition, Greaves and Linnett were able to correlate some of their results of oxygen atoms at oxide surfaces with "acidity" or "alkalinity" of the oxide. They found that the less active surfaces form acidic oxides, and the more active surfaces form basic oxides.

A general mechanism for surface catalysis includes adsorption, desorption, and surface diffusion of the active species and the active sites provided by the catalytic material (ref. 9). A number of workers observed that the gas adsorption on some surfaces is affected when the gas is excited (ref. 17). A weak Tesla coil discharge will greatly increase the rate of hydrogen adsorption on zinc oxide even after the surface is saturated with respect to the unexcited gas (ref. 18). On the other hand, a weak Tesla coil discharge causes a decrease in the rate of adsorption in an oxygen-iron system and a desorption in an oxygen-copper system (ref. 19). Since adsorption and desorption are part of the mechanism in catalysis, the nature of the discharge producing the dissociation may therefore have an effect on the number of atoms recombining at the surface.

Recombination results for nitrogen and oxygen atoms at acidic and basic oxide surfaces are presented in this report, and these results are compared with the work of Greaves and Linnett. The oxides of six metals were tested: three that form acidic oxides (chromium, germanium, and zinc) and three that form basic oxides (calcium, copper, and iron).

Results on the effect of a Tesla coil discharge on the recombination heat transfer with nitrogen and oxygen atoms are also presented in this report. Measurements for this part of the work were made at surfaces of metallic copper and iron and at surfaces of calcium oxide, copper oxide, iron oxide, and zinc oxide.

APPARATUS

The apparatus used is shown schematically in figure 1. It is a modification of that used in earlier work by this author (refs. 7 and 8). These modifications include: (1) an 800-watt power generator for the discharge which operates at 2450 megacycles per second; (2) a thermostatically controlled water jacket around the discharge tube to give a range of surface temperatures; (3) a porous catalytic disk, made of sintered glass painted with platinum paint, with a reference or control probe downstream of this disk; and (4) an improved low-flow valve for controlling the flow of the test gas.

The test gases used were commercial water-pumped nitrogen and oxygen. The mass-flow rates are given in table I. These flow rates give a gas velocity

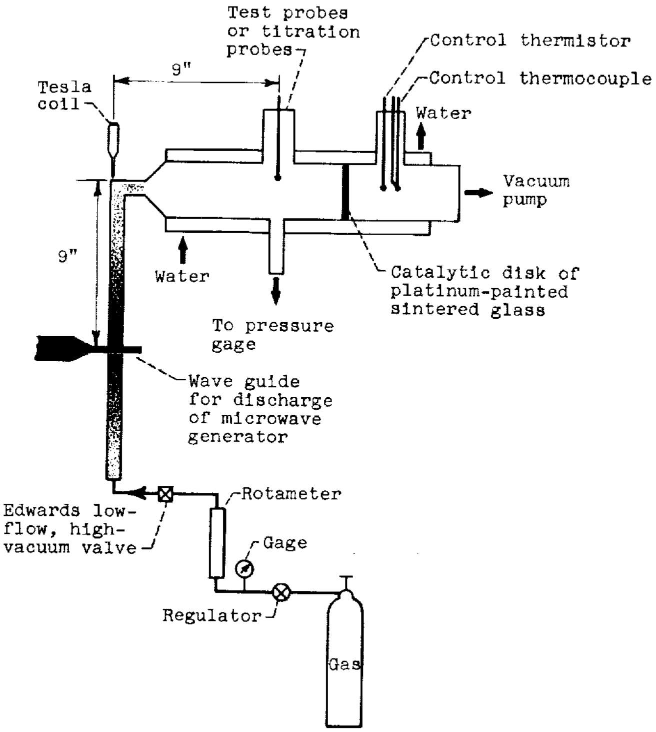


Figure 1. - New atom-recombination unit.

between 230 to 360 centimeters per second for nitrogen and 190 to 300 centimeters per second for oxygen, depending on the gas pressure and temperature.

TABLE I. - TEST CONDITIONS

Test gas	Oxygen		Nitrogen	
Test gas flow rate, g/min	0.196	0.349	0.183	0.326
Test pressure, mm Hg	1.7	2.5	1.7	2.5
Reynolds number per centimeter	3.00	5.29	2.82	4.91
Mass fraction of atoms	0.018	0.017	0.0079	0.0073

In this work the atom concentration of both the nitrogen stream and the oxygen stream was required. The nitrogen atom concentration was determined by a gas titration with nitric oxide (ref. 20), and the oxygen atom concentration was determined by a gas titration with nitrogen dioxide (ref. 21). Since nitrogen dioxide is a corrosive gas, the flow rate of titrant gas at the end point of the titrations was determined by a pressure-drop method in a completely glass system. This method consists of measuring the pressure drop per unit time of a known volume of titrant gas. The titration probe was a small-diameter stainless-steel tube positioned at the axis of the discharge tube and pointed in an upstream direction. A commercially available low-flow valve was used to regulate the flow of titrant gas.

Glass-bead thermistors were used to measure recombination heat in a manner similar to that used in reference 8. Thermistor resistances determined with an automatically balancing Wheatstone bridge and the voltage across the bridge circuit were used for determining the recombination heat transfer (ref. 8). The test thermistors replaced the titration probe after the completion of the gas titration (fig. 1).

PROCEDURE

The determination of the recombination coefficient of a substance requires both a gas titration for the atom concentration and recombination heat measurements. The effect caused by a Tesla coil discharge only requires recombination heat-transfer measurements with and without a Tesla coil discharge. Table I lists the various test conditions used for these experiments.

Titration of Atoms

The nitrogen atom concentration was measured by a titration with nitric oxide (ref. 20). The determination of the oxygen atom concentration involves the reaction of oxygen atoms with nitrogen dioxide (ref. 21). The reactions taking place during these titrations are:

$$N + NO \rightarrow N_2 + O \tag{1}$$

$$O + NO_2 \rightarrow NO + O_2 \tag{2}$$

$$NO + O \rightarrow NO_2 + h\nu \qquad \text{[Slow compared with reactions (1) and (2)]} \tag{3}$$

In both the determination of nitrogen atoms and oxygen atoms the light-emitting reaction (eq. (3)) is the indicator for the end point of the titration. In the titration for nitrogen atoms, reaction (1) takes place until the mole flow of nitric oxide exceeds that of the nitrogen atoms; then the excess nitric oxide reacts according to equation (3) with the oxygen atom produced during the first reaction. Thus, the end point is indicated by the appearance of the emitted light.

Things are a little different for the oxygen atom titration. As soon as nitrogen dioxide is added to the stream containing oxygen atoms, the reactions shown by equations (2) and (3) both take place, and light is emitted. When the mole flow rate of nitrogen dioxide exceeds that of the oxygen atoms, the light-emitting reaction (eq. (3)) can no longer take place because all the oxygen atoms are consumed. Therefore, the end point for the oxygen titration is reached when the emitted light disappears.

The titration for each of the test gases was carried out at one microwave generator output power and two different gas flow rates and pressures. The results are presented in table I. The $N_2O_4 \rightleftarrows 2NO_2$ equilibrium was taken into account in calculating the oxygen atom concentration (ref. 22).

Under the conditions of these experiments, the flow rate of the titrant gases at the end point was quite small, less than 0.013 gram per minute for nitrogen oxide and 0.007 gram per minute for nitrogen dioxide. Because of these low flow rates, the precision of measuring the titration end points was no better than ±10 percent.

Recombination Heat Measurements

As was done in some earlier work, the recombination heat on a test surface was determined by electrically measuring the difference in heat transfer to the test surface and a noncatalytic surface with glass-bead thermistors (ref. 8). This heat-transfer difference equals the heat released by surface recombination. Glass was used as the noncatalytic standard because it is a poor catalyst for both nitrogen and oxygen recombination (ref. 16).

For all the Tesla coil experiments, the Tesla coil discharge was turned off and on several times before the heat-transfer data were taken. This was done to make sure that any change in the recombination heat transfer was caused by the Tesla coil discharge. The effect of the strength of the Tesla coil discharge was measured by varying the input power to the Tesla coil from 0 to 25 watts. As a further check on the reality of the effect, Tesla coil discharge tests were also made on all surfaces with the microwave generator turned off.

Temperature Measurements

The temperature of the test gas was varied over a 17° to 87° C temperature range by varying the water temperature in the discharge tube water jacket. A noncatalytic calibrated thermistor was used to measure the gas temperature.

Test surface temperatures were governed by the recombination coefficient of the test material and by the water jacket temperature. The variation of the water jacket temperature provided at least a 30° C temperature range for the test surfaces. The temperature of the test surface was determined from the resistance of the coated test thermistor.

Surface temperature data for the Tesla discharge experiments followed the same Tesla coil discharge-off and -on procedure described in the section entitled Recombination Heat Measurements.

Test Surface Preparation and Conditioning

The surfaces tested are listed in table II. A newly prepared surface was made for each series of tests.

TABLE II. - TEST SURFACES FOR RECOMBINATION COEFFICIENT MEASUREMENTS AND TESLA COIL TESTS

Test surface	Recombination coefficient measurement	Tesla coil test
Calcium oxide	Yes	Yes
Chromium oxide	Yes	No
Copper	No	Yes
Copper oxide	Yes	Yes
Germanium dioxide I (from oxidation of vacuum-evaporated germanium)	Yes	No
Germanium dioxide II (from vacuum-evaporated germanium dioxide)	Yes	No
Germanium monoxide[a]	Yes	No
Iron	No	Yes
Iron oxide	Yes	Yes
Zinc oxide	Yes	No

[a] For nitrogen atoms only.

The copper and iron surfaces were prepared by vacuum evaporation of thermocouple grade wire from a tungsten filament. The oxides of chromium, copper, iron, and one of the germanium oxides (probably germanium dioxide) were prepared by oxidation of the vacuum-evaporated metal surfaces. Films of copper and iron were oxidized in a stream of oxygen at about 350° C. Higher temperatures were used for oxidation of the chromium and germanium films. Vacuum evaporation of germanium dioxide gave a surface that was probably germanium monoxide because of partial decomposition of the dioxide on the hot tungsten filament. Germanium monoxide was tested only with nitrogen atoms because a change in the color of the surface indicated that oxygen atoms quickly oxidized the monoxide to the dioxide. However, germanium dioxide formed by the oxidation of germanium monoxide was tested as a separate surface. Germanium dioxide prepared from the monoxide physically appeared to be a much thicker test surface than that prepared by oxidizing the metal film. (For simplicity, germanium dioxide prepared from oxidized germanium metal will be called germanium dioxide I, and germanium oxide prepared from oxidized germanium monoxide will be called germanium dioxide II.)

Zinc oxide films were prepared by vacuum evaporation of zinc oxide followed by heating the surface to 350° C in an oxygen stream. This last step made sure the surface was completely oxidized because some decomposition may have taken place during the vacuum evaporation.

Evaporation of lime water on a test thermistor bead provided the calcium oxide surface. This was followed by heating of the calcium oxide surface in the oxidizing part of a bunsen flame.

Tests on the oxide surfaces were always preceded by about 3 hours of oxygen atom bombardment. This was done to condition the test surface so that no surface changes would take place during the experimental measurements (ref. 7). For the calcium oxide surface, it was found that the atom bombardment had to include at least 1 hour of bombardment with nitrogen atoms to prevent erratic results. Erratic results mean that the oxygen atom data could not be repeated after the nitrogen data were taken. After the initial atom bombardment of these oxides, the recombination heat measurements were made. The oxygen atom tests were made first, and then the tests with the nitrogen atoms were made. A recheck of several points of the oxygen atom tests always followed the nitrogen atom tests to make sure the test surface did not change.

The conditioning of the two metallic surfaces, copper and iron, was done with 3 hours of nitrogen atom bombardment, because oxygen atom bombardment would oxidize the surface. For the same reason, the recombination heat-transfer measurements were made first with nitrogen atoms and then with oxygen atoms. Data for the oxygen atom tests on these two surfaces were taken rapidly before complete oxidation of the surface was accomplished. No recheck of the nitrogen atom tests was made with these surfaces because of observable surface oxidation.

Since it is important for comparisons that the nitrogen and oxygen atom results be for the same surface, all the tests on a given surface were completed in 1 day.

CALCULATIONS

The recombination coefficient γ is defined as

$$\gamma = \frac{g_i - g_r}{g_i}$$

and is calculated from the following equations from reference 8:

$$\gamma = \frac{G}{P\sqrt{\frac{M}{2\pi RT}}\frac{2m_s}{1 + m_s}}\left(\frac{1}{1 + \frac{G}{2P\sqrt{\frac{M}{2\pi RT}}\frac{2m_s}{1 + m_s}}}\right) \tag{4}$$

$$Nu' = \frac{Gd}{\rho D_{12}(m_\infty - m_s)} = 2 + 0.6\ Re^{1/2}Sc^{1/3} \tag{5}$$

where

D_{12}	binary diffusion coefficient
d	test thermistor diameter
G	net mass flux of atoms
g_i	number of atoms striking unit surface per second
g_r	number of atoms reflected from unit surface per second
M	molecular weight of atoms
m_s	mass fraction of atoms at surface
m_∞	mass fraction of atoms at stream
Nu'	mass transfer Nusselt number
P	pressure
R	gas constant
Re	Reynolds number
Sc	Schmidt number
T	surface temperature
ρ	gas density

The derivation of equation (4) is given in reference 8, and equation (5) comes from reference 23. The binary diffusion coefficient D_{12} and the viscosity used in calculating Sc and Re were determined from the alignment charts in reference 24.

PRECISION

The factor that has the greatest effect on the precision of the recombination coefficients is the precision of the gas titration. For the more catalytic surfaces, the ±10-percent reproducibility in the titration can cause the variation in the reproducibility of the recombination coefficient to be as high as ±30 percent. Also, since glass is used as a noncatalyst reference, there could be significant errors in the measurement of the recombination heat on the surfaces only slightly more catalytic than glass. When considering these and other less significant sources of error, it is felt that the precision of the recombination coefficient results is no better than ±30 percent. Other workers also have found the percent deviation in their reported results to be quite high (refs. 2 and 12).

It has been reported in the literature that in an electrodeless discharge several percent of the active species consists of metastable oxygen in the $^1\Delta g$ state, which has an energy of almost 1 ev (ref. 25). However, under the conditions of the present experiment, the titration is still the biggest source of error.

Because of the off-on technique described in the PROCEDURE section, the recombination heat-transfer measurements for the Tesla discharge experiments are quite precise. The voltage across the bridge circuit could be measured to better than 1-percent accuracy, and the thermistor resistance could be measured to ±1 ohm.

RESULTS

Recombination Coefficients

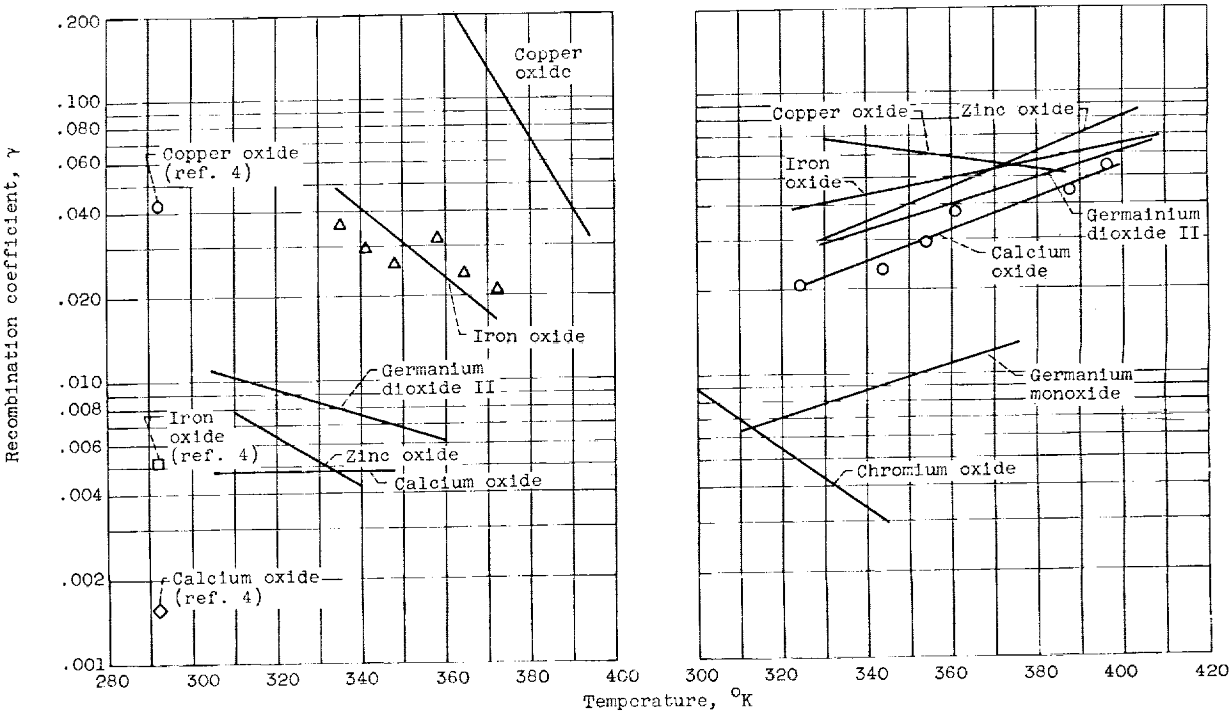
The results of the recombination coefficient measurements as a function of temperature are shown in figure 2 for oxygen atoms and nitrogen atoms. The test surfaces that were found to be about as noncatalytic as glass toward either of the atomic species are listed in table III. The reference 4 results for oxygen atoms with these same surfaces at room temperature are plotted in figure 2(a) if they were found to be good catalysts or are listed in table III if they were found to be poor catalysts.

TABLE III. - TEST SURFACES THAT ARE AS NONCATALYTIC AS A GLASS SURFACE

Test surface	Recombining atoms	Reference 4 value for oxygen atoms
Chromium oxide	Oxygen atoms	2.5×10^{-4}
Germanium dioxide I	Oxygen atoms	1.3×10^{-4}
Germanium dioxide II	Nitrogen atoms	--------
Zinc oxide[a]	--------------	4.4×10^{-4}

[a] Although in this work zinc oxide was not found to be as noncatalytic as glass, it is placed in this table to give published results of ref. 4 for comparison.

Because the plotting of all the data points could cause figure 2 to be confusing, the data points for only one surface are plotted in each figure. In figure 2(a) the points are for iron oxide; in figure 2(b) the points are for calcium oxide. Each point is the average of two or three determinations. Since reference 8 reports that the recombination coefficient is independent of pressure and atom concentration, the lines were drawn between the points because the three points to the right are for one set of pressure and atom concentration conditions and the three points to the left are for another set (table I). It can be seen quite clearly in figure 2(a) that the line drawn would be parallel to the lines drawn through the points for each test condition. The reason for this deviation is the ±10-percent expected error in the gas titration.



(a) Oxygen atoms.

(b) Nitrogen atoms.

Figure 2. - Effect of temperature on recombination coefficient.

For the recombination of oxygen atom, it was found that, in general, the order of catalytic activity is copper oxide > iron oxide > germanium dioxide II > zinc oxide > calcium oxide with both chromium oxide and germanium dioxide I as the poorest catalysts (fig. 2(a) and table III). The activity of the four best catalysts was found to decrease with increasing temperature. The activity of calcium oxide did not change with temperature.

Germanium dioxide I was the only oxide found to be as poor a catalyst as glass for nitrogen atoms (table III). In the temperature range tested, copper oxide, zinc oxide, iron oxide, germanium dioxide II, and calcium oxide were found to have roughly the same catalytic efficiency for nitrogen atoms (fig. 2(b)), namely, about 2 to 9 percent. The efficiencies of germanium monoxide and chromium oxide were intermediate in range, less than 1 percent. Unlike the oxygen recombination results, most of the oxides show an increase in the recombination coefficient with temperature for nitrogen atoms. Only copper oxide and chromium oxide show a negative temperature dependence.

Effect of a Tesla Discharge

The effect caused by a maximum input power of 25 watts to the Tesla coil on recombination heat transfer of the various surfaces tested is listed in table IV.

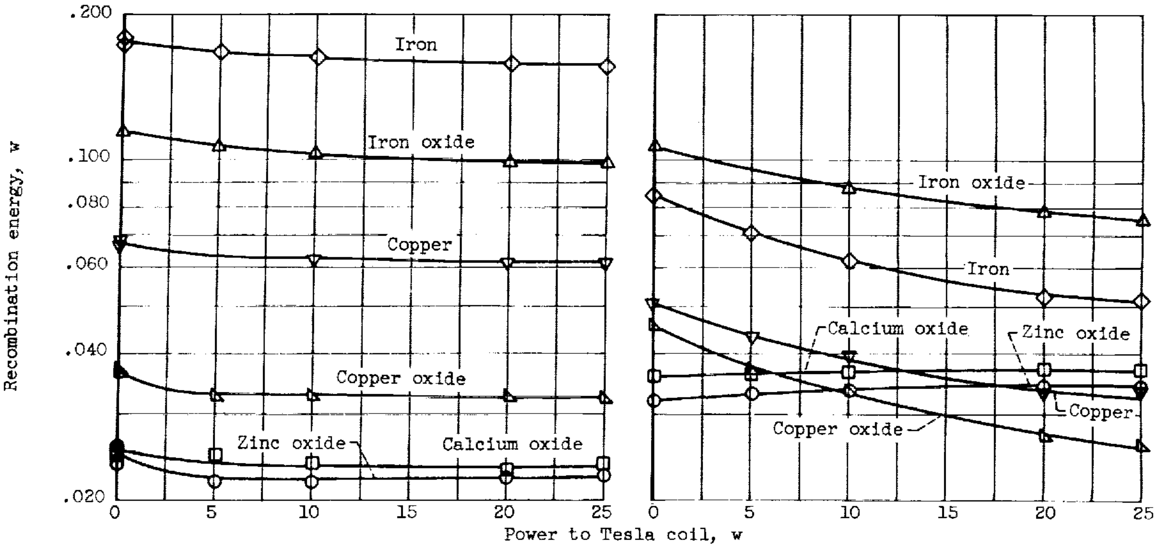
TABLE IV. - MAXIMUM PERCENT CHANGE IN RECOMBINATION

HEAT TRANSFER CAUSED BY A TESLA COIL DISCHARGE

Test surface	Oxygen		Nitrogen	
	1.7 mm Hg test pressure, percent	2.5 mm Hg test pressure, percent	1.7 mm Hg test pressure, percent	2.5 mm Hg test pressure, percent
Calcium oxide	-9.1	-10.0	+3.5	+2.1
Copper	-9.7	-14.5	-35.6	-17.0
Copper oxide	-12.3	-18.4	-43.7	-23.0
Iron	-10.1	-8.3	-39.3	-19.8
Iron oxide	-14.6	-12.2	-30.2	-17.6
Zinc oxide	-15.6	-16.5	+6.4	+2.4

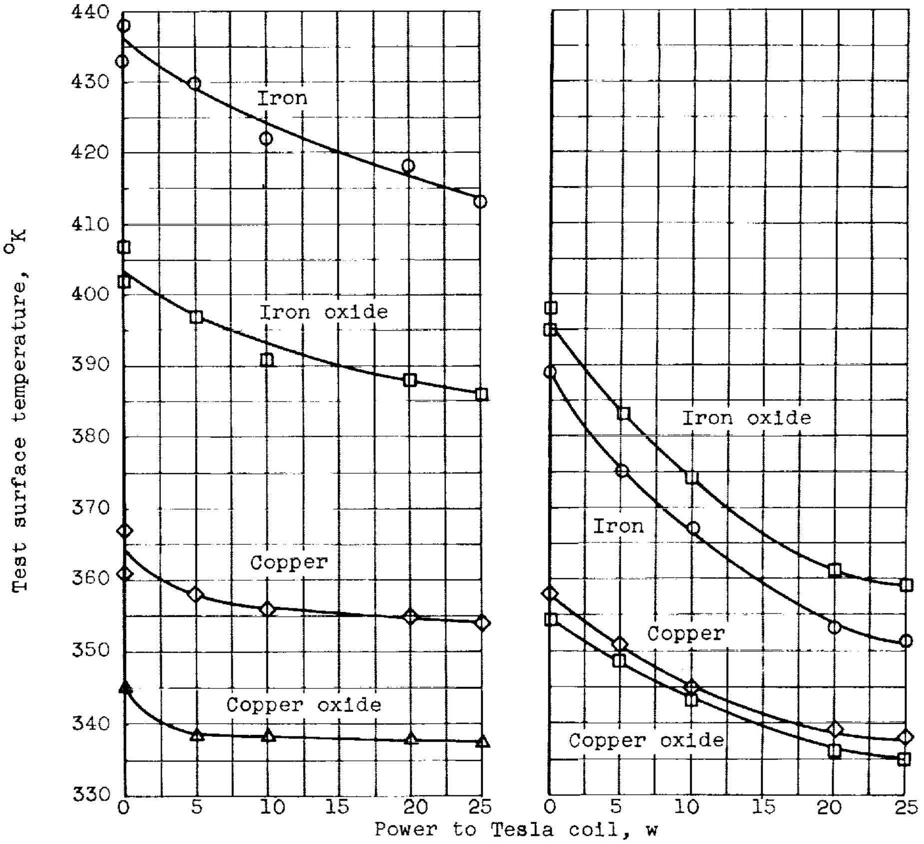
The negative signs indicate a decrease in heat transfer; the positive signs indicate an increase. The change in recombination heat transfer as a function of the strength of the Tesla discharge is shown in figure 3(a) for oxygen atoms and in figure 3(b) for nitrogen atoms. This effect in recombination heat transfer would affect the recombination coefficient by about the same amount. Since a change in recombination heat transfer causes the test surface temperature to change accordingly, the Tesla coil discharge also causes an effect on the surface temperature (fig. 4). This surface temperature effect is important in the catalytic-differential probe technique for measuring atom concentrations (ref. 26).

The Tesla discharge in a stream containing oxygen atoms always caused a decrease in the recombination heat transfer. The degree of this decrease depends on the surface and the pressure with measurements made at pressures of



(a) Oxygen atoms. (b) Nitrogen atoms.

Figure 3. - Effect of Tesla coil power on recombination energy transfer to test probe.



(a) Oxygen atom recombination. (b) Nitrogen atom recombination.

Figure 4. - Effect of Tesla coil power on test surface temperature.

1.7 and 2.5 millimeters of mercury (table IV). The Tesla discharge effect on calcium oxide and zinc oxide did not change much with increasing pressure. Calcium oxide changed from -9.1 to -10.0 percent, and zinc oxide changed from -15.6 to -16.5 percent. Both copper and copper oxide showed a greater effect by the Tesla discharge at the higher test pressure with copper varying from -9.7 to -14.5 percent and copper oxide varying from -12.3 to 18.4 percent. On the other hand, iron and iron oxide showed that the Tesla discharge had a greater effect at the lower pressure with -10.1 percent against -8.3 percent for iron and -14.6 percent against -12.2 percent for iron oxide. Sometimes the effect of the discharge leveled off at a low input power to the Tesla coil (5.0 w for a zinc surface and 10.0 w for a calcium oxide surface), and sometimes it continued to increase with increasing input power (e.g., iron and iron oxide, figs. 3(a) and 4(a)).

With nitrogen atoms, the Tesla coil discharge always showed a greater effect at the lower pressure (1.7 mm Hg) than at the higher pressure (2.5 mm Hg) (table IV). An increase in recombination heat transfer was caused by the Tesla discharge for nitrogen atoms at surfaces of zinc oxide and calcium oxide. However, as in the case for oxygen atoms, the Tesla discharge reduced the recombination of nitrogen atoms at surfaces of copper, copper oxide, iron, and iron oxide. The increase in recombination heat transfer for the calcium oxide and zinc oxide was, respectively, +3.5 and +6.4 percent at the lower test pressure and +2.1 and +2.4 percent at the higher test pressure. The greatest effect produced was the decrease in nitrogen atom recombination at a copper oxide surface, which was -43.7 percent at 1.7 millimeters of mercury and -23.0 percent at 2.5 millimeters of mercury. Rather large effects were also observed for surfaces of copper (-35.6 and 17.0 percent), iron (-39.3 and 19.8 percent), and iron oxide (-30.2 and -17.6 percent). A maximum effect of a Tesla discharge was observed for zinc oxide and calcium oxide when the input power to the Tesla coil was nearly at its maximum of 25 watts (fig. 3(b)). The curves for iron oxide, iron, copper, and copper oxide in figures 3(b) and 4(b) show that at the maximum Tesla input power of 25 watts the effect of the Tesla discharge has not leveled off.

To make sure these Tesla discharge effects were not false electrical effects, qualitative measurements were made at each of the test surfaces on the effect of the Tesla discharge in an undissociated gas. These measurements showed that the Tesla discharge itself always caused a slight heating of the test surface. Measurements with a time-of-flight mass spectrometer showed that a Tesla coil discharge increased the atom concentration of a dissociated oxygen or nitrogen stream by a factor of about 1.05. Consequently, the heating of the test surface caused by the Tesla discharge itself could be due to catalytic recombination at the surface.

To make the picture complete, qualitative measurements of the Tesla discharge effect were made on glass, and some measurements with hydrogen atoms were made on zinc oxide and copper oxide. The discharge had no effect on the glass measurements with either nitrogen or oxygen as the test gas. For the hydrogen atoms, both zinc oxide and copper oxide showed only a slight increase in heat transfer.

DISCUSSION OF RESULTS

The relative order of catalytic efficiency for oxygen atoms in the present results is copper oxide > iron oxide > germanium dioxide II > zinc oxide > calcium oxide > chromium oxide and germanium dioxide I (fig. 2(a) and table III). With the germanium oxide prepared from oxidized metallic germanium (germanium dioxide I), these results compare, on a relative basis, quite well with those of Greaves and Linnett (ref. 4). When absolute numbers are compared, however, the values of reference 4 are generally much lower than those presented here. Hoenig, in his atomic beam studies of oxygen atom recombination (ref. 13), finds that his measured recombination efficiencies are sometimes much higher than those of other investigators. In reference 4 the recombination coefficients determined by the side-arm method gave different results when a Wrede-Harteck gage measured the atom concentration than when a thermocouple was used. For example, magnesium oxide had a γ value that was increased by a factor of 8 using the Wrede-Harteck gage. On the other hand, γ for lead oxide showed a factor of 9 decrease with the Wrede-Harteck gage.

These differences in the measured value of recombination coefficients by the various investigators could be explained by the different experimental techniques. However, a more probable explanation is a difference in the actual surface tested. This surface variation is especially likely for vacuum-evaporated thin films (ref. 27). Reference 8 reports that a copper film 1 micron thick has a γ value three times that of a copper film 0.5 micron thick. In the present work, the thicker germanium dioxide II film (which, by the color of the film, appears to be the same oxide as germanium dioxide I) gave a γ that was orders of magnitude greater than that of germanium dioxide I.

Figure 2(b) shows that nitrogen atom recombination at oxide surfaces is not explained by Greaves and Linnett's mechanism of acidic and basic oxides. Neither does the position of the metal in the periodic table nor the filling of the d-shell explain these results. Only a general type mechanism including adsorption and desorption, as proposed in reference 9, seems appropriate.

The germanium dioxide II surface is much more catalytic than the germanium monoxide. Although the nitrogen atom γ was only determined for the two oxides of this one metal, these results do suggest a possible nitrogen-oxygen bond mechanism for adsorption of nitrogen atoms.

Most of the surfaces showed an increase with temperature in catalytic activity for nitrogen atom recombination (fig. 2(b). Other workers, in general, have also reported that the catalytic efficiencies of surfaces either increase with temperature or remain constant (refs. 8, 9, 10, and 12). The results for nitrogen atoms at two of the test surfaces and oxygen atoms at most of the test surfaces showed a decrease in γ with temperature (fig. 2). Most other investigators have not observed such a decrease in catalytic activity with increasing temperature. Reference 1 did observe this effect with a catalytic thermocouple probe. This effect was also observed in reference 12 with hydrogen at some of the surfaces tested; however, this effect was attributed to a change in the surface by poisoning of the surface or dissolving of the hydrogen by the surface.

The fact that the catalytic efficiencies of surfaces can increase, decrease, or remain constant with increasing temperature suggests that the overall effect of temperature on adsorption of atoms, desorption of atoms, and desorption of recombined molecules is the important factor. In other words, the temperature effect is not simply a direct effect on the rate of the recombination reaction itself.

The reduction in catalytic activity caused by a Tesla discharge (figs. 3 and 4) and the Tesla discharge effects on surface adsorption (refs. 18 and 19) further indicate the importance of adsorption and desorption on the recombination coefficient. The increase in recombination heat of nitrogen atoms at surfaces of zinc oxide or calcium oxide could be caused by the increased atom concentration. However, a decrease in the desorption rate of adsorbed atoms or an increase in the desorption rate of recombined molecules should not be ruled out.

If the adsorption results reported in reference 18 are considered, the qualitative results on the effect of a Tesla discharge on hydrogen recombination heat transfer at surfaces were not anticipated. One explanation could be that the Tesla discharge decreases the rate of desorption of recombined hydrogen without affecting the chemisorption kinetics of the hydrogen atoms.

From the Tesla discharge results, it seems possible that the nature of the discharge producing a dissociated gas for surface recombination studies can affect the results. At radio frequencies the spreading of the discharge indicates the existence of ions similar to those produced by a Tesla discharge. Since the frequencies of the discharges used by the various investigators are almost as numerous as the investigators, some of the discrepancies among the published results may be caused by this poorly understood and previously unrecognized variable.

CONCLUSIONS

Recombination coefficient measurements at the surface of some metallic oxides were determined for nitrogen and oxygen atoms. Also, the effect of a Tesla coil discharge on recombination heat transfer was determined. The following conclusions were reached:

1. Nitrogen atom recombination at oxide surfaces cannot be explained by an acidic - basic oxide mechanism successfully invoked for oxygen-atom recombination. Neither does the periodic table nor the filling of the d-shell for the transition metals explain the nitrogen atom results.

2. The recombination efficiency of a surface may increase, decrease, or remain constant with increasing temperature. The kinetics of the chemisorption processes will determine the temperature effect.

3. A Tesla coil discharge affects the number of atoms recombining at a surface. The degree and direction of this effect depend on the surface and type of atoms.

4. The thickness of an evaporated film of test material and the nature of the discharge producing the dissociated test gas are important in surface catalysis and may strongly influence measured recombination efficiencies.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, September 20, 1962

REFERENCES

1. Linnett, J. W., and Marsden, D. G. H.: The Kinetics of the Recombination of Oxygen Atoms at a Glass Surface. Proc. Roy. Soc. (London), ser. A, vol. 234, no. 1199, Mar. 6, 1956, pp. 489-504.

2. Linnett, J. W., Marsden, F. R. S., and Marsden, D. G. H.: The Recombination of Oxygen Atoms at Salt and Oxide Surfaces. Proc. Roy. Soc. (London), ser. A, vol. 234, no. 1199, Mar. 6, 1956, pp. 504-515.

3. Greaves, J. C., and Linnett, J. W.: The Recombination of Oxygen Atoms on Surfaces. Trans. Faraday Soc., pt. 9, vol. 54, no. 429, Sept. 1958, pp. 1323-1330.

4. Greaves, J. C., and Linnett, J. W.: The Recombination of Atoms at Surfaces. Pt. 5: Oxygen Atoms at Oxide Surfaces. Trans. Faraday Soc., pt. 8, vol. 55, no. 440, Aug. 1959, pp. 1346-1354.

5. Greaves, J. C., and Linnett, J. W.: The Recombination of Atoms at Surfaces. Pt. 6: Recombination of Oxygen Atoms on Silica from 20° C to 600° C. Trans. Faraday Soc., pt. 8, vol. 55, no. 440, Aug. 1959, pp. 1338-1362.

6. Green, M., Jennings, K. R., Linnett, J. W., and Schofield, D.: Recombination of Atoms at Surfaces. Pt. 7: Hydrogen Atoms at Silica and Other Similar Surfaces. TN 59-869, Office Sci. Res., Feb. 1960.

7. Prok, G. M.: Nitrogen Atom Recombination on Surfaces. Planetary and Space Sciences, vol. 3, 1961, pp. 38-45.

8. Prok, George M.: Effect of Surface Preparation and Gas Flow on Nitrogen Atom Surface Recombination. NASA TN D-1090, 1961.

9. Tsu, Kin, and Boudart, Michel: Molecular Problems in Heat and Mass Transfer: Recombination of Hydrogen Atoms on Glass. TN 60-1152, Office Sci. Res., 1960. (See also Ph.D. Thesis by K. Tsu, Princeton Univ., 1960.)

10. Wise, H., Ablow, C. M., and Wood, B. J.: Surface-Catalyzed Atom and Free-Radical Reactions. Semi-Annual Rep., Proj. Squid, Apr. 1960, p. 45.

11. Wise, H., Ablow, C. M., and Wood, B. J.: Surface-Catalyzed Atom and Free-Radical Reactions. Semi-Annual Rep., Proj. Squid, Oct. 1960, p. 29.

12. Wood, Bernard J., and Wise, Henry: Kinetics of Hydrogen Atom Recombination on Surface. Jour. Phys. Chem., vol. 65, no. 11, Nov. 1961, pp. 1976-1983.

13. Hoenig, S. A.: A Study of Oxygen Recombination on Metallic Surfaces by Means of an Atomic Beam. Tech. Rep. HE-150-173, Univ. Calif., Oct. 7, 1960.

14. Nakada, Kazuo: Recombination of Hydrogen Atoms on Various Transition Metal Surfaces. Bull. Chem. Soc. (Japan), vol. 32, no. 8, 1959, pp. 809-813.

15. Nakada, Kazuo: Recombination of Hydrogen, Nitrogen, and Oxygen Atoms on Copper and Silver Single-Crystal Surfaces. Bull. Chem. Soc. (Japan), vol. 32, no. 10, 1959, pp. 1072-1078.

16. Young, Robert A.: Pressure Dependence of the Absolute Catalytic Efficiency of Surfaces for Removal of Atomic Nitrogen. Jour. Chem. Phys., vol. 34, no. 4, Apr. 1961, pp. 1292-1294.

17. Low, M. J. D.: Kinetics of Chemisorption of Gases on Solids. Chem. Rev., vol. 60, no. 3, June 1960, pp. 267-312.

18. Low, Manfred J. D., and Taylor, H. Austin: Enhanced Surface Reactions. Jour. Electrochem. Soc., vol. 104, no. 7, July 1957, pp. 439-442.

19. Low, M. J. D.: Enhanced Surface Reactions. II. Oxygen Adsorption on Several Metals. Jour. Electrochem. Soc., vol. 105, no. 2, Feb. 1958, pp. 103-105.

20. Harteck, Paul, Reeves, Robert R., and Mannella, Gene: Rates of Recombination of Nitrogen Atoms. Jour. Chem. Phys., vol. 29, no. 3, Sept. 1958, pp. 608-610.

21. Kaufman, F., and Kelso, J.: Reactions of Atomic Oxygen and Atomic Nitrogen with Oxides of Nitrogen. Seventh Symposium (International) on Combustion, Butterworths Sci. Pub., 1959, pp. 53-56.

22. Gray, P., and Yoffee, A. D.: The Reactivity and Structure of Nitrogen Dioxide. Chem. Rev., vol. 55, 1955, pp. 1069-1154.

23. Ranz, W. E., and Marshall, W. R., Jr.: Evaporation from Drops, pt. II. Chem. Eng. Prog., vol. 48, no. 4, Apr. 1952, pp. 173-180.

24. Brokaw, Richard S.: Alignment Charts for Transport Properties, Viscosity, Thermal Conductivity, and Diffusion Coefficients for Nonpolar Gases and Gas Mixtures at Low Density. NASA TR R-81, 1961.

25. Foner, S. N., and Hudson, R. L.: Metastable Oxygen Molecules Produced by Electrical Discharges. Jour. Chem. Phys., vol. 25, no. 3, Sept. 1956, pp. 601-602.

26. Rosner, D. E.: The Theory of Differential Catalytic Probes for the Determination of Atom Concentrations in High Speed, Nonequilibrium Streams of Partially Dissociated Gases. Tech. Pub. 19, AeroChem Res. Labs., Inc., Oct. 1960.

27. Schmitt, R. W.: Thin Films. Science and Tech., no. 2, Feb. 1962, pp. 42-48.

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