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PHOTODESORPTION OF OXYGEN FROM NICKEL OXIDE POWDER

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SUMMARY

The photodesorption of oxygen from nickel oxide was studied at room temperature using 635, 705, and 1070 millimicron light. These wavelengths produced photodesorption similar to that of white light. First-order and logarithmic sorption processes are demonstrated to occur during illumination. The rate of logarithmic uptake kinetics, normally measured in the dark, appears to increase during illumination. Sorption kinetics after light cessation are first order with the rate constants k_A = 1.4 per minute and k_D = 1.1 per minute. Pretreatment of the nickel oxide surface with infrared light decreases the rate of oxygen uptake, presumably by decreasing the number of activated adsorption centers.

INTRODUCTION

The desorption of gases sorbed on semiconductor surfaces can be accomplished in several ways and has been the subject of many investigations. The general subject has been reviewed by Ehrlich (ref. 1). The use of incident light is one of the various techniques utilized to study the removal of gases from surfaces. The use of light to produce a desorption effect is a complex process (ref. 2). A complete understanding of the mechanisms involved requires additional experimental observations and theoretical interpretation. Rosenberg and Martel (ref. 3), Kotel'nikov (ref. 4), and Jogepier and Schuit (ref. 5) maintain that the photodesorption effect is caused by heating. Stone (ref. 2) and others suggest that desorption is caused by the absorption of light. If a heating effect is responsible for photodesorption, the disposition of the absorbed energy by radiative and/or nonradiative mechanisms can be an important factor which determines more or less the magnitude of the sorbent surface temperature and thus the degree to which thermal energy can cause desorption. At this time, a satisfactory differentiation between

a true photoeffect and a heat effect is yet to be made.

Of the many systems available for study, the photoeffects involving gaseous oxygen (O_2) on nickel oxide (NiO) were of particular interest and could be compared with some previous work. In particular, the suggestion made by Haber and Stone (ref. 6) that desorption of O_2 from NiO surfaces occurred when the surface was exposed to optical energies equivalent to the specific absorption energies found in NiO needed clarification. While these authors showed that enhanced desorption occurred for the band of wavelengths between 650 and 900 millimicrons, they did not report specifically on the desorption effects of the individual wavelengths deemed responsible for the effect. One of the purposes of this report is to clarify this point by presenting the results of an investigation of the "photodesorption" observed for the O_2-NiO system when specific wavelengths were used as optical stimulation.

In the dark, the uptake of O_2 by NiO follows logarithmic kinetics (ref. 6); this process does not change noticeably in normal room light. When more intense light is applied to the nickel oxide surface, first-order desorption kinetic reactions are obtained. Both of these results have been verified. The study of the kinetics has been extended, and it is shown herein that a logarithmic kinetics is operating during steady-state illumination and that first-order adsorption kinetic reactions follow light cessation.

EXPERIMENTAL APPARATUS AND PROCEDURE

Sorption measurements were performed using an apparatus (fig. 1) similar to the one described by Haber and Stone (ref. 6). The experiment consisted of measuring the change in oxygen pressure caused by adsorption or desorption over a sample of NiO powder before, during, and after exposure of the sorbent surface to light.

Reagent-grade polycrystalline NiO (black, approximately 99.85% pure) was obtained from a commercial source. A 1-gram sample was conditioned prior to each experiment by being heated in a vacuum of 2×10^{-5} torr (2.7 mN/m^2) for 6 hours at 450° C. Prior to the bakeout, the sample was heated in O_2 to the bakeout temperature. This conditioning procedure gave reproducible kinetics.

Pressure measurements were made using a Pirani gage, the output of which was recorded. Pressures were measured to 0.1 micron.

The light source was a 750/1000-watt quartz, tungsten iodine lamp (ref. 7). For most experiments, the light passed through 20 millimeters of water, which acted as a major heat filter and limited the white-light radiation applied to the NiO to wavelengths less than approximately 1.2 microns. An additional glass heat filter was placed nearer the sample on occasion to decrease the wavelength region even further. Provision was made for various Wratten, gelatin-type filters (prefix W) to be placed in the light beam.

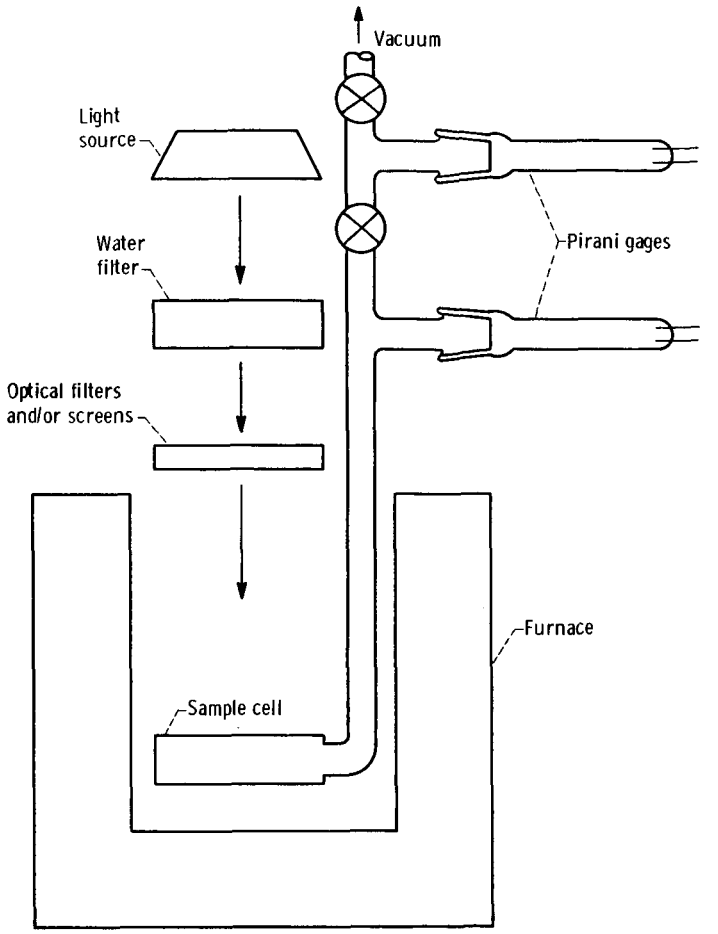
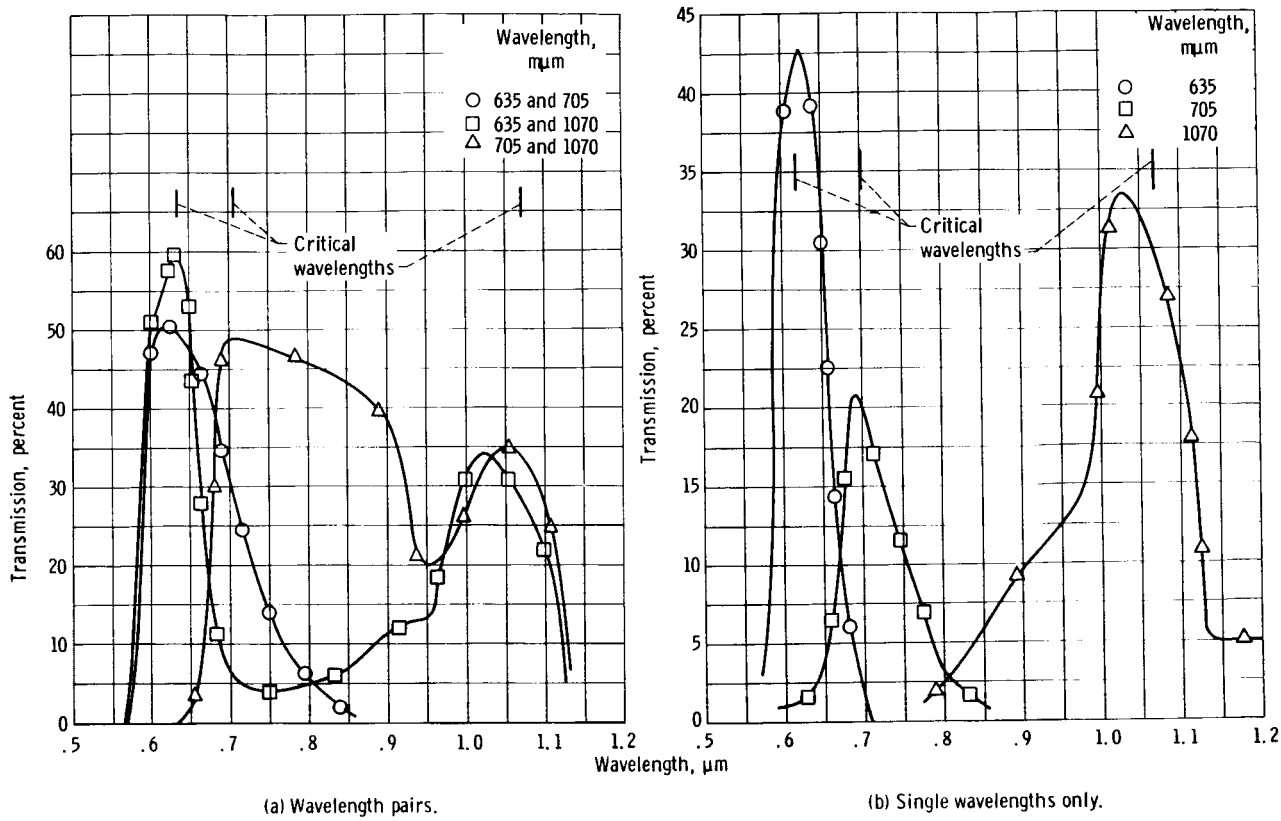


Figure 1. - Apparatus for photodesorption studies.

(Narrow band-pass interference filters did not give high enough intensity to be useful.) Several Wratten filters were usually combined to give compound filters that passed light at bands which included the proposed active wavelength region (NiO absorptions of 635, 705, and 1070 mμm (ref. 8)). The optical transmission properties of these filters (measured through water and quartz) are illustrated in figure 2. The intensity of the white light was about 75 milliwatts per square centimeter. Exposure of the NiO to illumination was accomplished through a photographic shutter and was used to minimize tailing of the light intensity. Intensities were measured with a calibrated thermopile and were changed by using wire screen grids.

When O_2 was admitted to a "clean" (heat-vacuum conditioned) NiO surface in the dark, an extremely rapid a adsorption occurred. This process was too rapid to be measured and identified in the present system. This behavior has been observed in other systems (ref. 9) and by Dell (ref. 10) for NiO. Logarithmic adsorption kinetics (ref. 11) was observable almost immediately (ref. 10) and indicated that the initial uptake process had rapidly subsided.



(a) Wavelength pairs.

(b) Single wavelengths only.

Figure 2. - Filter transmissions used to isolate specific wavelengths.

When the surface was subsequently illuminated with white light, the pressure in the system rose as oxygen was desorbed. After cessation of illumination when a steady-state condition had been achieved, additional adsorption kinetic reactions (first order) were observed. The total duration of this sorption process was at least 30 minutes at room temperature and, in general, was measured at pressures between 30 and 50 microns. By switching the illumination on and off, similar kinetic reactions were observed for many cycles. After several days, the maximum pressure difference observed with illumination decreased. After several weeks, the photodesorption effect became virtually constant but still indicated labile oxygen on the surface; the total pressure of the system steadily decreased toward an equilibrium.

RESULTS AND DISCUSSION

That light causes some change in the surface properties of the NiO sorbent is quite evident. If the surface condition present during and immediately after illumination were present prior to the initial sorption, the sorption kinetics, apparent immediately after light cessation, should have been observed. Since it was not, illumination must somehow alter the surface properties of the oxide. At this stage in the study, it cannot

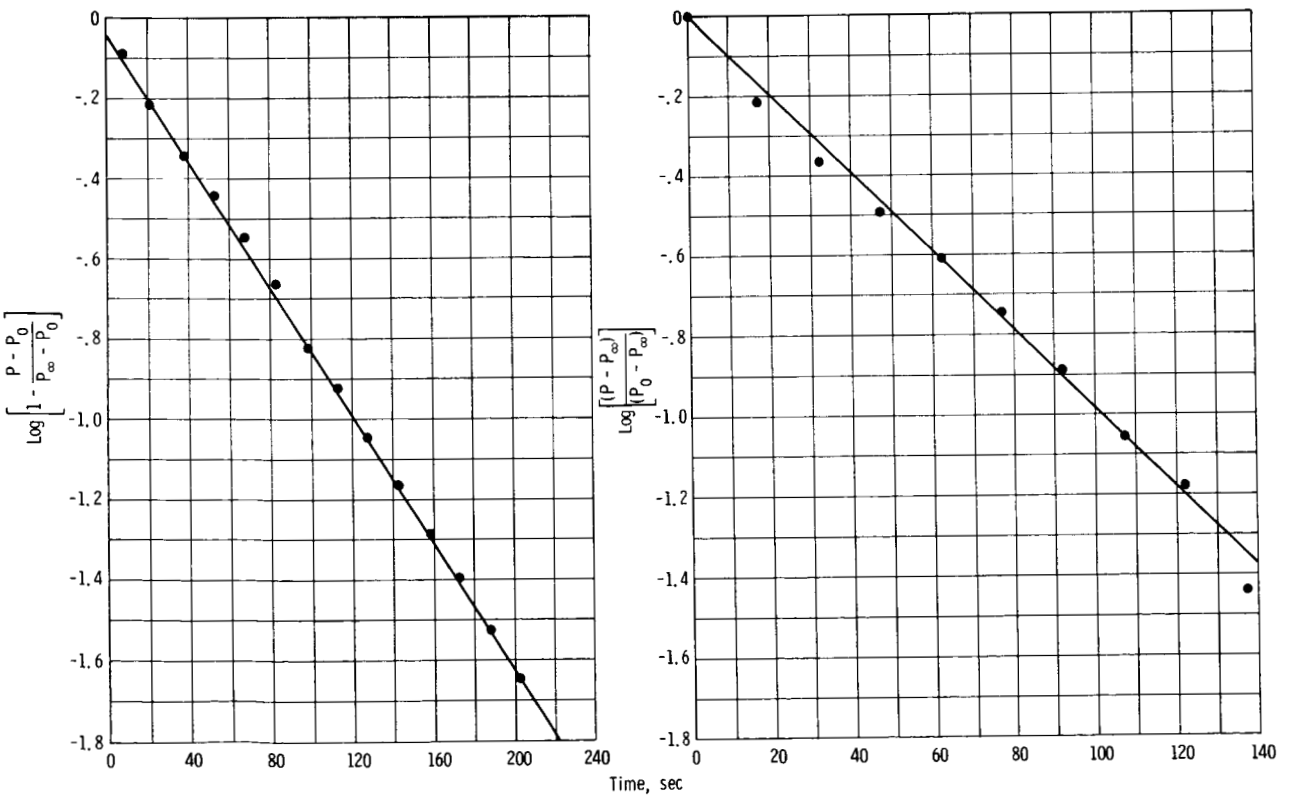
be said, however, that the rapid initial uptake (dark) and the uptake after light cessation are not the same process. It is not likely that light in the energy regions studied herein would be absorbed directly by the O_2 molecule. Consequently, the following discussion is limited primarily to properties of the solid.

The results of this study indicate that the total sorption process of O_2 on NiO is the sum of at least two and possibly more processes (i.e., a slow logarithmic and a fast first-order process.) A dual sorption process for the sorption of O_2 on NiO has been suggested by Charmen, et al. (ref. 10). At least one of these processes can be described by logarithmic (Elovich) kinetics (ref. 11) according to the equation

$$\frac{dq}{dt} = ae^{-\alpha q}$$

where q is the uptake, and a and α are constants. The photodesorption process has been shown to be first order (ref. 4). Little is known about the kinetics of the sorption process observed immediately after light cessation except that it appears to be first order also. These first-order processes can be described by

$$P_\infty - P = (P_\infty - P_0)e^{-k_D t} \quad \text{(Photodesorption)} \tag{1}$$



(a) During illumination with white light; rate constant, k_D, 1.10 per minute.

(b) After light cessation; rate constant, k_A, 1.36 per minute.

Figure 3. - Typical photodesorption.

and

$$P - P_\infty = (P_0 - P_\infty)e^{-k_A t} \quad \text{(Sorption)} \tag{2}$$

where P is the pressure at time t, P_0 and P_∞ are the initial and final pressures, respectively, and k_A and k_D are rate constants. A typical photodesorption using white light and subsequent dark sorption is illustrated in figure 3. The rate constants for these processes are k_D, 1.10 per minute, and k_A, 1.36 per minute, about twice the values reported in reference 6. The fact that these two values are nearly the same suggests that photodesorption and subsequent sorption (light off) may require approximately the same activation energy and, therefore, may involve only a single site species.

Haber and Stone (ref. 6) offer an explanation of the observed kinetics of photodesorption and adsorption rates, that is,

$$\left(\frac{dP}{dt}\right)_{obs} = \left(\frac{dP}{dt}\right)_D + \left(\frac{dP}{dt}\right)_A \tag{3}$$

They further assume that the desorption rate is proportional to the number of quanta absorbed I_{obs}

$$\left(\frac{dP}{dt}\right)_D = k_D I_{obs} \tag{4}$$

and that the adsorption rate is proportional to the displacement from the initial coverage that has taken place

$$-\left(\frac{dP}{dt}\right)_A = k_A(P - P_0) \tag{5}$$

After integration and the application of steady-state conditions, Haber and Stone's equation describing photodesorption is

$$\ln (P_\infty - P) = -k_A t + \text{constant} \tag{6}$$

This expression is the same as the empirical relation found in the present study for photodesorption, if k_A is substituted for k_D in equation (1). The near equivalence of k_A and k_D in the preceding equation suggests that Haber and Stone's assumption of a first-order adsorption process (during illumination) is probably correct. Furthermore,

because of the identity of k_A and k_D as proposed by Haber and Stone and found in this study, it probably can be assumed that the first-order sorption process occurring after light cessation is the same as the competing sorption process occurring during illumination.

Wavelength Dependency of Photodesorption

Haber and Stone suggest that the photodesorption of O_2 from NiO is correlated with the internal absorption of NiO. In particular, the wavelengths 635, 705, and 1070 millimicrons were considered to be effective. The effect of these wavelengths of light on the photodesorption of O_2 from NiO was investigated in more detail than in the study presented by Haber and Stone. The measurements were carried out at room temperature. White light (water filtered) was used as a standard measure of the photodesorption capacity of the system. The maximum desorption pressure ΔP_m for maximum light intensity I_m was measured and also the desorption pressures ΔP for lesser light intensities I. Figure 4 is a plot of such data for the NiO - O_2 system. The solid data points and the curve represent $\ln \Delta P/\Delta P_m$ as a function of I/I_m for white light.

After exposure of the nickel oxide surface to the specific wavelengths in the presence of O_2, the following observations were made. The wavelengths 635, 705, and

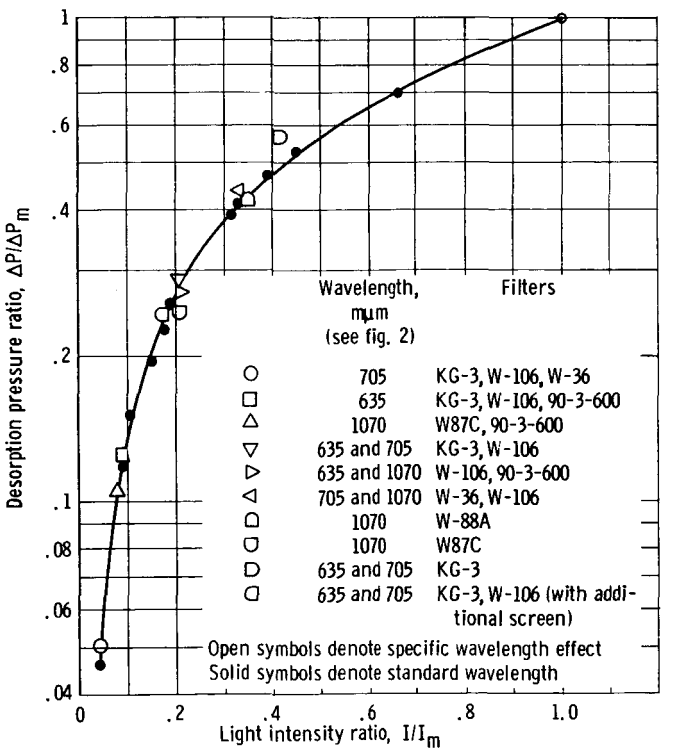


Figure 4. - Effect of various wavelengths of light on desorption of gaseous oxygen from nickel oxide.

TABLE I. - MEASURE OF EFFICIENCY OF VARIOUS

WAVELENGTHS USED INDEPENDENTLY

Wavelength, mμm	Power, mW/cm^2	Pressure units	Ratio of pressure units to power in
705	3.1	1.1	0.4
635	6.7	2.7	.4
1070	6.0	2.4	.4

1070 millimicrons (and their combinations) produced the same degree of photodesorption as white light. The same conclusion can be drawn when these wavelgnths are compared to each other (table I). This result indicates that, while there is little doubt that these wavelengths are effective in producing photodesorption, desorption may not be dependent on the direct absorption of these wavelengths by the sorbed species. A somewhat similar conclusion was made by Kotel'nikov (ref. 4), who used rather broad optical regions, and by Jogepier and Schuit (ref. 5), who examined wavelengths less than 635 millimicrons.

Many photoexcited processes are caused not by the primary radiation applied (ref. 12) but by the radiation emitted when an excited state is deactivated. Two energy schemes (fig. 5) can be constructed to account for the photodesorption either as a heat

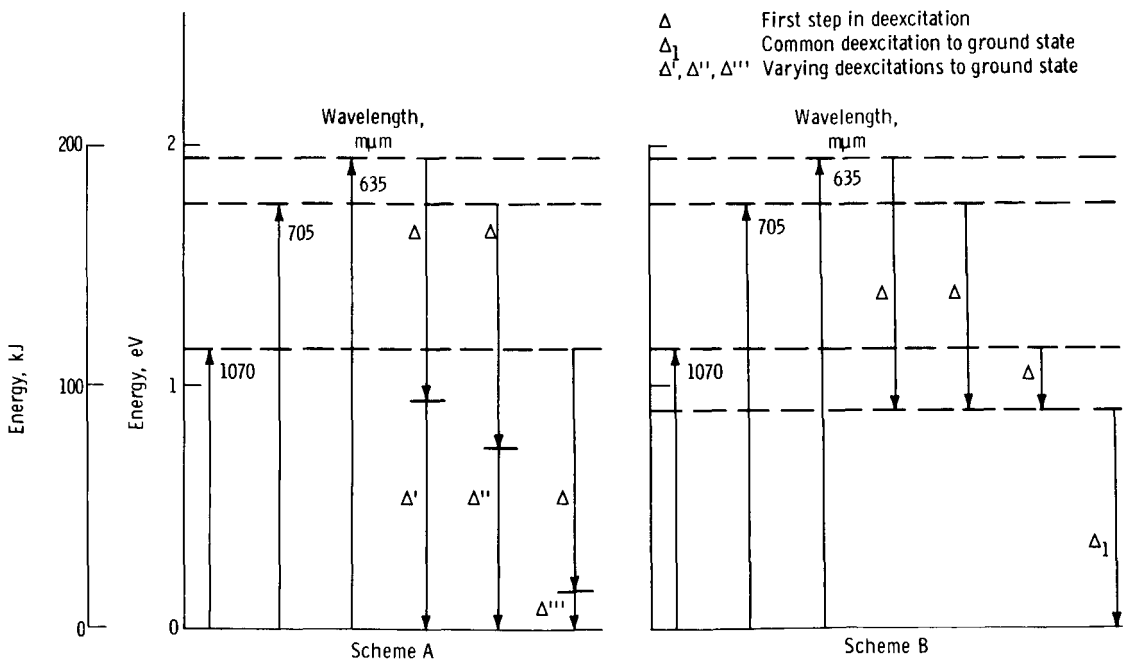


Figure 5. - Energy schemes showing possible decay paths which could result in photoexcitation or thermal excitation.

effect or a true photoeffect. Scheme A illustrates the case where the first energy step in the deexcitation is equivalent for each of the excited states (all Δ are equal); scheme B illustrates the case where all excited states decay to a common excited state and then have a common deexcitation Δ_1 to the ground state. In these cases, Δ and Δ_1 are the energies responsible for the desorption of O_2. The values of Δ and Δ_1 are arbitrary, and since they could be radiative and/or nonradiative transitions, the question of a thermal effect or a photoeffect can not be settled. Emission studies of NiO may provide significant information in this respect. At this time scheme B is more appealing since scheme A implies that additional absorptions, of less than 1 electron volt (96 kJ), might be observed for Δ, Δ' and Δ''. These absorptions have not been observed.

Scheme B provides a more reasonable approach. All excited states might be close to the ground state, and, therefore, the value of Δ_1 could be small. Newman and Cherenko (ref. 8), using reflection methods, observed a surface absorption at about 0.08 electron volt (7.7 kJ or $\sim 15 \mu m$), which might be related to the adsorption process. The value 0.08 electron volt (1.8 kcal or 7.7 kJ) is also in the appropriate range for adsorption activation energies. An alternate explanation of the apparent lack of specific wavelength dependency could be that the optical energies applied are all in excess of the threshold energy needed to dissociate an oxygen complex from the surface.

Light and Logarithmic Kinetics

Haber and Stone rule out a heat effect by demonstrating that illumination during the early stages of dark adsorption does not produce an increased adsorption. An increase in adsorption rate would be expected from the Elovich kinetics if an increase in temperature were present. On the other hand, Kotel'nikov (ref. 4), using a similar procedure, demonstrates that a pressure reversal does occur. The reversal occurs at longer elapsed times than those used in the study by Haber and Stone.

A pressure reversal was observed in the present study and was somewhat similar to the one observed by Kotel'nikov. If white-light illumination was permitted to continue for times exceeding that necessary to produce steady-state values of the desorption pressure, the pressure of the system began to decrease with time. These data were plotted and were found to follow Elovich kinetics, as illustrated in figure 6. Immediately after light cessation first-order kinetics reactions were observed. At long times after light cessation, the uptake kinetics reactions again were logarithmic, but the slope of the plot was not exactly equivalent to that of the early time data (fig. 7, dashed curve), which shows the dark system and indicates that a change in slope is to be expected at long times. A comparison of the slopes of the Elovich plots under the two conditions of illumination suggests that during illumination the rate of uptake was more rapid than when the light was absent.

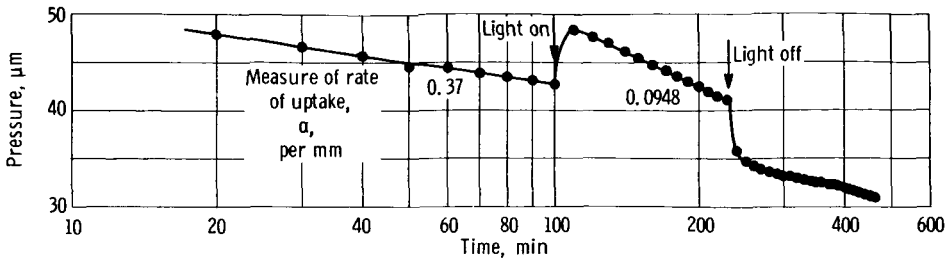


Figure 6. - Effect of illumination on Elovich rate of uptake.

Considering α as some measure of the rate of uptake and comparing the room-temperature ratio of α for light off to α for light on with the values of α for heating obtained by Haber and Stone (ref. 6) at room temperature, it is indicated that a proportional decrease in α for heating corresponds to an increase in the temperature of the surface of approximately 150° C.

A separate experiment was conducted to determine the heating effect of the light on the sample. A thermocouple placed in the NiO under illumination showed only a 4° to 5° C increase in temperature, comparable in magnitude to other observations made on zinc oxide (ref. 13). This small increase in temperature seems to eliminate the possibility of a heat effect. However, the value of Δ or Δ_1 could be small and could produce a relatively small increase in temperature.

Effect of Pretreatment on Logarithmic Kinetics

Several additional experiments were conducted to observe the effect of various pretreatments on the dark kinetics. In all cases, the oxide was heated in vacuum to 450° C and cooled overnight in vacuum in the dark to obtain a reproducible surface before any treatment was attempted. The pressure decreases observed as a function of log t are illustrated in figure 7. The dark kinetic reaction of an experiment, prior to which the sample was simply heat-vacuum conditioned and cooled in the dark, is shown as the dashed curve. A deviation in the curve is noted at about 150 minutes. From approximately 1500 minutes to about 9000 minutes the curve is linear and slope increases. The break in the curve was not observed by Haber and Stone, whose experiments were limited to about 15 minutes. The break in the curve is possibly indicated at higher temperatures in the work performed by Charmen, Dell, and Teale (ref. 10).

In a second experiment, the sample was conditioned and kept in the dark in vacuum for 1 week before sorption was attempted. This experiment was performed to determine if the activity of the surface decreased spontaneously. This treatment produced only a slight decrease, if any change, in the uptake characteristics and can be represented also by the dashed curve in figure 7.

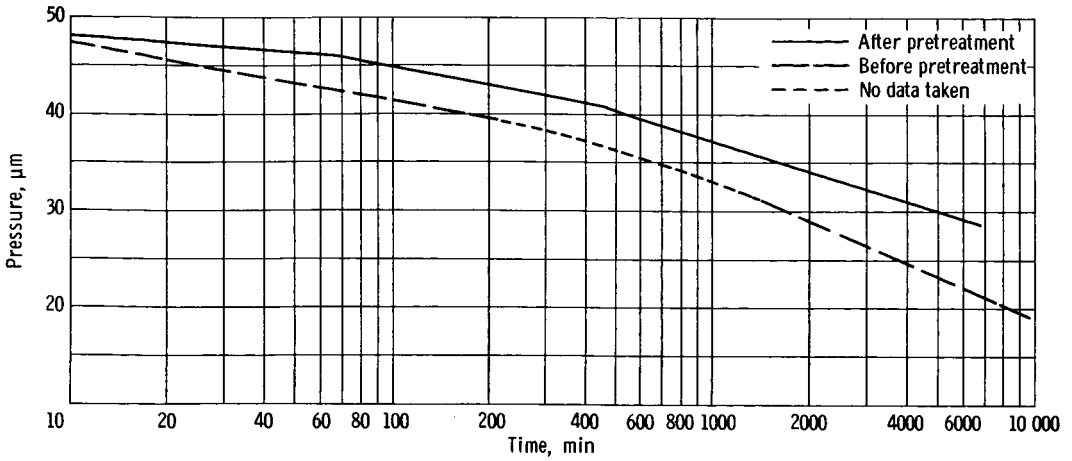


Figure 7. - Effect on dark kinetics before and after pretreatment with infrared.

A third experiment was conducted during which the sample was exposed directly (no water filter) for several hours in vacuum to the radiations from an infrared heat lamp and was returned to the dark after illumination. Subsequent sorption of O_2 several hours later, when the sample had cooled showed a dramatic change in the uptake kinetic reactions, illustrated by the solid curve of figure 7. This curve, obtained after radiation, is considerably flatter up to about 70 minutes. After 70 minutes, the slope parallels the slope of the original dark-sorption curve at early times and then increases again. The slope of the final segment, however, is flatter than the standard (dashed) curve. A similar curve was obtained if the sample was illuminated with light from filter W87 (wavelength > 900 mμm). Such a qualitative experiment demonstrates that the surface sites can be adversely affected by optical radiation prior to sorption, and that such treatment can effect the rate of subsequent uptake kinetics, most probably by altering the concentration of active sites. The effect of the light pretreatment is that which one would expect to observe if the sites were electrons located in surface traps. A similar experiment using white-light illumination produced no change in the uptake kinetics.

The preceding results indicate that a large heat effect is not present during illumination. The increase in rate of the Elovich kinetics is not definitive proof that thermal energy is involved. The increase in rate could be caused by an increase in the trapped electron population due to illumination. If such a slight increase in temperature as was found experimentally is indicative of the surface temperature, a true photodesorption effect is indicated.

It is obvious from the experiments that, during illumination, photosorption and photodesorption occur simultaneously. This effect is demonstrated by the observation that, when the illumination is turned on initially, the pressure increases and approaches a steady state (oxygen is desorbed). Sorption is indicated by the simultaneous increase in the rate of the Elovich kinetics during illumination. Such evidence seems to support

a hypothesis of two different sorption mechanisms which operate on the surface of NiO at one or more types of sites.

CONCLUSIONS

The following conclusions were drawn from this experiment on the photodesorption of oxygen from nickel oxide powder:

1. The assumption by Haber and Stone of a pseudo-first-order adsorption process during illumination is correct. As they predicted, the measured values of the rate constants k_A and k_D are reasonably close. The value of k_A, therefore, can be obtained by measuring the uptake kinetics after light cessation.

2. When compared with white light of the same intensity, the wavelengths 635, 705, and 1070 millimicrons, used in combination and/or separately, produce photodesorption similar to that of white light. The efficiency of the process is the same as that found by Jogepier and Schuit for wavelengths less than 635 millimicrons.

3. The rate of logarithmic uptake of gaseous oxygen by nickel oxide is changed by the application of white light. Since the temperature does not increase appreciably during illumination, the apparently increased rate may be caused by an increase in the concentration of active sites.

4. The pretreatment of a nickel oxide surface with infrared light decreases the rate of oxygen uptake, presumably by decreasing the number of active centers. This deactivation might be caused by the emptying of electrons from surface-trapped sites to the bulk of the solid.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, June 7, 1967,
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