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# PHOTORESPONSES FOR THE OXYGEN ADSORBED ON ZINC OXIDE POWDER

By

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The effect of light-irradiation on the oxygen adsorbed on zinc oxide powder samples was investigated with lights having wave lengths near fundamental absorption of zinc oxide. Photodesorption of oxygen was found to occur on the outgassed sample whereas the photoresponse turned out to be an irreversible sorption on the oxidized sample. Initial rates of these photoresponses were determined against light intensity, oxygen pressure and temperature.

The pressure-temperature relation of oxygen in contact with zinc oxide was investigated without light by raising the temperature of the adsorption vessel from room temperature to 300°C at a constant rate. A distinct maximum appeared in the plot of  $p$  against  $T$  in the temperature range 150°~200°C particularly on the outgassed zinc oxide. From the shape of the  $p$ ~ $T$  curve as well as other informations available it was thought that dissociative chemisorption of oxygen may appear near and above the maximum temperature or that some weakly chemisorbed oxygen presumably of molecular form may be present as an adsorption intermediate on the surface below the maximum temperature, *i. e.*, the temperature range where the photodesorption has actually been observed.

Photodesorption or photoadsorption phenomenon was discussed as the reaction of such an adsorbed intermediate with either electron or positive hole injected in zinc oxide on illumination. The role of adsorbed oxygen in the electrical conductivity as well as in the photoconductivity of zinc oxide was also discussed.

## Introduction

Photosensitized oxidation reaction on metallic oxides or sulfides has been increasingly investigated from the point of fundamental interest as well as from industrial requirement during the recent years. It has thus become known<sup>1)</sup> that the formation of hydrogen peroxide from oxygen and water is remarkably accelerated by zinc oxide when irradiated by light. The oxidation of carbon monoxide by cuprous

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1) M. C. MARKHAM and K. J. LAIDLER, *J. Phys. Chem.* **57**, 363 (1953); J. R. RUBIN, J. G. CALVERT, G. T. RANKIN and W. M. MACNEVIN, *J. Am. Chem. Soc.* **75**, 2850 (1953); J. G. CALVERT, K. THEURER, G. T. RANKIN and W. M. MACNEVIN, *J. Am. Chem. Soc.* **76**, 2575 (1954); R. E. STEPHENS, B. KE and D. TRIVICH, *J. Phys. Chem.* **59**, 966 (1955).

oxide shows similar photosensitization<sup>2)</sup>. On the other hand, these oxides and sulfides have been known to be photoconductive semiconductors and the rise in photoconductivity or its decay of these semiconductors has been extensively investigated<sup>3)</sup> by physicists.

Unfortunately there is great gap of knowledge yet between these two photoresponses, *i.e.*, photocatalysis and photoconductivity, or there still remains a question of interest in how these two phenomena should correlate each other. To bridge the gap it seems desirable to investigate at least the photoresponse for the gases adsorbed on these materials since any kind of photoresponse revealed in the adsorbed phase may be reflected also in the surface reaction in which the gases participate, hence giving rise to photocatalytic reaction. On the other hand, there are some investigations which show that photoconductivity of semiconductors is not independent on the ambient gas<sup>4)</sup>, in other words, photoconductivity could be understood only insufficiently without knowledge of photoresponse which might occur simultaneously in the adsorbed phase.

The purpose of the present paper is to show the effect of light irradiation in particular on the oxygen adsorbed on zinc oxide. Some of the features reached are as follows. There is a very considerable difference between the photoresponse on reduced zinc oxide sample on one hand and that on oxidized sample on the other, which might be interpreted partly by the current electronic theory of semiconductors. Photoresponses on these samples appear to depend on the past history for illumination so that a fresh portion of the surface was needed to expose in every measurement to obtain reproducible photoresponse. In conjunction with these results, photocatalysis works were undertaken using the oxide as catalyst, which will be reported separately.

### Experimental

**Materials:** Zinc oxide was prepared by igniting basic zinc carbonate precipitated from a mixture of zinc nitrate and ammonium carbonate solution at about 500°C in air. Spectroscopic purity of zinc oxide was

2) W. M. RITCHEY and J. G. CALVERT, *J. Phys. Chem.* **60**, 1465 (1956).

3) T. S. MOSS, *Optical Properties of Semiconductors*, p. 201 (1959), Butterworths Scientific Publications, London.

4) D. A. MELNICK, *J. Chem. Phys.* **26**, 1136 (1957); R. H. BUBE, *J. Chem. Phys.* **21**, 1409 (1953); R. H. BUBE, *Phys. Rev.* **83**, 393 (1951); W. MUSCHIED, *Ann. Physik* **13**, 305, 322 (1953).

99.9%, main impurity being iron. Its B.E.T. surface area, measured by nitrogen adsorption at liquid nitrogen temperature, was 6.2m<sup>2</sup> per gram. A 0.28 g. sample of the oxide was placed in the adsorption vessel of Pyrex glass and outgassed or oxidized prior to adsorption measurements. Oxygen was prepared by heating potassium permanganate in vacuum and purified by repeated distillations. Other gases used in the experiment were prepared by the generally accepted procedure.

Apparatus: As shown in Fig. 1, the apparatus was consisted of adsorption vessel, gas reservoir, McLEOD gauge and vacuum pump, each being connected by the greaseless cock or mercury seal. The adsorption

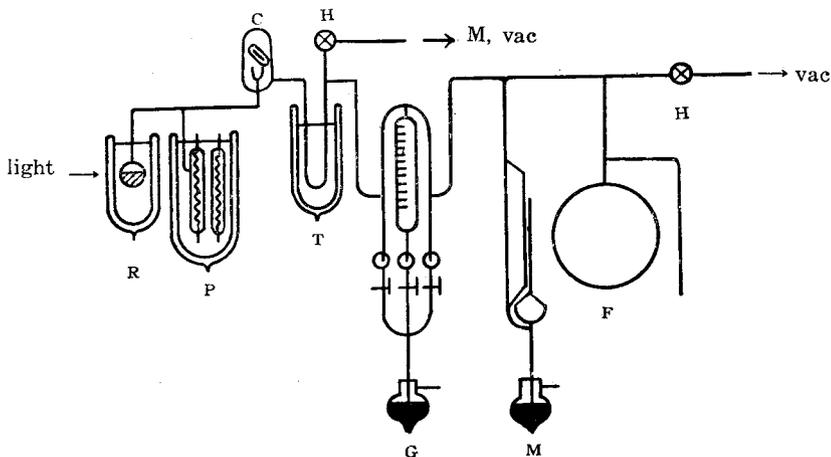


Fig. 1. Apparatus for the measurement of photoadsorption or photodesorption.

R: Adsorption vessel. C: Greaseless cock. P: PIRANI gauge.  
 G: Mercury gas burette. T: Liquid nitrogen trap.  
 H: Mercury cut off. M: McLEOD gauge. F: Gas reservoir.

vessel was accompanied by a PIRANI gauge and a gas burette by which gases were introduced. The volume of the adsorption vessel including PIRANI gauge was about 40 cc. The sensitivity of PIRANI gauge was  $1 \times 10^{-6}$  mm Hg/div. for oxygen. Zero point shift was occasionally checked and, if necessary, revised on the basis of McLEOD gauge.

The light from Mazda Super High Mercury Lamp, SHL 100 UV (100 W), was employed to illuminate zinc oxide sample. About ten minutes were required for aging the lamp *i.e.*, to reach steady intensity. The intensity of light was varied in some experiments by inserting

one or two blackened copper nets into the light path. The transmission coefficient of the net was beforehand determined as 37.5% per unit. In most experiments we used a combination of Mazda glass filter VC1B and copper sulfate solution (100 g  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}/\text{l}$ ) in 5 cm diameter quartz flask to remove the light of long wave lengths in the absence of copper net. It was confirmed in advance that the glass filter cut off the light of wave length shorter than 3300 Å and the solution does the visible and infrared light longer than 6000 Å, and that the light having wave lengths between 3600 Å and 4350 Å was filtered through by this combination of the filters.

Procedure: Zinc oxide sample placed in the adsorption vessel was outgassed at 300°C and a small portion of oxygen was introduced from the gas burette into the vessel kept at a desired temperature. When the adsorption of oxygen was nearly completed, the greaseless cock was closed to isolate the adsorption vessel and the irradiation of light onto the vessel was made through the above mentioned filters and then in most cases through the window of the Dewar vessel working as thermostat. The change of pressure inside the vessel was followed by the PIRANI gauge every 15 seconds. The working pressure was within  $10^{-4}$ — $10^{-3}$  mm Hg.

Outgassed zinc oxide sample was sometimes subjected to oxidation treatment under 10 mm Hg oxygen at 300°C. The measurement of photoresponse with this oxidized zinc oxide was made in the following way. The temperature of the vessel was allowed to cool down to room temperature in this atmosphere of oxygen, and a portion of oxygen was admitted on the zinc oxide sample evacuated to  $10^{-5}$  mm Hg. The measurement of photoresponse was then made similarly as above.

## Experimental Result

### *Photodesorption of oxygen*

Preliminary experiment indicated that the pretreatment of zinc oxide gives rise to somewhat divergent photoresponses. Standard procedure for the pretreatment of the sample was therefore needed to determine any kind of photoresponse. The following procedure was adopted. The zinc oxide sample was first outgassed at 300°C for one hour, and then oxygen was introduced into the vessel kept at room temperature. Adsorption equilibrium was nearly completed within ten minutes at this temperature, equilibrium pressure being about

$10^{-4}$  mm Hg. Irradiation of light without filters caused immediate desorption of oxygen from the surface. Spectral response was then investigated for the photodesorption. Light having wave lengths near  $5500 \text{ \AA}$  gave very faint photodesorption and the one longer than this gave no response. Desorption of oxygen was fairly quick on illumination of the light having wave length  $3650\text{--}4350 \text{ \AA}$  *i.e.*, the light near the fundamental absorption of zinc oxide<sup>5</sup>.

A typical result of photodesorption of oxygen on the outgassed zinc oxide is shown in Fig. 2 which was obtained at room temperature on illumination of the light  $3650\text{--}4350 \text{ \AA}$ . As shown in Fig 2, quick desorption of oxygen took place followed by a slower process. Photo-stationary state was attained within ten or more minutes.

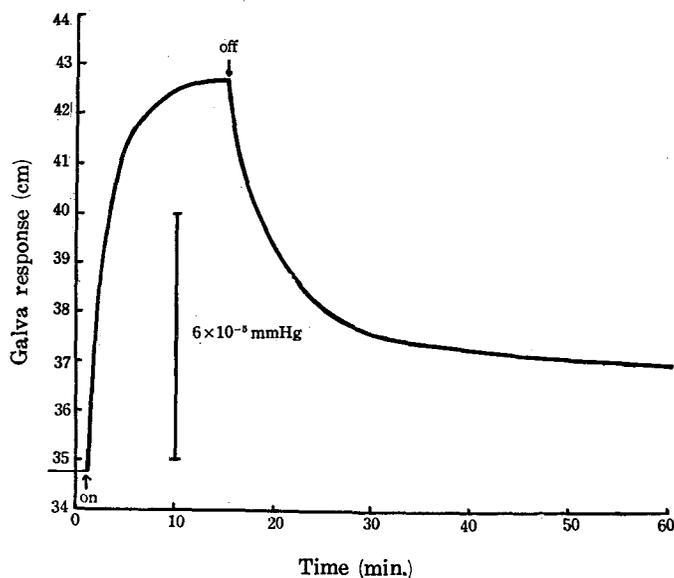


Fig. 2. Photodesorption of oxygen.  $T$ :  $18.2^{\circ}\text{C}$ . Oxygen pressure before illumination:  $4 \times 10^{-4}$  mm Hg.

When the light was shut off, the adsorption of oxygen occurred immediately but soon slowing down. Thus, far beyond the period of the preceding illumination, the pressure of oxygen was never attainable to the original value, *i.e.*, the pressure before illumination. Thus, the adsorption-desorption of oxygen was fairly reversible but not entirely.

Repeated illuminations of zinc oxide were found to decrease the

5) E. SCHAROWSKY, Z. Physik 135, 318 (1953).

initial rate of photodesorption as well as the pressure increment of the photostationary state. However, reproducible photodesorption rate was obtained when the reaction vessel was vibrated, in the absence of illumination, by knocking slightly the tube connecting the adsorption vessel. The phenomenon may suggest that the illuminated surface of the sample was actually a very small portion of the whole sample and that by the every slight shake of the vessel virgin surface was brought into exposure to the light. The observation of photodesorption in this way gave almost reproducible rate data with respect to the given zinc oxide sample. Kinetic investigation of this phenomenon, as will be shown later, was carried out always in this manner. The sample, which was outgassed at 300°C, will be called *reduced zinc oxide* in what follows.

*Photoresponse of nitrogen and other various gases*

In order to see the photoresponse of gases other than oxygen, *i.e.*, helium, hydrogen, nitrogen, carbon monoxide, carbon dioxide and water vapour were brought into contact with the reduced zinc oxide at room temperature. On illumination none of these gases was found to desorb nor adsorb within experimental accuracy. The finding would mean at least that the photodesorption of oxygen is not caused by the photolysis of the zinc oxide sample. Desorption of these gases, on the other-hand, might occur on illumination thermally as krypton was found to do so, according to ROSENBERG and MARTEL<sup>6)</sup>, on germanium surface. The fact that no photoeffect was observed with the gases other than oxygen may exclude therefore the possibility that the photodesorption of oxygen took place thermally.

The d.c. electrical resistance of the zinc oxide powder of the same stock was measured, the sample in this case being compressed in about 2 mm thick between two platinum plates. The resistance was several meg ohms at room temperature. On heating and outgassing the sample, the resistance did not change appreciably below 200°C but rapidly decreased and reached to several ten ohms at 300°C. The sample was then cooled down to room temperature in vacuum. Introduction of a few mm Hg oxygen to this sample caused instantaneous increase in resistance to several kilo ohms. On heating the zinc oxide again to about 200°C, the resistance was found to restore the value before the introduction of oxygen. Similar observation with the ad-

6) A. J. ROSENBERG and C. S. MARTEL, Jr., J. Phys. Chem. **61**, 512 (1957).

sorption of various gases mentioned above showed no particular change in resistance. Thus, the type of adsorption that influences electrical resistance may be considered to give photoresponses.

*Adsorption character of oxygen and photoresponses*

The shape of adsorption isobar provides a means of differentiation for the adsorption bond; monotonously decreasing or increasing curve would mean a single kind of adsorption bond involved. An attempt was made therefore to obtain pressure-temperature relation for the oxygen adsorbed on zinc oxide in a constant volume. This should not be identified of course as adsorption isobar, but be sufficient for the present purpose.

A portion of oxygen was introduced to the adsorption vessel containing reduced zinc oxide and kept at room temperature. The vessel was then heated at a constant rate, *i.e.*,  $dT/dt = 4.5^\circ\text{C}/\text{min}$  without illumination and the change of oxygen pressure was recorded by PIRANI gauge against the temperature of the vessel. The result is shown in Fig. 3. As shown there, the desorption of oxygen took place with increasing temperature but tended toward adsorption sharply at about  $150^\circ\text{C}$ . Further increase in temperature however led again to gradual desorption. Consequently a maximum appeared in the plot of oxygen pressure against temperature. This maximum, which may correspond

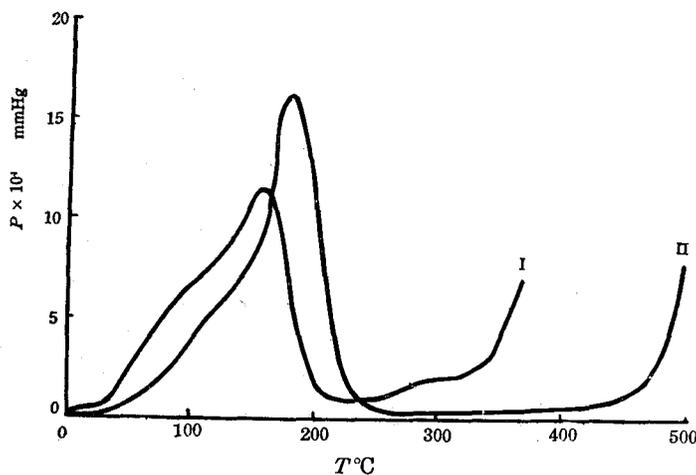


Fig. 3.  $p \sim T$  relation of oxygen on reduced zinc oxide.

I: Zinc oxide outgassed at  $300^\circ\text{C}$ .

II: Zinc oxide outgassed at  $500^\circ\text{C}$ .

to the *valley* of adsorption isobar, indicates that adsorption bond of different type is involved over the temperature range investigated.

At lower temperature range, *i.e.*, around room temperature, adsorption of oxygen was quick and almost reversible and hence may be considered to be of low adsorption heat and low activation energy. At higher temperature, *i.e.*, near and above 150°C, the adsorption was activated type and not reversible with respect to temperature variation. This adsorption ought to be of high adsorption heat and high activation energy.

The position of maximum in the plot of  $p$  against  $T$  was found to shift depending on the mode of pretreatment of the zinc oxide sample. On outgassing the sample at 500°C for about one hour, the maximum moved toward higher temperature with much more distinct peak as shown also in Fig. 3. Adsorption of oxygen increased by this severe treatment to a certain extent.

At first sight, Fig. 3 might show that there are two types of adsorption bond for oxygen; one is physical and appears in the desorbing curve below the maximum and the other chemical in the adsorbing curve beyond this. However it may be reminded that oxygen adsorption at room temperature gives rise to an increase in electrical resistance by a factor of  $10^3$ , hence suggesting ionic adsorption of oxygen involved even around room temperature. Thus the desorption may be considered as that from some weakly chemisorbed oxygen and not from the VAN DER WAALS layer alone. Further discussions will be made on the character of adsorption bond later.

To see whether or not the adsorbed oxygen at higher temperature is accessible to desorption on illumination, photoresponses were investigated at about 150°C. Oxygen was introduced, after outgassing treatment of zinc oxide sample at 300°C, into the vessel maintained at 150°C and allowed to contact zinc oxide for some time. On illumination, a slight yet definite *adsorption* of oxygen occurred. The sample was then heated to 300°C and subjected again to illumination. No photoresponse was obtained however in this case. The sample was then kept at 150°C and reinvestigated for the photoeffect. Photodesorption was not reproduced at this time. These observations suggest that the photoresponse is considerably sensitive to the state of zinc oxide. Particular the opposite phenomenon obtained with the adsorption of oxygen on perhaps oxidized surface of zinc oxide stimulated us to extend this sort of observation on the zinc oxide sample oxidized under

a well defined condition. The result will be mentioned in a later section.

*Photodesorption kinetics*

Initial photodesorption rates were measured at constant light intensity at room temperature against coverage by oxygen. At low coverages or low equilibrium pressures photodesorption rates were almost proportional to the equilibrium pressure. With increasing equilibrium pressure, the rates were found to be proportional to some less power of the equilibrium pressure. On the other hand photodesorption rates were measured at constant equilibrium pressure against light intensities. The result is given in Fig. 4 as logarithmic plot. The

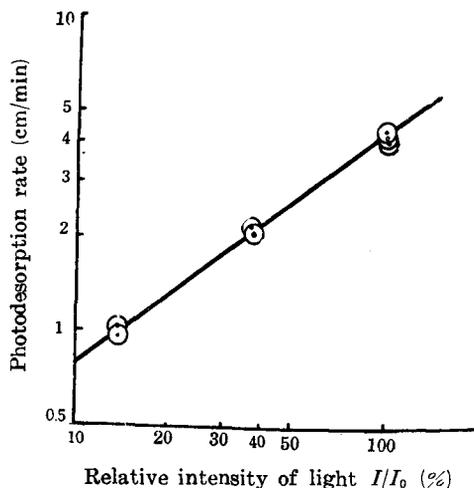


Fig. 4. Initial photodesorption rates of oxygen as a function of light intensity.

$T$ : 19.3°C. Oxygen pressure before illumination:  $4.5 \times 10^{-4}$  mm Hg. 1 cm/min. of ordinate is equivalent to  $1.2 \times 10^{-5}$  mmHg/min.

figure shows that photodesorption rates are proportional to a power of light intensity. Consequently the rates were expressed approximately by

$$(dp/dt)_{i, it.} = k_a \frac{bp}{1 + bp} I^n$$

where  $k_a$  and  $b$  are constants,  $I$  the light intensity and  $p$  the equilibrium

*Photoresponses for the Oxygen Adsorbed on Zinc Oxide Powder*

TABLE 1.

Temperature °C	23.5	19.3	-195
<i>n</i>	0.73	0.73	0.74

pressure of oxygen. The value of *n* was little dependent on temperature as shown in Table 1.

Temperature coefficient of the photodesorption rate was determined at constant oxygen pressure and at constant light intensity in the temperature range 0–50°C. The change of surface coverage by oxygen due to temperature variation was estimated to be very small or 1.0–0.1%. As shown in Fig. 5, photodesorption rates were almost independent on temperature. The activation energy for the photodesorption should hence be zero approximately since *n* depends little upon temperature.

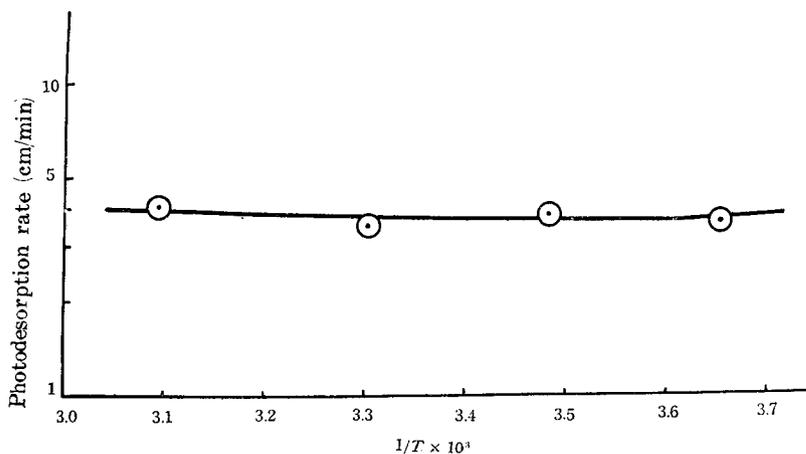


Fig. 5. Temperature dependency of initial photodesorption rate. Oxygen pressure before illumination was  $3.5 \times 10^{-4}$  mm Hg.

*Photoadsorption of oxygen*

It was quite certain that photodesorption occurs on zinc oxide of reduced state. However the photodesorption became faint or even turned out to be photoadsorption on presumably oxidized surface at and above 150°C. Further experiments were needed therefore to investigate the photoresponse with zinc oxide oxidized under a well defined condition as possible.

Outgassing of zinc oxide sample was followed by a treatment with 10 mm Hg oxygen at 300°C for one hour. The adsorption vessel was then cooled down to room temperature and evacuated at this temperature to  $10^{-5}$  mm Hg. The measurement of d. c. resistance, carried out with another sample of the same pretreatment, was found to be as large as several meg ohms.

The sample is called as oxidized zinc oxide. The adsorption of oxygen on this sample was well measurable but it was estimated to be about one-tenth of that on reduced zinc oxide.

Photoresponse was investigated similarly as before with this sample. On direct illumination of mercury lamp photoadsorption of oxygen took place in contrast with the effect on reduced zinc oxide. Moreover this state of adsorption remained unchangeable even when the light was intercepted. The light filtered through VC1B-CuSO<sub>4</sub> solution was again effective for the adsorption in this case. Repeated illuminations on the same surface of zinc oxide caused a depression of the effect but gave almost reproducible photoresponse when the vessel was slightly shaken between runs. So the behavior of photoeffect resembled that on reduced zinc oxide. Most contrasted phenomena would be that the effect of illumination appears to be opposite and that the response is

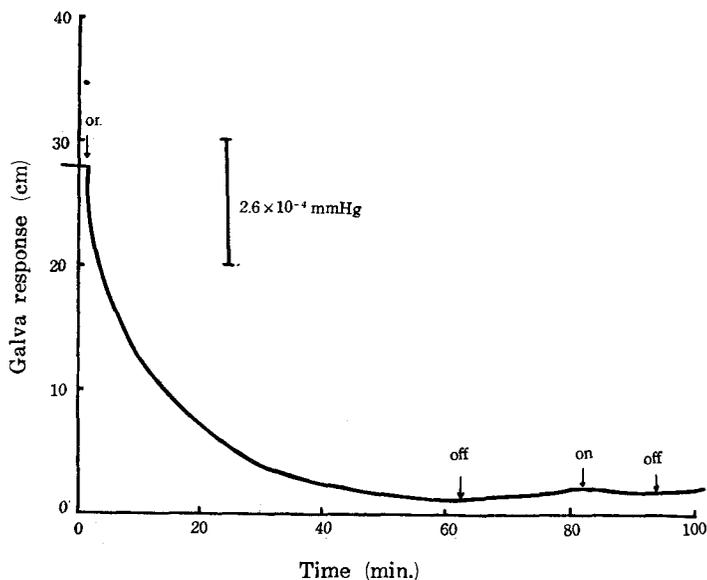


Fig. 6. Photoadsorption of oxygen.  $T$ : 18.0°C. Oxygen pressure before illumination:  $6.3 \times 10^{-3}$  mm Hg.

*Photoresponses for the Oxygen Adsorbed on Zinc Oxide Powder*

entirely irreversible with respect to on or off of the light.

A typical example of photoadsorption is shown in Fig. 6. Initial photoadsorption rates at constant oxygen pressure were described according to

$$-(dp/dt)_{\text{init.}} =: k_a I^m$$

where  $k_a$  is a constant. The value of  $m$  was almost independent on temperature over the temperature range 0-50°C as shown in Table 2.

TABLE 2.

Temperature °C	0	17.1	19.7	21.7	48
$m$	0.67	0.67	0.63	0.60	0.61

The activation energy for photoadsorption at the initial stage was calculated to be -3 kcal/mole. Fig. 7 shows the temperature dependency of the photoadsorption rate at constant light intensity.

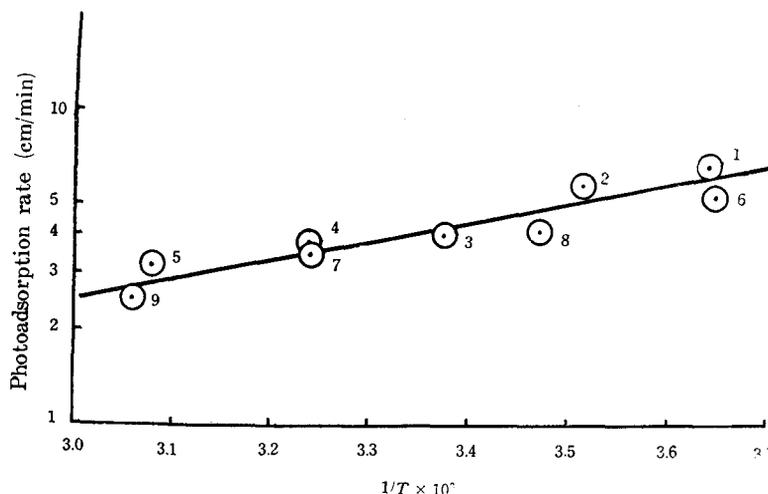


Fig. 7. Temperature dependency of initial photoadsorption rate. Oxygen pressure before illumination was approximately  $5 \times 10^{-4}$  mm Hg. Annexed figure indicates the order of measurement.

The adsorption vessel containing oxygen and oxidized zinc oxide was heated at a constant speed without illumination to obtain  $p$ - $T$  curve and to compare it with that on reduced zinc oxide. The result is shown in Fig. 8. Curve I is the one obtained on zinc oxide oxidized

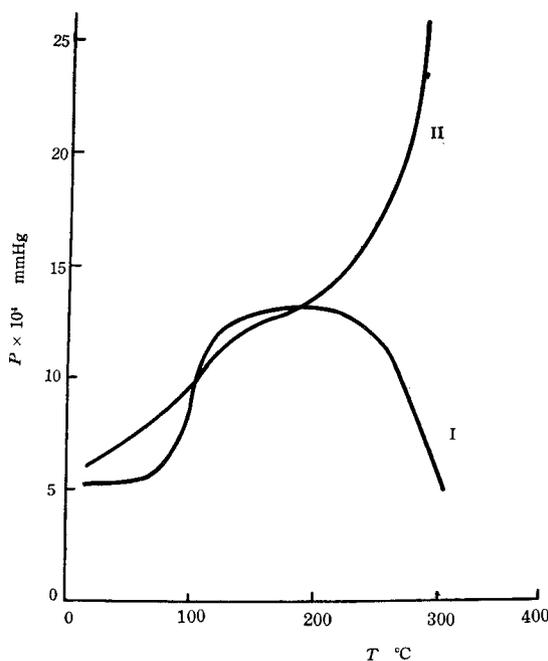


Fig. 8.  $p$ - $T$  relation of oxygen on oxidized zinc oxide.  
 I: Zinc oxide oxidized at 300°C for one hour.  
 II: Zinc oxide oxidized at 300°C for three hours.

at 300°C for one hour while curve II is that on zinc oxide oxidized at 300°C for three hours under a few cm Hg oxygen pressure. The figure shows that the curve I at least qualitatively resembles that obtained on reduced zinc oxide, *i.e.*, it possesses a flattened maximum near 200°C whereas the curve II merely gives an inflection point at the temperature. This would mean that two types of chemical adsorption are still involved on oxidized zinc oxide as well as on reduced sample. Closer inspection of the figure shows however that oxidation treatment of zinc oxide suppresses the adsorption of oxygen of both low and high temperature types. This result is to be expected if electrons become less and less available by the oxidation treatment.

### Discussion

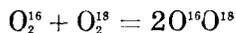
The shape of the  $p$ - $T$  curve obtained with oxygen in contact with reduced zinc oxide will first be discussed to see what kind of adsorbed state has been responsible for the photodesorption of oxygen at room

temperature. The adsorption of oxygen below 150°C, as judged from Fig. 3, should be VAN DER WAALS type or chemical while above 150°C it must be of much stronger chemical bond. It is improbable that adsorbed oxygen in the VAN DER WAALS layer is able to desorb on illumination because if this could happen thermally similar phenomenon may appear with the gases such as nitrogen, carbon dioxide and others in contrary to the experiment.

The adsorption of oxygen at room temperature was found several times greater on zinc oxide outgassed at 500°C than that outgassed at 300°C. VAN DER WAALS adsorption should never be expected to increase on the surface of severely heated and outgassed zinc oxide. On the other hand, chemical adsorption may increase appreciably on the surface of such a zinc oxide sample as in the case of carbon dioxide adsorption<sup>7)</sup>.

So it is conceivable that oxygen bound to reduced zinc oxide kept below 150°C is weak yet chemical in nature. In addition, the fact that the electrical resistance of zinc oxide markedly increases on adsorbing oxygen may suggest that adsorbed oxygen removes conduction electrons from zinc oxide and hence is negatively charged. The work by KOBAYASHI and KAWAJI<sup>8)</sup> who observed the change of surface potential due to illumination for the adsorption of oxygen on zinc sulfide showed that adsorbed oxygen is negatively charged.

In the light of these observations it would not be unrealistic to postulate the presence of negatively charged oxygen ion in the form,  $O_2^-$ , on the surface of zinc oxide kept below 150°C. The adsorption of oxygen above 150°C, on the other hand, may perhaps result in dissociation of this molecular ion to yield  $O^-$  or  $O^{--}$  on the surface since the  $p$ - $T$  curve shows that another chemical adsorption of activated type set in around this temperature. In this connection it is interesting to see that the exchange reaction of oxygen



on an outgassed zinc oxide is measurable, according to WINTER<sup>9)</sup>, only above 120°C. Although non-occurrence of the exchange reaction below 120°C does not necessarily mean that the adsorption of oxygen is molecular, the above postulate is sound enough in the exchange datum of this kind as well.

7) T. KWAN, T. KINUYAMA and Y. FUJITA, *J. Res. Inst. Catalysis* **3**, 28 (1953).

8) A. KOBAYASHI and S. KAWAJI, *J. Phys. Soc. Japan* **10**, 270 (1955).

9) E. R. S. WINTER, *J. Chem. Soc.* 1522 (1954).

There are many observations relating to the electrical conductivity of semiconductors as a function of temperature. Generally accepted relationship might be

$$\ln \sigma = A - \frac{E}{RT}$$

where  $\sigma$  is the specific conductivity of the semiconductor and  $E$  and  $A$  are constants.

However, according to STÖCKMANN<sup>10)</sup> who observed the conductivity of zinc oxide film (0.1  $\mu$  thick) kept in air there exists an abnormal maximum in the curve of  $\ln \sigma$  against  $1/T$  when the temperature of the sample is raised at a constant speed. The position of the maximum was between 150–250°C just as in the  $p$ - $T$  curve for the adsorption of oxygen on zinc oxide. FRITSCHÉ<sup>11)</sup> reinvestigated the phenomenon using zinc oxide of the same thickness and with a similar technique but in a vacuum and found no maximum in the plot of  $\ln \sigma$  against  $1/T$ .

Thus it is evident that the anomalous curve in the  $\sigma$ - $T$  relation may be ascribed to the consequence of the desorption-adsorption of oxygen; as the temperature rises the adsorbed oxygen ion,  $O_2^-$ , may desorb from the surface donating an electron to zinc oxide, hence causing the conductivity of zinc oxide to increase. On further raising of temperature chemical adsorption may appear near the maximum temperature to yield  $O^-$  or  $O^{--}$  by accepting electrons from zinc oxide. As a result the conductivity may decrease beyond this temperature with increasing temperature.

Similar interpretation can be made on the observation by MORRISON<sup>12)</sup> who studied the variation of conductivity of sintered zinc oxide sample against time when the sample was heated from 23 to 100°C. The initial anomalous peak in the plot of the conductivity against time is naturally expected if rapid desorption of molecular oxygen ion is followed by a slow dissociative chemisorption.

Since spectral response for the photodesorption of oxygen almost coincides with that of the characteristic absorption of zinc oxide and moreover the direct absorption by oxygen molecule is not possible with the light of the wave length used, the observed photoresponse should be considered as caused by the reaction of adsorbed molecular oxygen

10) F. STÖCKMANN, *Z. Physik* **127**, 563 (1950).

11) H. FRITSCHÉ, *Z. Physik* **133**, 422 (1952).

12) S. R. MORRISON, *Advances in Catalysis*, VII, p. 259 (1955), Academic Press. New York.

ion with either electron or hole injected in the zinc oxide on illumination. The participation of atomic oxygen ion is not needed in the desorption of this kind, for its reverse reaction, *i. e.*, the dissociative adsorption of oxygen is not expected to proceed readily at room temperature in contrary to the experiment.

For the photodesorption of oxygen from the surface the following scheme seems most compatible with the experiment.



where  $\oplus$  denotes the hole. On the other hand photoadsorption ought to be the reaction of electron with either oxygen molecule in the VAN DER WAALS layer or chemisorbed molecular oxygen ion to form  $\text{O}^-$  or  $\text{O}^{--}$ .



where  $\ominus$  denotes electron.

Because, the photoadsorption was found to be irreversible or the excess adsorption due to illumination could not desorb when the light was shut off. It is reminded that the reversible adsorption in the form of  $\text{O}^-$  or  $\text{O}^{--}$  at the surface can only take place far beyond the maximum temperature. Therefore the photoadsorption once occurred near the room temperature should never restore the original state quickly or substantially irreversible.

While the photochemical reaction scheme (1) and (2) have been proposed respectively to account for the observed photoresponses, no explanation is given there as to why positive hole (or electron) should participate in the photoresponse on reduced (or oxidized) and not on oxidized (or reduced) zinc oxide. In this connection the suggestion by BRATTAIN<sup>13)</sup> may be cited. In discussing the photooxidation behavior of *n*- and *p*-type germanium he suggested that the *minority charge carrier* of semiconductor plays dominant role generally in the photoresponse. Since conduction electrons are much more abundant in reduced than in oxidized zinc oxide, these may not participate, according to BRATTAIN, in the photoresponse at least on reduced zinc oxide. The scheme (1) satisfies this principle. On the other hand, the electrons might be entitled to minority carriers on oxidized zinc oxide to participate in the photoresponse such as given by the scheme (2).

A similar theoretical conclusion was reached by WOLKENSTEIN and

13) W. H. BRATTAIN, *Semiconductor Surface Physics*, p. 26 (1957), Pennsylvania Univ.

KOGAN<sup>14)</sup> who derived an expression for the change of adsorbed species on semiconductor as a function of relative increase of electron or hole upon illumination. Two types of adsorption bond were postulated by these authors to derive the expression: one is weak and neutral and the other strong and ionic. Photoadsorption occurs when relative increase of electron overcomes that of hole while photodesorption *vice versa*. Thus, the theory requires that as one passes from reduced to oxidized sample photoadsorption turns to photodesorption just as found by us. So as far as the direction of photoresponse concerns, there is no contradiction between the experiment and the theory. Experiments on the other hand showed that the photochemical process involves at least three types of adsorbed oxygen, namely,  $O_2$ ,  $O_2^-$  and  $O^-$  or  $O^{--}$  as given by (1) and (2).

If electron and hole decay or recombine only through the adsorbed oxygen as given in the above scheme (1), the pressure change due to illumination or interception should be entirely reversible. Experiments showed however that this is not true, *i.e.*, the interception of light did not reproduce the original pressure, for instance, on reduced sample. Moreover the rate of photodesorption or adsorption appeared to depend strongly on the past history for illumination. So some irreversible trapping of electron or hole may be considered to occur besides the reaction of these carriers with adsorbed oxygen at the surface. The irreversible change in the concentration of conduction electron by trapping should lead to the change in conductivity before and after illumination. This is what TRIVICH *et al.*<sup>15)</sup> actually found with zinc oxide with or without doped impurities.

Let us now turn to the numerous photocurrent investigations reported in the literature. Most of these seem to ignore the effect of surrounding gas on the photocurrent. MELNICK<sup>3)</sup> very recently emphasized the importance of oxygen pressure in the photoconductivity response. Unfortunately adsorption or desorption of oxygen was not observed by him. The present work confined itself to the photoresponse in the adsorption and not to photoconductivity response.

MEDVED<sup>16)</sup> recently measured the rise of photoconductivity of evaporated zinc oxide and the rate of photodesorption of oxygen from the surface simultaneously and found that there is approximate parallelism

14) Th. WOLKENSTEIN and S. M. KOGAN, J. Chim. Phys. 55, 483 (1958).

15) H. H. PAPA ZIAN, P. A. FLINN and D. TRIVICH, J. Electrochem. Soc. 103, 84 (1957).

16) D. B. MEDVED, J. Chem. Phys. 28, 870 (1958).

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between these two photoeffects. BORISSOV *et al.*<sup>17)</sup> and MYASNIKOV *et al.*<sup>18)</sup> reported that *negative photoconductivity* occurs with zinc oxide kept in air. Since the latter authors confirmed that such phenomenon never appears with samples kept in a vacuum, the phenomenon might be interpreted as due partly to photoadsorption of oxygen occurring simultaneously.

It is obvious now that the present work in conjunction with the works by MELNICK and others exhibits the importance of the adsorbed oxygen in the interpretation of photoconductivity of zinc oxide.

17) M. BORISSOV and St. KANEV, Z. physik. Chem. **61**, 512 (1957).

18) I. A. MYASNIKOV and S. Ya. PSHEZHETSKII, Prob. Kinet. in Cata. Akad. Nauk, SSSR **8**, 34 (1955).