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Electrical Conductivity of Pure and Doped Zinc Oxides, Catalysts of the Hydrogenation of Ethylene

I. Activation of the Catalyst and Adsorption of Oxygen on Pure Zinc Oxide

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The influence of the activation of zinc oxide *in vacuo* and of the poisoning by oxygen on electrical conductivity of the catalyst is examined. The chemical approach to the equilibrium of defects gives a consistent picture for the chemisorption of oxygen as O^- and O^{2-} ions.

INTRODUCTION

It has been shown (*1*), (*2*) that zinc oxide is a good catalyst for the hydrogenation of ethylene at 150°C, provided that it has been previously activated by heating *in vacuo* at 250°C. Kinetic results interpreted in terms of Langmuir mechanism have disclosed that ethylene and hydrogen are likely to be adsorbed on two kinds of sites, the hydrogen adsorption being weak. The purpose of the present study is to give more details on the kind of sites involved in chemisorption of reagents and on intermediate steps of the reaction. This has been attempted by following the electrical conductivity changes of zinc oxide in the presence of reagents and by applying the statistical concept of lattice defects, first developed by Wagner (*3*) and then by Bevan and Anderson (*4*), Hauffe and Block (*5*), Fritzche (*6*), Heiland (*7*), Hogarth (*8*), and others. Conductivity electrons are considered as reacting species, participating in reactions between the surface and adsorbed complexes. Frequently these reactions are simply adsorptions or desorptions of gases and are equilibrated. The introduction of equilibrium constants may lead to well-defined relationships between the conductivity and the pressure of the gas at a given temperature. These relationships in turn give some information on the nature both of the chemisorbed complex and of the surface site involved.

It may be mentioned that this approach leads to the same general conclusions as an approach based on the equilibrium between electrons, holes, their traps, and adsorbed species, derived by Cimino *et al.* (*9*).

Finally, it must be pointed out that all the electrical measurements are carried out on powdered, nonsintered, samples of ZnO, presenting a high surface-to-volume ratio. Surface effects therefore predominate, even at temperatures well above room temperature. As the chemisorption is also a surface process, the correlation between the two phenomena should be easier to follow. However, a semiconductor in powdered form is difficult to analyze quantitatively. Accordingly, the conclusions to be drawn are mainly of a qualitative nature. So, no attempt is made to correlate the amount of the gas adsorbed to conductivity changes. In other words, it is proposed to consider conductivity measurements of a catalyst in contact with a gaseous reagent as a convenient way of discriminating between several kinds of chemisorption and to draw some information as to the sufarce sites involved.

METHODS

The conductivity cell for powdered zinc oxide is derived, with some modifications, from the apparatus described by Chapman *et al.* (*10*). Figure 1 gives the scheme of the cell made out of Pyrex glass and connected

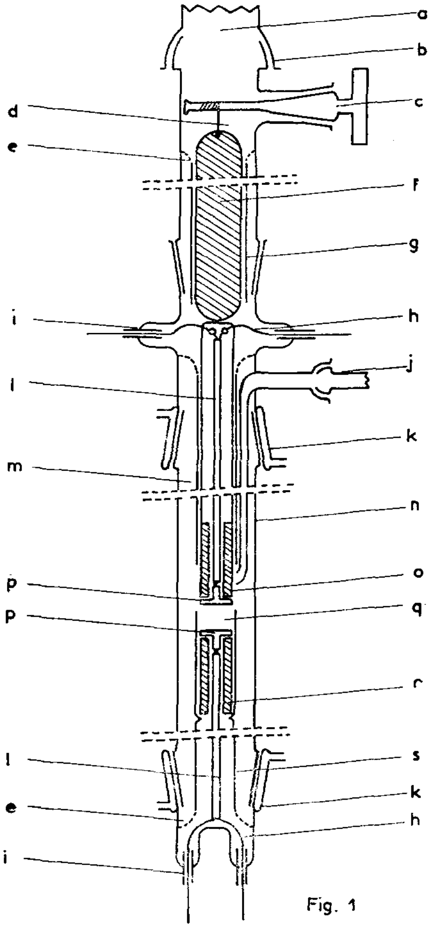

FIG. 1. Conductivity cell for powdered samples.

through the tubing (a) and the spherical ground joint (b) to the vacuum line.

The mercury-containing sealed bulb (f) can be raised and lowered by a nylon wire (d) wound on to a lifting device (c). A guide (g) contains evacuation holes (e). The piston (o) terminated by a platinum disc (p) which is the upper electrode, is suspended to the bulb (f). The cylindrical cavity (q), whose bottom is a fixed platinum electrode (p) holds the sample in powdered form. A chromel-alumel thermocouple (h) is soldered to each electrode and is isolated by silica rods (l). The thermocouple wires pass through the Pyrex–Kovar seals (i). The powder is compressed by the upper electrode under the effect of the mercury bulb (f). The pressure is 1 kg/cm^2. Gases for adsorption are introduced through the inlet (j). The central part (n) may be placed inside an electric oven which opens along its generatrix. For this reason the ground joints (k) are water-cooled. The oven is of a non-inductive type and has no temperature gradient in its central part. An electronic regulation system maintains through the thermocouples the temperature constant within 0.5°C in the range from 50° to 500°C and within 1° to 2°C in the range from 500° to 900°C.

One wire of each thermocouple serves as the lead for resistance measurements with an AC bridge of Leeds and Northrup (type 1554 A2). The resistance values are determined at a frequency of 1000 Hz, with a precision of 1% in the range of 1 Ω to 10M Ω. For higher values of resistance, DC measurements are made with an Iso-R-Metre of Lemouzy. The precision is of 1% up to $10^{11}\Omega$, 2–3% up to $10^{13}\Omega$, and 3–5% up to $10^{16}\Omega$.

Zinc oxide is directly prepared in the conductivity cell (unless otherwise stated) by dehydration of a pure zinc hydroxide (*11*) at 110°C in high vacuum (10^{-6} mm Hg). The initial surface area of ZnO is 30 m^2/g which becomes 31 m^2/g after activation at 250°C, 10 m^2/g after activation at 400°C, and 1 m^2/g after activation at 900°C.

According to Morrison (*12*), when the surface-to-volume ratio for the zinc oxide increases to 10^3 cm^{-1}, surface effects in the conductivity become predominant. This ratio corresponds to a surface of 0.1 m^2/g or to a linear dimension of particles of 10 microns. Conductivity measurements of activated samples are then relevant mainly to surface properties.

The resistivities of zinc oxide may be measured by both AC and DC methods in the range from 5×10^5 to $10^8\Omega$. Successive determinations by the two methods gave identical values of the resistance in this range. No polarization effect has been observed with DC measurements when the voltage applied is of 12.5 volts only. For a resistance of $10^6\Omega$ this corresponds to an intensity of 12.5 μA. Ohm's law has been observed in every case, which shows that the resistance on the surface of the particles is not disturbed by the contact resistance between the particles.

Results and Discussion

A. Activation of the Zinc Oxide

It has been shown that the conductivity of zinc oxide is independent of the nature of the gas atmosphere for pressures below 10^{-4} mm Hg and therefore varies only with temperature (*4*). For this reason the experiments described below were carried out at a pressure of 10^{-6} mm Hg. Zinc hydroxide was decomposed *in vacuo* at 110°C for 15 hr and then slowly heated up to 900°C and cooled *in vacuo*. During this stage conductivities were registered and are reproduced in Fig. 2, curve A showing the variation of the logarithm of the conductivity versus the reciprocal of the absolute temperature. Above 200°C the conductivity rises abruptly. At 900°C the conductivity is very stable even after 10 hr of this treatment. During the cooling the conductivity increases as shown by the straight line A, which accounts for a metallic behavior.

When these experiments are carried out with the heating being interrupted at 400°C or at 250°C, curves B or C, respectively, are obtained. The main difference between these curves and curve A is the slope during cooling. The conductivity decreases for the linear

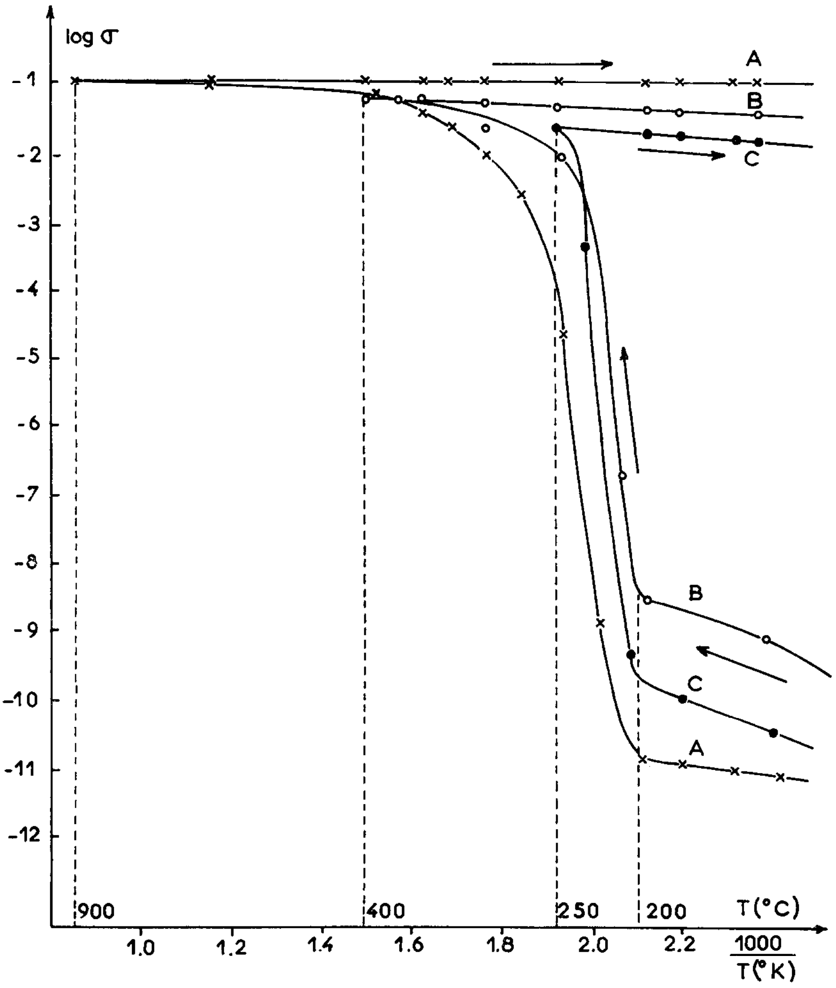

FIG. 2. Conductivity of zinc oxide sample heated and cooled *in vacuo*.

portion of curves B and C as the temperature decreases, which accounts for a semiconducting behavior. The temperature coefficient of the conductivity, E_a, is 0.029 ev for line B and 0.065 ev for line C. The fact that during the heating, curves A, B, and C do not coincide may be explained by small differences in the rate of increase of the temperature for the three samples. However, the straight lines during the cooling correspond to a reversible process. In fact, the conductivity of any sample A, B, or C registered during the second heating and cooling, always follows its respective straight line of Fig. 2.

The decrease of the activation energy E_a of conductivity, as the final temperature of heating increases from 250° to 400°C, is probably due to the creation of new electron donors, at least in the surface layer of zinc oxide. These donors also contribute to an increase in conductivity and their energy level is being brought closer to the lower limit of the conductivity band. When the Fermi level reaches this limit or goes beyond it, the semiconductor is degenerated. Its behavior is that of a metal, which accounts for a negative value of the activation energy (curve A).

Seebeck effect determinations for samples heated up to 400°C show a negative sign at any temperature between 150° and 400°C, either in vacuum or after introduction of oxygen. This accounts for an *n*-type conductivity, in agreement with the determinations made by different authors (*8*, *13*). No inversion from the *n*-type to the *p*-type, after admission of oxygen (*14*), has been observed in the previous temperature range.

A formation of a nonstoichiometric oxide after heating *in vacuo* is a well-established phenomenon, even for such refractory oxides as alumina (*15*) or titania (*16*). There is good evidence (*17–19*) that zinc oxide is dissociated, at least on its surface, according to the equilibrium

$$\mathrm{ZnO} \rightleftharpoons \mathrm{Zn_i} + 1/2\mathrm{O_2} \qquad (1)$$

The high vacuum and the divided state of the solid favor the formation of the zinc "interstitial" surface atoms which, it is assumed, are ionized according to the equilibria

$$\mathrm{Zn_i} \rightleftharpoons \mathrm{Zn_i^{+}} + \mathrm{e^-} \qquad (2)$$

$$\mathrm{Zn_i^{+}} \rightleftharpoons \mathrm{Zn_i^{2+}} + \mathrm{e^-} \qquad (3)$$

At moderate temperatures equilibrium (3) probably represents a small fraction of the total ionization (see below).

Near the Tamman temperature of zinc oxide (900°C) the dissociation may also occur in the bulk of the solid heated *in vacuo*. At the same time, on the surface, the concentration of conductivity electrons increases and reaches degeneracy value. Surface-degenerated zinc oxide then shows a metallic behavior during cooling. However this behavior may also be explained by nucleation, at least on the surface, of a zinc metal phase. This hypothesis is reinforced by the observation of condensation of metallic zinc on the walls of the conductivity cell when the temperature exceeds 500°C.

Catalytic activity of the zinc oxide in the hydrogenation of ethylene is observed when the solid has been activated *in vacuo* at 250°C. An activation below this temperature does not lead to catalytic activity. This behavior may be connected with the abrupt increase in conductivity in this temperature range shown in Fig. 2. Therefore, the formation of a nonstoichiometric zinc oxide, at least on the surface, according to Eq. (1), with a concomitant ionization according to Eq. (2), seems to be a necessary condition for the catalytic activity in the hydrogenation of ethylene.

B. Conductivity of the Zinc Oxide in Oxygen

It has been shown that zinc oxide catalyst is poisoned by oxygen for the hydrogenation of ethylene (*1*, *2*). The conductivity of the activated zinc oxide also decreases in the presence of oxygen. It varies with the pressure of oxygen, with the temperature, and with the previous treatment of the sample. A systematic investigation has been made by trying to maintain two of these parameters constant and varying the third one. The variation of the conductivity with time for a given temperature and oxygen pressure starts too fast and has not been measured.

1. The Influence of the Pressure of Oxygen. The sample is first activated *in vacuo* for 15 hr. Temperatures of activation T_a are

400° and 900°C. Oxygen is introduced at a temperature T_e of either 150°, 400°, or 600°C. The pressure is established by steps from 10^{-4} to 160 mm Hg. For each step the apparent equilibrium pressure and conductivity are measured. The time necessary for this equilibrium to be established varies from 20 min to a few hours. In Fig. 3, representing the logarithm of oxygen pressure, curves D and D′ established at 150°C, and G established at 400°C, refer to samples activated at 400°C. For samples activated at 900°C curve E is established at 150°C and curve F at 600°C.

Besides curve E, which is almost horizontal, curves D, D′, G, and F exhibit linear portions whose slopes are 1/2 for curves D, D′, and G, and 1/4 for curve F. Thus, in the range of a linear variation of these plots, the conductivity σ follows the equations

$$\log \sigma = \log k - 1/m \log P_{O_2} \qquad (4)$$

or

$$\sigma = kP_{O_2}^{-1/m} \qquad (5)$$

This law of variation of the conductivity with oxygen pressure was established by different authors for different temperatures and the values of m are given in Table 1.

The particular case of curve E may be interpreted by remembering that activation *in vacuo* at 900°C gives a surface phase which may be metallic zinc. It is probable that oxygen at 150°C cannot oxidize this zinc and therefore conductivity hardly varies when increasing pressures of oxygen are established. However, zinc oxide activated at 900°C shows quite a different behavior in oxygen at 600°C (curve F). The oxidation of metallic zinc is probably possible here and then an equilibrium between zinc oxide and gaseous oxygen takes place.

Curves D, D′, G, and F of Fig. 3 and the values of m from Table 1 show the existence of at least two temperature ranges for the influence of the oxygen pressure on conductivity. According to Morrison and Miller (*21*) chemisorption of oxygen on zinc oxide

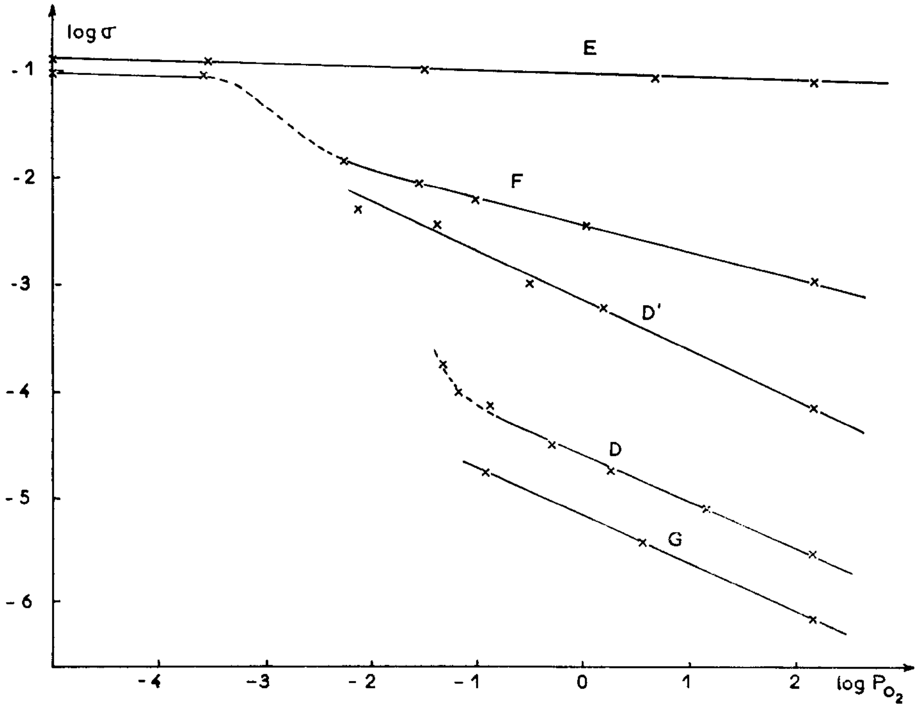

FIG. 3. Variation of the conductivity of zinc oxide samples, activated *in vacuo* at $T_a = 400°$ or 900°C, with oxygen pressure at $T_e = 150°$, 400°, or 600°C. Curve D: $T_a = 400°C$, $T_e = 150°C$, $m = 2.1$. Curve D′: $T_a = 400°C$, $T_e = 150°C$, $m = 2.2$. Curve G: $T_a = 400°C$, $T_e = 400°C$, $m = 2.1$. Curve F: $T_a = 900°C$, $T_e = 600°C$, $m = 4.2$. Curve E: $T_a = 900°C$, $T_e = 150°C$.

TABLE 1

VALUES OF m IN THE EQUATION $\log \sigma = \log k - (1/m) \log p_{O_2}$

Temperature (°C)	m	Authors (Ref.)
150° curve D	2.1	This work
curve D′	2.2	This work
300°	1.5	Uchida and Ogino (*20*)
400° curve G	2.1	This work
600° curve F	4.2	This work
530–630°	4.1–4.5	Baumbach and Wagner (*3*)
560–977°	4.6–3.6	Hogarth (*8*)
560–792°	3.7–4.3	Bevan and Anderson (*4*)
665°	5.5	Hauffe and Block (*5*)

is reversible above 450°C and this corresponds to a value of m of about 4. It is partially irreversible below 450°C and the corresponding value of m is about 2.

Indeed, it has been established that, for instance, at 150°C, the thorough evacuation of oxygen gives a smaller conductivity value than that before adsorption of this gas, which accounts for a lack of equilibrium, at least for the time allowed before measurements. The conductivity after thorough evacuation of oxygen at this temperature is of 5.4×10^{-4} ohm^{-1}cm^{-1} compared to 6.9×10^{-2} ohm^{-1}cm^{-1} before introduction of this gas and 7.5×10^{-5} ohm^{-1}cm^{-1} for a pressure of oxygen of 160 mm Hg. It seems then that only a fraction of the total adsorbed oxygen may be desorbed below 450°C and only this fraction represents an experimentally reversible phenomenon, shown by curves D, D′, or G.

On the other hand, at 600°C, the initial high conductivity is recovered after evacuation of oxygen. A different interpretation of the chemisorption of oxygen on zinc oxide may be envisaged for each temperature range.

Temperatures above 450°C. Nonstoichiometric zinc oxide contains interstitial zinc atoms, more or less ionized with liberation of electrons to the conductivity band. The decrease of the conductivity by chemisorption of oxygen (Fig. 3) may correspond to a recombination of interstitial zinc atoms with oxygen, at least on the surface, which leads to a decrease of the concentration of free electrons. The equilibrium on the surface of ZnO would then be

$$ZnO \rightleftharpoons Zn^{+} + e^{-} + 1/2O_2 \qquad (1) + (2) = (6)$$

$$ZnO \rightleftharpoons Zn^{2+} + 2e^{-} + 1/2O_2 \qquad (1) + (3) = (7)$$

The law of mass action gives

$$K_6 = [Zn^{+}][e^{-}]P_{O_2}^{1/2} \qquad (6')$$

$$K_7 = [Zn^{2+}][e^{-}]^2P_{O_2}^{1/2} \qquad (7')$$

or $[Zn^{+}] = [e^{-}] = n$ for (6) and $2[Zn^{2+}] = [e^{-}] = n$ for (7) where n is the concentration of conductivity electrons. Then

$$K_6 = n^2P_{O_2}^{1/2} \qquad (6'')$$

$$K_7 = n^3P_{O_2}^{1/2} \qquad (7'')$$

The conductivities being proportional to the concentrations of charge carriers if the mobilities are assumed to be constant, it follows that

$$\sigma \sim n = k_1P_{O_2}^{-1/4} \qquad (6''')$$

$$\sigma \sim n = k_2P_{O_2}^{-1/6} \qquad (7''')$$

Curve F of Fig. 3 is representative of an equation of this type, the value of m being closer to 4 than to 6, which seems to indicate that single ionization of zinc atoms would be predominant.

These considerations tend to show that the reversible adsorption—desorption process may be represented by an equilibrium

$$1/2O_{2(g)} + 2e^{-} \rightleftharpoons O^{2-} \qquad (8)$$

The law of mass action for this equilibrium gives the variation of the conductivity with the oxygen pressure expressed by Eq. (6‴).

$$K_8 = \frac{[O^{2-}]}{P_{O_2}^{1/2}[e^{-}]^2}$$

As $[O^{2-}]$ is very high in the zinc oxide, practically, it does not vary. Then

$$[e^-]^2 = n^2 = K_8 P_{O_2}^{-1/2}$$

and

$$\sigma \sim n = kP_{O_2}^{-1/4} \qquad (6''')$$

This form of chemisorption of oxygen (O^{2-}) is representative of a so-called type B high-temperature chemisorption. It was already postulated by Bevan and Anderson (*4*) and more recently by Barry and Stone (*22*). Electron spin resonance measurements on zinc oxide containing adsorbed oxygen at high temperature lead Kokes (*23*) to the same conclusion.

Temperatures below 450°C. The irreversible part of the adsorption of oxygen at these temperatures may be due (*23*) to the process, occurring during the first increase of oxygen pressure, expressed by Eq. (8), the reversible part being representative of the adsorption with a formation of O^- ions (type A adsorption) according to

$$1/2O_{2(g)} + e^- \rightleftharpoons O^- \qquad (9)$$

Uchida and Ogino (*20*) gave a derivation analogous to that shown above, by which it can be demonstrated that the conductivity varies according to the law

$$\sigma = kP_{O_2}^{-1/2} \qquad (10)$$

if the process is represented by Eq. (9). This accounts for $m = 2$ in curves D, D′, and G of Fig. 3.*

At intermediate temperatures chemisorption of oxygen should proceed according to two schemes at the same time and a reversible transformation

$$O^- + e^- \rightleftharpoons O^{2-} \qquad (11)$$

may be envisaged. This is also the conclusion reached by Glemza and Kokes (*23*), according to whom when oxygen is admitted on the zinc oxide, at an intermediate temperature, type B adsorption (O^{2-}) proceeds through a first adsorption as O^- (type A). Barry and Stone (*22*) also postulate that low-temperature type A adsorption leads to an O^- ion.

2. The Influence of the Temperature

In the preliminary experiments zinc oxide was first heated in air at 900°C for 1 hr and then rapidly cooled to room temperature and conserved in dry air. Conductivity measurements in air on this sample as a function of the temperature are shown in Fig. 4 where curves 1 and 3 correspond to the heating and curves 2 and 4 to the cooling of the same sample. For the second heating (curve 3) the extrema exhibited during the first heating (curve 1) are very much attenuated. The linear portions of curves in Fig. 4 lead to the values of activation energy of conductivity given in Table 2.

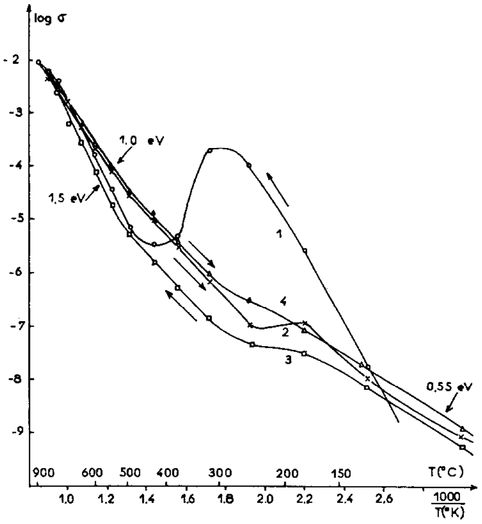

FIG. 4. Conductivity of zinc oxide sample heated and cooled in air.

TABLE 2
ACTIVATION ENERGIES OF CONDUCTIVITY FROM FIG. 4

Temperature range	25–200°C	275–500°C	500–900°C
		E_a(ev)	
Curve 1	1.30	—	1.50
Curve 2	0.55	0.8	1.00
Curve 3	0.55	0.8	1.50
Curve 4	0.55	0.8	1.00

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* It may be pointed out that for the equilibrium $O_{2(g)} + e^- \rightleftharpoons O_2^-$ m in Eq. (5) would be 1. This value is found for lithium-doped zinc oxide, as will be shown in a forthcoming paper.

The interpretation of these results may be made by considering equilibrium (1) between the solid and the gas phase. At any temperature the conductivity of ZnO during heating or cooling in air is stabilized within a few minutes, which shows that the process, at least on the surface of the solid, is fast. Depending on a rise or a decrease of the temperature, desorption or adsorption of oxygen takes place and modifies the number of surface "interstitial" zinc atoms according to (1) and simultaneously the number of conductivity electrons, according to (2) and (3). It was, however, previously shown that the second ionization interferes to a small extent only and, at first approximation, equilibrium (3) may be neglected. Simultaneous equilibria (1) and (2) result in equilibrium (6) whose constant is

$$K_6 = [\mathrm{Zn}^+][\mathrm{e}^-]P_{\mathrm{O}_2}{}^{1/2}/[\mathrm{ZnO}] = K_1 \times K_2$$

As the solid must be electrically neutral $[\mathrm{Zn}^+]$ is equal to $[\mathrm{e}^-]$ and besides [ZnO] and $P_{\mathrm{O}_2}{}^{1/2}$ may be considered as constant for these experiments. The conductivity is proportional to $[\mathrm{e}^-]$ if it is assumed that the mobility of the electrons does not vary very much. Then

$$\sigma = kK_6{}^{1/2} = kK_1{}^{1/2}K_2{}^{1/2}$$

or

$$\ln \sigma = k' + 1/2 \ln K_6$$

According to the equation of Van't Hoff

$$\ln \sigma = 2.303 \log \sigma = k' - (\Delta H_6{}^\circ/2RT) \tag{12}$$

where $\Delta H_6{}^\circ$ is the enthalpy of reaction (6)

$$\Delta H_6{}^\circ = \Delta H_1{}^\circ + \Delta H_2{}^\circ$$

Equation (12) shows that the plot of $\log \sigma$ vs $1/T$ gives a means of calculating $\Delta H_6{}^\circ$ from the slope. However, the linear portions of curves in Fig. 4 do not correspond to the same slope (Table 2). The differences in activation energies of curves in Fig. 4 and the anomalies like maximum and minimum (curve 1) have been explained by Morrison (*12*) with the help of a theory developed by Weisz (*24*). The rate v of the chemisorption of oxygen follows a relationship

$$v = A \exp [(-E_b + \mu)/kT]$$

where E_b is the potential barrier on the ZnO surface that must be crossed by the electron from the donor level to the adsorbed oxygen, μ being the Fermi level. The value of E_b depends on the number of chemisorbed oxygen species and increases with surface coverage by this gas. When the temperature decreases during cooling in air the surface coverage by oxygen increases, E_b increases, and v decreases practically to zero. A pseudo-equilibrium is then established at low temperatures. At high temperatures the rate of adsorption is fast enough and equilibrium (*1*) may be established. The conductivity depending on the number of free electrons follows equilibria (2) and (1) at the same time, or (6). For temperatures above 450°C, the activation energy of conductivity

$$E_a = \tfrac{1}{2}\Delta H_6{}^\circ = \tfrac{1}{2}(\Delta H_1{}^\circ + \Delta H_2{}^\circ)$$

according to Eq. (12). The experimental value of E_a in the range 500–900°C (Table 2) is 1.50 ev or 34.5 kcal/mole if the value of 1.00 ev is for the moment discarded. Then $\Delta H_6{}^\circ = \Delta H_1{}^\circ + \Delta H_2{}^\circ = 69$ kcal. For the same temperature interval Deren *et al.* (*25*) and Bevan *et al.* (*26*) found for the activation energy E_a the values, respectively, of 1.61 and 1.60 ev.

For temperatures below 450°C the rate of adsorption of oxygen decreases exponentially and it can be assumed that finally equilibrium (1) is no longer involved in the conductivity changes which follow only equilibrium (2). In the low-temperature range the slope of curves 2, 3, and 4 gives $E_a = 0.55$ ev (Table 2). It follows that

$$\Delta H_2{}^\circ = 2E_a = 1.1 \text{ ev} = 25.0 \text{ kcal/mole}$$

and

$$\Delta H_1{}^\circ = 69 - 25 = 44 \text{ kcal/mole}$$

Now, the thermodynamic value of $\Delta H_1{}^\circ$ for reaction (1) in the high-temperature range is of the order of 83 kcal. Taking into account all previous assumptions made and the fact that reaction (1) occurs mainly on the surface, the thermodynamic properties of which are different from those of the bulk (*15*), the calculated enthalpy, $\Delta H_1{}^\circ$, is of the correct order of magnitude.

Finally, it has been pointed out that for the high-temperature range (500–900°C) E_a is 1.5 ev for heating curves 1 and 3 and 1.0 ev for cooling curves 2 and 4 (Fig. 4 and Table 2). During the heating at increasing temperatures (curves 1 and 3) oxygen is desorbed and the potential barrier E_b can only decrease. At 900°C this barrier is minimum and during cooling (curves 2 and 4) it increases due to adsorption of oxygen. It then follows that $E_{b\,\max}$ is of the order of 0.5 ev, which is in agreement with the values already reported (*12*). This value for the potential barrier is also found for curves 2, 3, and 4 for temperatures below 200°C where only equilibrium (2) is presumed to be established.

The maximum and minimum of curve 1 for the first heating may be explained by the following surface phenomena. During this heating E_b is maximum, which means that a potential difference of 0.5 ev is created between the surface and the chemisorbed layer, whose thickness is of the order of 10^{-5} cm (*27*). The electric field is then of the order of 10^5 v/cm. Such a high value may induce migration of ions or atoms of excess zinc from below the surface but the formation of a regular surface lattice by chemisorption of oxygen (*22*) is slow. At the same time, the rate of chemisorption v increases with increasing temperature and a new amount of this gas is chemisorbed which decreases the conductivity of the surface. It therefore follows that in the range 25–500°C (curve 1) a compensation at the surface may occur between electron consumption due to oxygen chemisorption and electron liberation due to the thermal activation of migrating donors [equilibrium (2)]. According to the predominance of each of these factors a maximum and a minimum of conductivity are observed at variable temperatures, depending on the state of the surface and previous treatment. Curve 1 of Fig. 4, which is representative of the heating of a zinc oxide sample, previously heated at 900°C in air and then rapidly cooled, with quenching of excess zinc, and conserved in dry air at 25°C for a few days, clearly shows these extrema.

It seems probable that the extrema observed by Cimino *et al.* (*14*) below 130°C and explained by these authors as a p-type to n-type inversion of surface layer due to the desorption of oxygen during this heating do not correspond to the phenomenon observed in the present work, as the p-type inversion has never been observed in the temperature range (Fig. 4) in which the extrema occur.

In Fig. 5 this phenomenon is also observed for a sample of ZnO first heated in air at 900°C, cooled rapidly to room temperature, and then heated in the conductivity cell *in vacuo* from 25° to 900°C (curve ABCD). On the other hand, subsequent cooling *in vacuo* (curve DE) of this sample shows the same behavior as for the sample heated only *in vacuo* (Fig. 2, curve A). During this cooling the only phenomenon is the thermal activation (or deactivation) of donors now present in a great number and the activation energy is a few hundredths of an electron volt (Fig. 5).

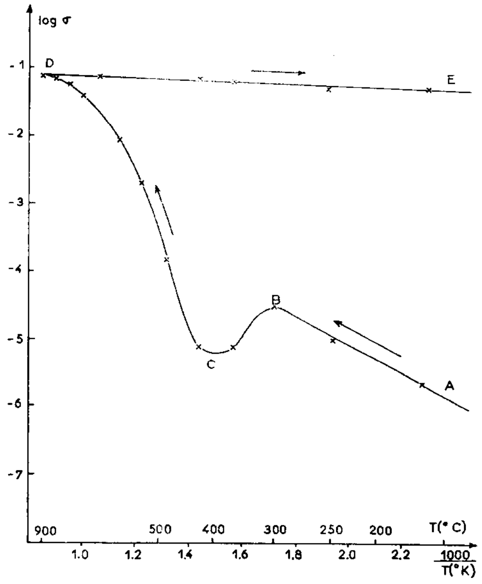

FIG. 5. Conductivity of zinc oxide sample previously heated in air at 900°C and then heated (ABCD) and cooled (DE) *in vacuo*.

If the previous anomalies are due to the migration toward the surface of interstitial zinc formed by heating in air at 900°C and quenched by rapid cooling to 25°C, they would be suppressed if the number of these defects were equilibrium dependent. The corresponding experiments are shown in Fig. 4, curves 2, 3, and in particular 4, and also in Fig. 6. For the experiments in Fig. 6 zinc oxide, prepared by decomposition of $Zn(OH)_2$ *in vacuo* at 110°C (point A) is then heated *in vacuo* up to 900°C (point B) and cooled *in vacuo* to 150°C (curve BC). During the heating to 900°C zinc oxide became nonstoichiometric first on the surface and then, at higher temperatures, interstitial zinc would migrate in the bulk (*19*). This situation is also conserved at point C for subsequent cooling *in vacuo*. From the point C a second heating up to 900°C is carried out in oxygen (160 mm Hg). As the temperature rises to 500°C excess surface zinc disappears by combination with oxygen and the conductivity decreases, which accounts for the minimum observed. From 500°C up, the progressive desorption of oxygen [equilibria (1) and (2)] results in an increase of the conductivity. At point D the equilibrium concentration of interstitial zinc in the lattice is probably achieved. The final slow cooling in oxygen gives curve DEA which is similar to curve 4 of Fig. 4 as it does not show any extremum. No substantial quenching of zinc excess occurs here and the equilibrium conditions during the slow cooling in oxygen are probably realized.

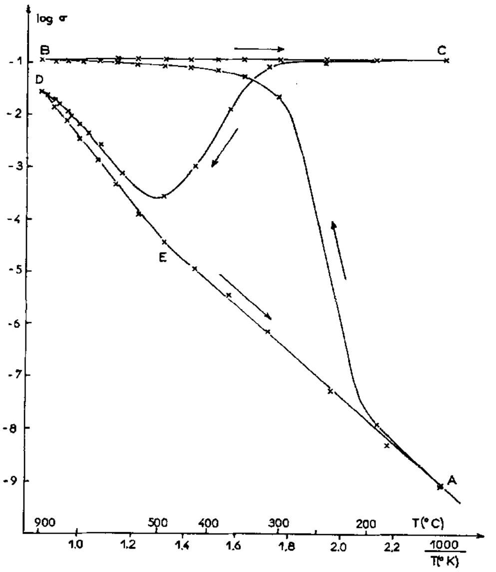

FIG. 6. Conductivity of zinc oxide sample heated (AB) and cooled (BC) *in vacuo*, then heated (CD) and cooled (DA) in oxygen.

To sum up, conductivity measurements on zinc oxide in the presence of oxygen or air tend to show that in the interval 200°–500°C the desorption–adsorption of oxygen is only partially equilibrated and may be perturbed by the migration of quenched zinc excess atoms or ions from the bulk toward the surface. For temperatures above 500°C the reversible adsorption of oxygen is achieved more readily.

The experiments described here also aim at showing that conductivity measurements on zinc oxide powders, carried out in this work, give essentially the same results as those made by different authors on sintered samples, films, or single crystals. Accordingly the study by the method described here of other adsorptions on zinc oxide, such as those of hydrogen and ethylene was envisaged, as well as the study of zinc oxide doped by lithium or gallium, with a view to attempting to establish the mechanism of the catalytic hydrogenation of ethylene.

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