351. *Properties of Some Simple Oxides and Spinels at High Temperatures.*

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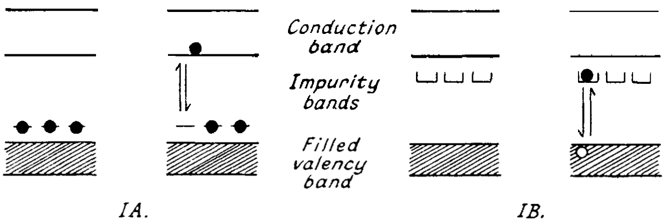
The electrical conductivity of the solid oxides ZnO, Fe_2O_3, Cr_2O_3, $ZnFe_2O_4$, $ZnCr_2O_4$, $MgFe_2O_4$, and $MgCr_2O_4$ has been determined at temperatures up to 1000°. Measurements in different gaseous atmospheres (air or oxygen, vacuum, hydrogen, or carbon monoxide) show that, as expected from general principles, ZnO, Fe_2O_3, $ZnFe_2O_4$, and $MgFe_2O_4$ are metal-excess (electron) conductors; Cr_2O_3 is an oxygen-excess or metal deficiency (positive hole) conductor. Zinc and magnesium chromites, potentially amphoteric, display positive hole conduction only.

The conductivity in each case responds reversibly to changes in oxygen pressure at temperatures below $0{\cdot}5T_m$ but above about $0{\cdot}25T_m$ (T_m = m. p. in ° K.), showing that impurity semiconduction can originate from the production of lattice defects in surface atom layers only. $ZnCr_2O_4$ at high temperatures shows evidence of changes in the concentration of a built-in stoicheiometric excess of oxygen in the air-sintered material. $ZnCr_2O_4$ formed by reaction of ZnO and Cr_2O_3 in hydrogen is a very poor conductor.

Three roughly defined ranges of temperature can be recognised as determining the properties of solid oxides. (A) A high-temperature range, in which self-diffusion permits of attainment of true thermodynamic equilibrium. (B) An intermediate range, in which lattice equilibrium is frozen, but surface mobility is manifest. (C) Temperatures too low for equilibration of the surface, all properties varying non-reproducibly. Semiconducting properties behave reversibly over temperature ranges A and B. The primary processes of chemical reaction by solid oxides involve (i) chemisorptive equilibrium of oxygen (or reducing gases) with fully tenanted or partially stripped crystal lattice surfaces, and (ii) diffusion processes whereby lattice defects migrate into the interior of the crystal lattice. The second stage can occur only in temperature range A.

According to the statistical thermodynamic model of solids (Schottky and Wagner, *Z. physikal. Chem.*, 1930, *B*, **11**, 165), an equilibrium must be set up, at temperatures where diffusion permits, between a solid metallic oxide and oxygen, present at a certain partial pressure in the surrounding gas phase. Any change in the partial pressure of oxygen should, theoretically, lead to changes—even if analytically indetectable—in the composition of the solid oxide, the direction of departure from the ideal composition depending upon the valency properties of the cations. For oxides derived from the highest valency state of a metal (*e.g.*, ZnO), the ideal formula represents an upper limiting composition. By loss of oxygen from the ideal crystal, an oxide is formed with an excess of metal atoms (*i.e.*, of Zn^{2+} cations + 2 electrons each); the excess electrons are trapped in the neighbourhood of an interstitial Zn^{2+} cation, or of a vacant anion site. In terms of the band theory of solids, such supernumerary metal atoms constitute filled impurity levels in the energy scheme of the crystal lattice, the distribution of electrons between the impurity levels and the conduction band being governed by a Boltzmann distribution (Fig. 1A). Similarly, for oxides derived from the lower of two valency states, the stoicheiometric

FIG. 1.



compound should represent a lower limiting composition; with increasing oxygen pressure, additional O^{2-} ions may be built on to the crystal lattice, electrons being withdrawn in corresponding number from cations which are thereby converted into cations of higher valency. These constitute empty impurity levels, or trapped positive holes; a temperature-dependent concentration of mobile positive holes results from the Boltzmann distribution of electrons between these levels and the filled valency band of the cations (Fig. 1B).

The conductivity of oxides at high temperatures thus depends upon the oxygen pressure in a manner which reflects the mechanism of conduction, and provides an extremely sensitive index of deviations from stoicheiometric composition. For simple oxides the dependence of conductivity upon oxygen pressure should evidently be predictable (Friederich, *Z. Physik*, 1925, **31**, 813; Meyer, *ibid.*, 1933, **85**, 278); some double oxides, *e.g.*, the chromite spinels, such as $ZnCr_2O_4$, might *a priori* be of the type designated by Schottky as amphoteric conductors, giving rise to impurity conduction of either kind. As is shown below, $ZnCr_2O_4$ and $MgCr_2O_4$ are, in fact, positive hole conductors under all conditions.

There is already an extensive literature relating to the conductivity of certain metallic oxides. In adding to this it has been our intention to elucidate further the nature of the equilibrium established between a solid oxide and the gas phase, and, in particular, the processes whereby equilibrium is established. The results may be correlated, not only with the theoretical model, but also with the considerable body of information amassed during recent years on the phenomenology of reactions involving solids.

EXPERIMENTAL.

Measurements of conductivity were made potentiometrically on sintered, compressed plates of the oxides. Jander and Stamm (*Z. anorg. Chem.*, 1930, **199**, 165) showed that the ionic contribution to the conductivity of a number of typical oxides and spinels, is, at the most, very small, so that direct current measurements are permissible. The specimens were made by compressing the individual oxides, or the reacted spinels, in a hardened steel die under a pressure of 5—10 tons per square inch, to form plates 25 mm. × 5 mm. × 1—1·5 mm. thick. Plates so obtained were, in most cases, very fragile and troublesome to handle; when they were heated at temperatures above the Tammann point (*e.g.*, to 1000—1050°, for 4—12 hours) the particles fritted together to give plates of excellent mechanical strength. Alternatively, the unreacted oxide mixtures were pelleted and then heated at 1000—1050°. The processes of reaction and fritting then proceeded concurrently, forming compact, hard plates.

FIG. 2.

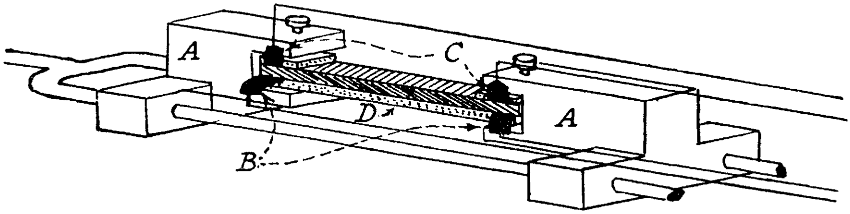
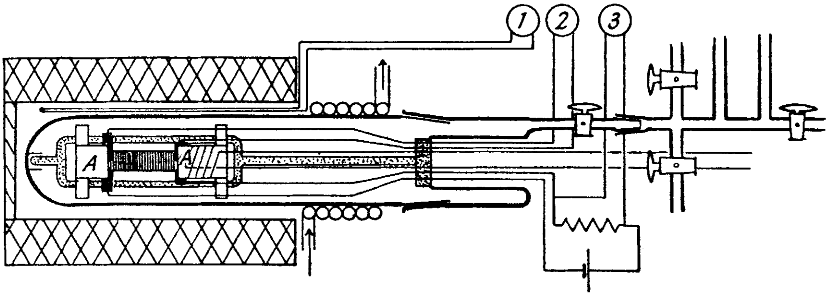


FIG. 3.



The plates were mounted between electrode holders (*A*, *A*, Figs. 2, 3) of heat-resistant steel (25% Cr, 20% Ni), supported by a silica-rod framework. Silica slips *D*, which served also as insulators, clamped the plates firmly in contact with two platinum-foil electrodes (*B*, *C*) at each end, one on either face; these served as current leads and potential leads respectively. The specimen, in its electrode assembly, was fitted through a silica-to-Pyrex standard ground joint into a silica jacket. The jacket was connected to vacuum pumps, manometer, McLeod gauge, and reservoirs for air, hydrogen, or carbon monoxide (Fig. 3).

Materials.—Zinc oxide. This was prepared by heating zinc oxalate at 550° (Rosencranz, *Z. physikal. Chem.*, 1931, *B*, **14**, 407).

Magnesium oxide. Magnesium hydroxide was precipitated from magnesium nitrate solution by means of a slight excess of sodium hydroxide. The precipitate was repeatedly washed by decantation with a large volume of water, dried at 110°, and ignited for 2 hrs. at 500°. According to Fricke and Lüke (*Z. Elektrochem.*, 1935, **41**, 174) the oxide so obtained is in a highly reactive state.

Ferric oxide. Amorphous ferric hydroxide was precipitated, by means of silica-free ammonia, from a solution made by oxidising A.R. ferrous sulphate with bromine. After prolonged washing by decantation, the precipitate was ignited at 450° for 3 hrs. The product is α-Fe_2O_3 in a reactive state (Fricke and Ackermann, *ibid.*, 1934, **40**, 630).

Chromic oxide. Chromic anhydride was dried at 150° (2 hrs.) in a current of dry, filtered air. The temperature was raised to 350° (2 hrs.) and ultimately to 450° (3 hrs.). The product was a very fine, dark green powder.

All materials were of A.R. quality, and distilled water was used throughout. The washing of precipitates was, in every case, prolonged for some time after the last detectable traces of electrolytes had been removed. After ignition, the oxides were very hygroscopic, and were stored in a desiccator over phosphoric oxide.

Mixtures of $ZnO + Fe_2O_3$, $MgO + Fe_2O_3$, $ZnO + Cr_2O_3$, $MgO + Cr_2O_3$ were made up in exactly stoicheiometric ratio, allowing for the ignition loss of the components. The oxides were intimately mixed by tumbling and grinding. It has been shown by various workers (Hüttig, Schröder, etc.) that spinel formation from ferric oxide proceeds freely above about 720°, the Tammann temperature of ferric oxide, at which the requisite freedom of diffusion of Fe^{3+} cations becomes appreciable. The reaction temperature of chromic oxide in air is rather lower. The oxide mixtures were, in general, submitted to reaction at 1050° for 24 hrs.; under these conditions reaction was substantially complete, as was verified analytically for several samples.

General Procedure.—The conductivity of each material was measured over a wide range of temperature, extending in each case above the Tammann temperature ($= 0{\cdot}5T_m$, where $T_m =$ m. p. in ° K.), since only above this temperature is the speed of self-diffusion enough to establish true equilibrium of lattice defects. Oxygen pressure was varied by measurement in oxygen (1 atm.), in air at the atmospheric or reduced pressures down to 10^{-3} to 10^{-4} mm., or in hyrodgen or carbon monoxide to establish very low effective partial pressures of oxygen.

RESULTS AND DISCUSSION.

For all the substances studied, the conductivity $\kappa(T)$ (at T° K.) conforms to the usual law

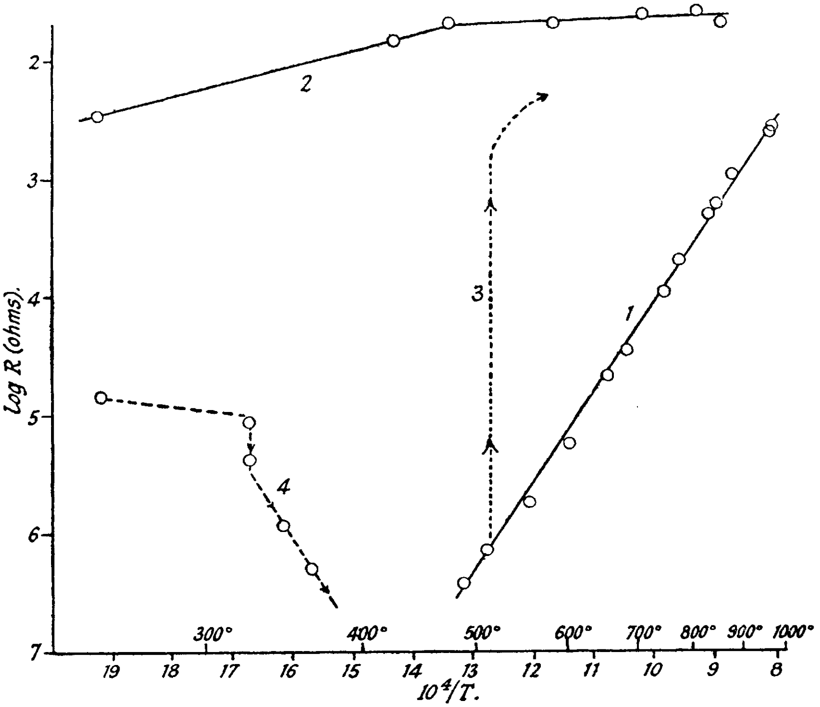
$$\kappa(T) = Ae^{-E/kT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

where A, involving the number of potentially conducting centres (and hence the stoicheiometric excess of metal or oxygen) and the mean free path of the conductivity electrons, is practically independent of the temperature, and E is an energy increment which determines the Boltzmann distribution of electrons between the impurity levels and the energy bands of the crystal. The effect of changes in partial pressure of oxygen is to control the concentration of impurity levels. Absolute values of $\kappa(T)$ have little significance, since the conducting cross section of a fritted granular material is very indeterminate and the contribution made by surface conduction (cf. Dubar, *Ann. Physique*, 1938, **9**, 5) is unknown. Through these and other factors, the values of κ found for semiconductors are notoriously dependent on past thermal history and structural factors. Nevertheless, results obtained for duplicate plates prepared from the same samples of oxide were satisfactorily reproducible, as the appended curves show.

Zinc Oxide.—Measurements on zinc oxide at high temperatures have been made previously by Jander and Stamm (*loc. cit.*), von Baumbach and Wagner (*Z. physikal. Chem.*, 1933, *B*, **22**, 199) and Miller (*Physical Rev.*, 1941, **60**, 890). As expected from the Friederich–Meyer rule, and as verified by von Baumbach and Wagner, the conductivity is greatly enhanced at low pressures of oxygen (cf. curves 1 and 2, Fig. 4), the enhancement being truly reversible at high temperatures. Von Baumbach and Wagner adduced sound evidence that the augmented conductivity could not be attributed to the formation of free zinc, and they considered that the variation of κ with oxygen pressure, between 10 and 760 mm. of oxygen, and at one temperature (650°) agreed with Wagner's model for non-stoicheiometric conducting solids (*Z. physikal. Chem.*, 1933, *B*, **22**, 181), which leads to the relation $\log \kappa = B - \frac{1}{6} \log p_{O_2}$. However two assumptions are implicit in Wagner's model: (*a*) that changes in conductivity arise solely from changes in the temperature-independent factor A of equation (1), this being taken as directly proportional to the concentration of excess metal atoms; (*b*) that one can ignore the surface, assuming that true equilibrium is attained within a crystal lattice of infinite extent.

Our results, over a wider range of oxygen pressure, and at temperatures between 470° and 1000°, show clearly, however, that the energy increment E of the conduction process changes greatly [curve 2, p_{O_2} about 10^{-4} mm., $E = 0{\cdot}038$ e.v., $\kappa(600°) = 0{\cdot}51$; curve 1, $p_{O_2} = 150$ mm., $E = 1{\cdot}60$ e.v., $\kappa(600°) = 1{\cdot}5 \times 10^{-4}$], the profound change in conductivity arising principally from this factor. The detailed relation between the conductivity of zinc oxide and the oxygen pressure is of some theoretical interest and importance, and will be dealt with in a later paper. Fig. 4 accordingly represents results relating to the two extreme conditions only. The incorrectness of the second assumption is discussed below, in relation to the results obtained with other oxides. We may here draw attention to curve 3, representing the slow, progressive rise of conductivity of a zinc oxide plate at 500° when the oxygen pressure was reduced from 150 to 10^{-4} mm. Response to any change of oxygen pressure, and attainment of equilibrium with the environment, was not achieved at temperatures much lower than 500°; at high temperatures, change of resistance on evacuation or on admission of oxygen was immediate. The melting point of zinc oxide is probably about 2000° (Hüttig and Toischer, *Z. anorg. Chem.*, 1932, **207**, 273), so that processes involving self-diffusion through the crystal lattice can hardly be important below about 860°. The inference is clear that at 500°, at least, the process which gives rise to the highly conducting state can only involve the superficial layers of atoms of the crystalline particles.

FIG. 4.

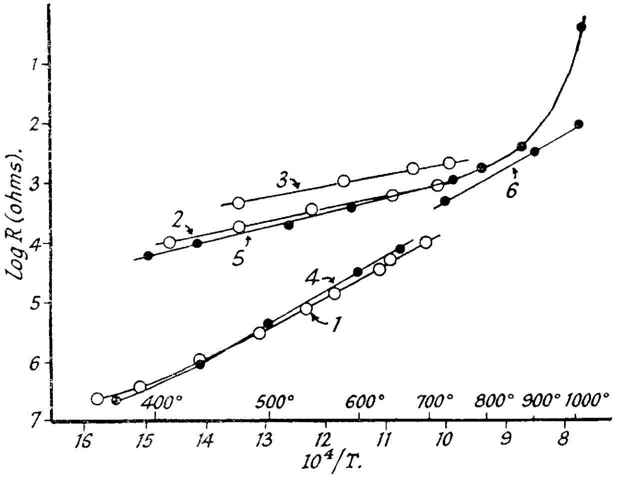


It may be noted, further, that in none of our experiments with zinc oxide prepared from zinc oxalate did we obtain the inflexion of curvature of the conductivity–temperature curve found by Jander and Stamm, von Baumbach and Wagner, and Miller. Von Baumbach and Wagner state that the measurements were reproducible with both ascending and descending temperatures. As the inflexion was found at temperatures where diffusion processes may just become important, it may possibly involve some factor connected with the interplay of surface and bulk processes, in respect of which our " active " zinc oxide differed from the zinc oxides of unspecified history used by the other workers.

Ferric Oxide.—Results for two plates are summarised in Fig. 5. Variation of conductivity with oxygen pressure shows that, as would be expected, ferric oxide is a metal-excess conductor. No drift of conductivity occurred on prolonged heating in a vacuum at 730°, as would have been the case if magnetite had been formed as a new phase (cf. plate 2). A second plate, similarly treated in air (curve 4) and in vacuum (curve 5) behaved similarly, but on raising the temperature to 1000°, formation of magnetite in continually increasing amount was shown by a rapid 100-fold rise in the conductivity; reversal of this dissociation, on admission of air, is shown by curve 6.

Wagner and Koch (*Z. physikal. Chem.*, 1936, *B*, **32**, 439) measured the conductivity of ferric oxide at 1000° only, and concluded that it was independent of the oxygen pressure. As may be seen from Fig. 5, curves 1 and 2, 4 and 5 would, in fact, intersect rather above 1000°, so that at that temperature the effect of reducing the oxygen pressure would be but small. The inference that ferric oxide is an intrinsic semiconductor is, therefore, unjustified, being based upon inadequate experimental material. It is, however, surprising that Wagner and Koch did not observe any thermal decomposition of the ferric oxide at that temperature.

FIG. 5.



Fe_2O_3.

Plate I. Heated in air to 702°.	Curve 1 :	E = 1·06 e.v.,	$\kappa(600°) = 5{\cdot}5 \times 10^{-4}$
Evacuated at 700° to 10^{-3} mm.	Curve 2 :	0·38 e.v.	$9{\cdot}7 \times 10^{-3}$
Evacuated at 410° to 10^{-5} mm.	Curve 3 :	0·38 e.v.	$2{\cdot}4 \times 10^{-2}$

In accord with the melting point of ferric oxide (*ca.* 1570° c.), processes of reaction, etc., which depend on self-diffusion are imperceptible below 650°, and become rapid above 700°. The conductivity of ferric oxide responds to changes in oxygen pressure at 410°, whereas formation of magnetite—a process involving the diffusion of cations through the crystal lattice—was observed only at temperatures well above 720°.

Our observations have some bearing on the problem of the mutual miscibility of α-ferric oxide and magnetite. Sosman and Hostetter (*J. Amer. Chem. Soc.*, 1916, **38**, 807) and, later, White (*Iron and Steel Inst.*, Carnegie Schol. Mem., 1938, **27**, 1) concluded from tensimetric evidence that between 1100° and 1450° the Fe_2O_3 and Fe_3O_4 phases each had a fairly wide range of existence. Sosman's later work (Greig, Posnjak, Merwin, and Sosman, *Amer. J. Sci.*, 1935, **30**, 239) indicated, however, that when true equilibrium was attained by proper annealing, the degree of mutual solid solution of the two oxides was extremely small. Conductivity measurements are extremely sensitive to the formation of the highly conducting magnetite as a second phase, and to the growth of the amount of magnetite. Our observations strongly suggested that magnetite was formed as a separate phase when a very small stoicheiometric proportion of oxygen had been removed from the ferric oxide; although not conclusive, this would be in accord with the work of Greig, Posnjak, Merwin, and Sosman.

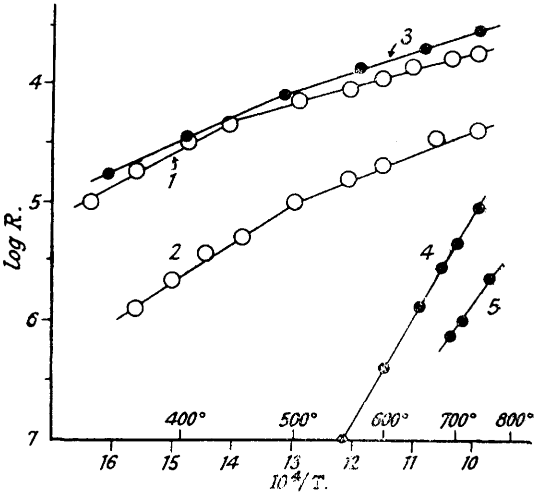
Chromic Oxide.—The conductivity of chromic oxide has apparently not been recorded previously, but the relative stabilities of the valency states of chromium indicate that the oxide should be an oxygen-excess (positive hole) conductor. This is confirmed by the results summarised in Fig. 6.

Curve 1 [E = 0·60 e.v., below 450°; E = 0·30 e.v., $\kappa(600°) = 3{\cdot}7 \times 10^{-3}$ at higher temps.] represents the conductivity of plate 1 in air; curve 2 [E = 0·67 e.v., below 500°; E = 0·50 e.v., $\kappa(600°) = 7{\cdot}4 \times 10^{-4}$ at higher temps.] that obtained when the oxygen pressure was reduced (at 740°) to about 10^{-3} mm. The decrease in conductivity corresponds to a decrease in the stoicheiometric excess of oxygen, and consequent conversion of higher-valent chromium cations into Cr^{3+} cations. Much lower effective partial pressures of oxygen are obtainable by admission of hydrogen or carbon monoxide; these do, in fact, lower the conductivity still further. Thus, at 740°, the resistance of plate 1 in different gaseous atmospheres varied successively as follows :

In air (p_{O_2} = 150 mm.)	$5{\cdot}2 \times 10^3$ ohms.
In vacuum (p_{O_2} about 10^{-3} mm.)	$2{\cdot}5 \times 10^4$,,
In 2 cm. electrolytic hydrogen (0·1% O_2, *i.e.*, ultimate $p_{H_2} : p_{H_2O}$ = about 500)	$3{\cdot}0 \times 10^5$,,
In 10 cm. electrolytic hydrogen	$9{\cdot}5 \times 10^5$,,
In 70 cm. oxygen	$5{\cdot}2 \times 10^3$,,
In 3 cm. carbon monoxide	$8{\cdot}0 \times 10^5$,,

The conductivity of " reduced " chromic oxide was more fully investigated on a second specimen (conductivity in air, curve 3), for which the conductivity curves in 2-cm. pressure of carbon monoxide, admitted at 740° [curve 4, E = 1·79 e.v., $\kappa(600°) = 1{\cdot}26 \times 10^{-3}$] and in 20 cm. of hydrogen [curve 5, E = 1·38 e.v., $\kappa(600°) = 4{\cdot}4 \times 10^{-3}$] are shown in Fig. 6.

FIG. 6.



Cr_2O_3.

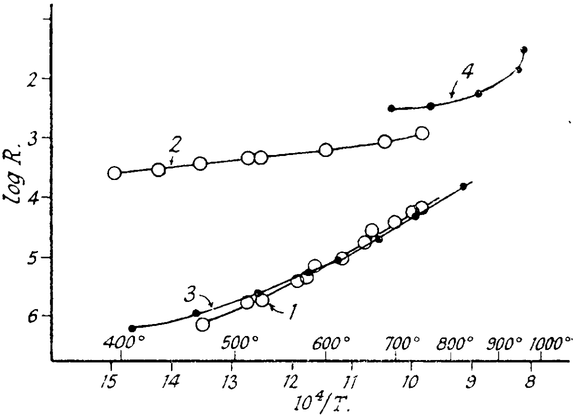
Chromic oxide, as prepared and ignited in air, evidently owes its conductivity to a small stoicheiometric excess of oxygen, and the states giving rise to the conductivity curves 2, 4, and 5 represent oxide approximating increasingly closely to the ideal composition Cr_2O_3. Nevertheless, the rapid response of the conductivity to changes in the oxygen pressure, and the fact that the conductivity is the same in air and in oxygen at 70 cm. pressure, preclude the view that any extensive reaction is involved in the change from the badly conducting " reduced " oxide to the better conducting oxide formed in air. Harbard and King (*J.*, 1938, 955; see also Cameron, Harbard, and King, *J.*, 1939, 55, for a bibliography of reported non-stoicheiometric oxides of chromium) stated that chromic oxide formed by the thermal decomposition of ammonium dichromate had the approximate composition $Cr_2O_{3\cdot13}$. It would appear from their paper that this was slowly converted into Cr_2O_3 on prolonged ignition in air, and was rapidly reduced in hydrogen, these changes being irreversible (since the ignition of Hg_2CrO_4 in air furnishes stoicheiometric Cr_2O_3). The processes involved in the change from curve 1 (Fig. 6) to curves 2, 4, or 5 were, however, reversible. We conclude that the oxide obtained by Harbard and King was metastable, and was not indicative of the stable range of existence of the Cr_2O_3 phase. Our results suggest that the range of composition of this phase is, in fact, only narrow. A minute stoicheiometric excess of oxygen would suffice to account for the observed conductivity.

Zinc Ferrite.—Neither cation in this structure is normally capable of any increase in valency, so that $ZnFe_2O_4$ should be an electron (metal excess) conductor. This is confirmed by the results plotted in Fig. 7. Curve 1 [combining three sets of measurements; E = 1·22 e.v., $\kappa(600°) = 8{\cdot}3 \times 10^{-5}$] represents the conductivity in air, curve 2 [E = 0·25 e.v., $\kappa(600°) = 7{\cdot}9 \times 10^{-5}$] that in vacuum. At the highest temperature of curve 2 (734°) the conductivity showed no drift on prolonged heating in vacuum. The change from curve 1 to curve 2 was reversible. A second plate (conductivity in air, curve 3), when heated to 960° in vacuum, showed a pronounced drift in conductivity which was not perfectly reversible on cooling, nor was the original low conductivity restored on admission of air; at 710° a slow reaction with oxygen was apparent, in addition to the initial rapid change. The increase of conductivity clearly indicates some chemical dissociation, bringing about a permanent change of composition. Schröder (*Z. Elektrochem.*, 1940, **46**, 680; 1941, **47**, 196) found that $CdFe_2O_4$ underwent decomposition, attended with a loss of cadmium, above 900°, although Schröder and Schmäh (*ibid.*, 1942, **48**, 241, 301) and Schröder, Lähr, and Müller (*ibid.*, 1943, **49**, 38) found no evidence of any similar reaction with $ZnFe_2O_4$. However, under the conditions of our conductivity measurements, a specimen of zinc ferrite weighing 2·51 g. underwent a loss of weight of 0·06 g. in 4 hours at 1000° and a dynamic vacuum (p_{O_2} about 10^{-4} mm.). The product was black and had a high conductivity. The composition (as determined by direct analysis) changed from $Fe_2O_3 : ZnO = 1·055$ initially to $Fe_2O_3 : ZnO = 1·143$ ultimately, indicating that zinc (or zinc oxide) and oxygen had been lost simultaneously, according to the equation

$$ZnFe_2O_4 \longrightarrow \underbrace{(1 - x)ZnFe_2O_4 + \tfrac{2}{3}xFeFe_2O_4}_{\text{Mixed crystals.}} + xZnO + \tfrac{1}{6}xO_2$$

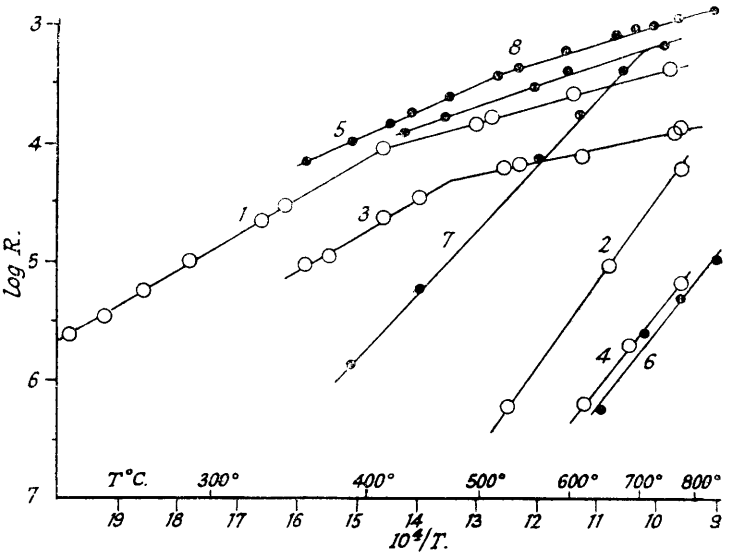
According to this equation, the composition corresponding to the observed loss in weight would be $Fe_2O_3 : ZnO = 1·135$, in fair agreement with the observed change.

Fig. 7.



$ZnFe_2O_4$.

Fig. 8.



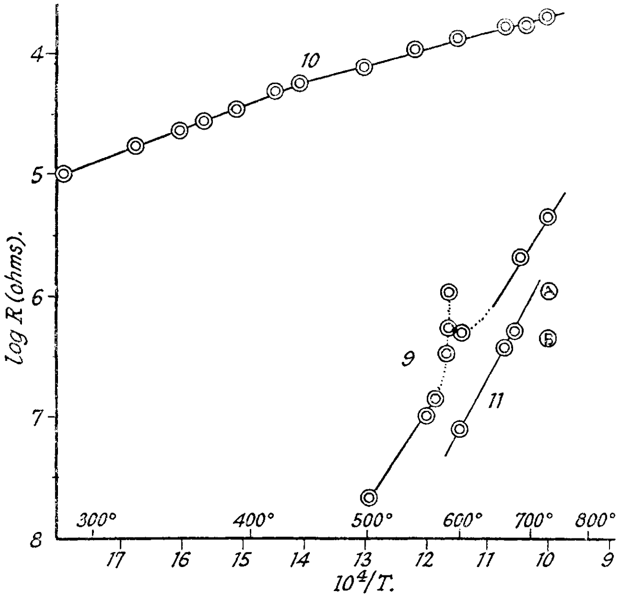
$ZnCr_2O_4$—I.

Zinc Chromite.—Some interest attaches to the properties of $ZnCr_2O_4$ since its surface properties and catalytic properties have been extensively studied, and also because the phenomena associated with the union of ZnO and Cr_2O_3 have been repeatedly investigated under varied experimental conditions. Data for two plates, sintered in air, are summarised in Fig. 8. Loss of oxygen, with formation of a stoicheiometric excess of interstitial zinc, or the building on of excess oxygen atoms, with corresponding increase in the valency of Cr^{3+} cations, would *a priori* both be possible. The results show that zinc chromite is solely a positive hole conductor, due to the latter mechanism, and they suggest that a small stoicheiometric excess of oxygen must already be present in $ZnCr_2O_4$ formed by reaction in air.

The initial conductivity, in air, of plate 1 [curve 1, $E = 0{\cdot}59$ e.v., below 420°; $E = 0{\cdot}29$ e.v., $\kappa(600°) = 6{\cdot}5 \times 10^{-3}$ at higher temperatures] was substantially decreased in vacuum [curve 2, $E = 1{\cdot}47$ e.v., $\kappa(600°) = 6{\cdot}3 \times 10^{-5}$]. Admission of air at 530° restored the high conductivity (curve 3). Although the original conductivity of curve 1 was not completely regained, even after prolonged heating in air at 800°, the oxidised state represented by curve 3 was completely reproducible. In hydrogen [10 mm. pressure, admitted at 750°; curve 4, $E = 1{\cdot}23$ e.v., $\kappa(600°) = 1{\cdot}3 \times 10^{-5}$] the conductivity was reduced below the value obtained in vacuum. Readmission of oxygen at 620° restored the conductivity to that of curve 3.

A second plate (conductivity in air, curve 5) was heated in hydrogen (100 mm.) at 835°. The immediate initial increase in resistance of the plate was followed by a further effect, increasing progressively with time; after 14 hours the conductivity–temperature curve was as shown in curve 6 [$E = 1{\cdot}37$ e.v., $\kappa(600°) = 6{\cdot}8 \times 10^{-6}$]. When air was readmitted at the ordinary temperature, a partial restoration of conductivity was observed [curve 7, $E = 1{\cdot}08$ e.v., $\kappa(600°) = 3{\cdot}5 \times 10^{-3}$]; after heating in air at 800°, the original conductivity of the air-sintered spinel was essentially restored (curve 8).

FIG. 9.



$ZnCr_2O_4$—II.

The hypothesis that a certain concentration of positive holes, *i.e.*, a small stoicheiometric excess of oxygen, is built into the crystal lattice of air-sintered $ZnCr_2O_4$ would account for the prolonged, slow interaction with hydrogen at 830° (a temperature probably about 100° above the Tammann point), and would enable the relation between curves 7 and 8, as also perhaps the discontinuities of slope of curves 1, 3, and 5, to be interpreted in terms of the interplay of surface and bulk-phase reactions, as discussed below. It would, then, be expected that zinc oxide and chromic oxide should react, in the absence of oxygen, to form a spinel of lower conductivity. This is, indeed, the case. Material sintered in hydrogen at 1050° had an extremely low initial conductivity; after exposure to the air at the ordinary temperature, the conductivity on heating in a vacuum (p_{O_2} about 10^{-4} mm.) followed curve 9 (Fig. 9) [$E = 1{\cdot}61$ e.v., $\kappa(600°) = 1{\cdot}05 \times 10^{-5}$]. Under these conditions the conductivity was comparable with that of the previous plate in hydrogen, but the higher value of E is indicative of a smaller concentration of built-in positive holes; the effect of exposure to the small partial pressure of oxygen in the evacuated apparatus would be to displace the conductivity curve, as indicated by the—much larger—displacement of curve 7 relative to curve 6 (Fig. 8). An accidental small leakage of air at 510° produced a 10-fold increase of conductivity; admission of hydrogen (50 mm. pressure) reduced the zinc chromite to its original state. Air at 730° immediately raised the conductivity to a value somewhat less than that of air-sintered spinel [curve 10, $E = 0{\cdot}39$ e.v., below 440°; $E = 0{\cdot}26$ e.v., $\kappa(600°) = 3{\cdot}4 \times 10^{-3}$ at higher temperatures]. Finally, prolonged treatment with hydrogen or with carbon monoxide [curve 11, $E = 1{\cdot}83$ e.v., $\kappa(600°) = 2{\cdot}6 \times 10^{-6}$] lowered the conductivity still further, to an extent dependent on the partial pressure of reducing gas. Thus, the points *A* and *B* (Fig. 9) represent the resistance at 730° in 220 mm. pressure of hydrogen (after 16 hours) and in 410 mm. pressure of hydrogen (after 10 hours), respectively. These may be compared with the corresponding point on curve 9, in hydrogen at 50 mm. pressure.

These results can be correlated with experimental data on the formation of zinc chromite from the constituent oxides. The extensive work of Hüttig and of W. Jander, in particular, has shown that in the course of spinel formation and in similar reactions between solids, the changes brought about successively in a variety of physical and chemical properties provide an indication of the onset of surface mobility and of bulk diffusion respectively. The temperatures corresponding to the successive stages of the reaction process are, in general, related to the absolute melting point (T_m) of the compounds concerned, and can in fact be represented fairly well in terms of a common reduced temperature scale, expressed as T/T_m. In the formation of spinels, the mobility of the tervalent cations appears to be the factor chiefly determining the temperature of successive stages. Hence, the formation of ferrite spinels (m. p. of Fe_2O_3 = 1570°) should proceed throughout at lower temperatures than the formation of chromite spinels (m. p. of Cr_2O_3 = 1990°). Hüttig, Radler, and Kittel (*Z. Elektrochem.*, 1932, **38**, 442; Hüttig, *ibid.*, 1935, **41**, 527) found, however, that whereas the temperatures indicative of surface mobility, incipient inner diffusion, and spinel crystallisation in the system $ZnO + Fe_2O_3$ were 400—450°, less than 625°, and 675° respectively, the corresponding temperatures for $ZnO + Cr_2O_3$, heated in air, were 300°, 330—350°, and 400—500°. Jander and Weitendorf (*ibid.*, p. 435) showed that chromate could be leached out of the surface of such mixtures after they had been heated in air at temperatures as low as 400°, and also out of Cr_2O_3 itself after ignition in the presence of oxygen. They considered that the reaction $2ZnO + Cr_2O_3 + \frac{3}{2}O_2 \longrightarrow 2ZnCrO_4$ proceeded faster than the direct union to form $ZnCr_2O_4$. In hydrogen or in vacuum they found that the maximum surface activity was attained after heating at 500—550°, *i.e.*, at temperatures higher than obtain in the $ZnO + Fe_2O_3$ system.

An alternative interpretation of these results, which emerges from our work, is that chromic oxide and zinc chromite in air pick up a stoicheiometric excess of oxygen, which confers on them the observed electrical conductivity, but does not necessarily lead to the formation of $ZnCrO_4$ or—less likely still—CrO_3 as separate phases. The oxidising properties, or the extraction of chromate ion on leaching, could result from a disproportionation process, akin to the selective extraction of Mn^{2+} or Pb^{2+} when the higher oxides of manganese or lead are leached with nitric acid. It has been shown (Wagner, *Z. physikal. Chem.*, 1931, Bodenstein Festschr., 177; Anderson and Richards, *J.*, 1946, 537) that small departures from ideal stoicheiometric composition can result in a marked increase in rates of diffusion in solids, so that the greater reactivity of chromic oxide in the presence of oxygen might be interpreted as due to this factor. The influence of the gaseous atmosphere upon the conductivity and on the reactivity of the oxides would then both arise from the same primary process of interaction between the solid oxides and the gaseous phase.

It may be noted that the conductivity curve for zinc chromite given by Verwey, Haayman, and Romeijn (*J. Chem. Physics* 1947, **15**, 181) accords in slope with our air-sintered material. Evidently through fritting their $Fe_3O_4 + ZnCr_2O_4$ solid solutions in an atmosphere containing sufficient oxygen to inhibit the decomposition of the magnetite, they incorporated positive holes in their mixed crystals rich in zinc chromite. Their measurements on $Fe_3O_4 + ZnCr_2O_4$ and $Fe_3O_4 + MgCr_2O_4$ systems must, accordingly, refer to material capable of conduction both by free electrons and by positive holes. The operation of this second mechanism, with a higher activation energy, probably accounts for the form of their conductivity curves for solid solutions containing 50% and 60% of zinc chromite.

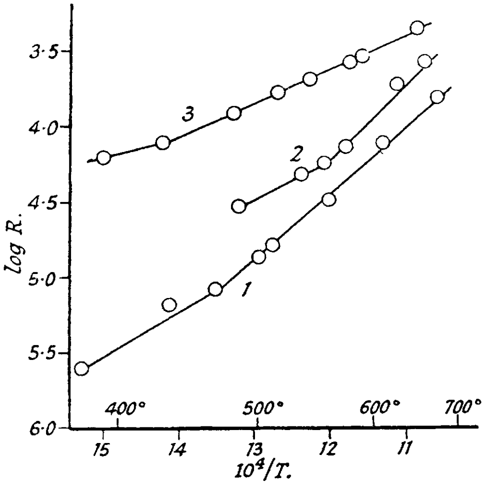
Magnesium Ferrite.—Measurements on the magnesium spinels were made at an early stage in the work, and were not extended over such a wide range of conditions as those on zinc spinels. The magnesium compounds resembled the latter in behaviour. Magnesium ferrite is an electron (metal excess) conductor. Curve 1 (Fig. 10, $E = 0{\cdot}92$ e.v.) represents the conductivity in air

(1 atm.), curve 3 ($E = 0{\cdot}46$ e.v.) that in vacuum, and curve 2 that in 4 mm. pressure of oxygen. Changes of conductivity with oxygen pressure were quite reversible.

Magnesium Chromite.—This is, as expected, a positive hole conductor. Measurements for an air-sintered specimen are shown in Fig. 11, on which is indicated also (dotted) the conductivity curve found by Jander and Stamm (*loc. cit.*), whose experimental method would inevitably include high contact resistances in the measured values, leading to a displacement of their curve relative to ours; the slope of their curve agrees with that found by us. Curve 1 (Fig. 11) represents the conductivity in air ($E = 0{\cdot}75$ e.v.), and curve 2 conductivity in 0·1 mm. pressure of air, after evacuation at 650° ($E = 0{\cdot}85$ e.v.).

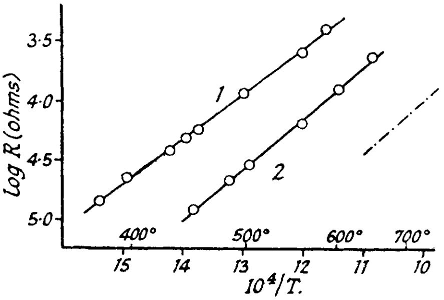
The results just summarised can be related to the recent discussion by Verwey and Heilmann (*J. Chem. Physics*, 1947, **15**, 174) and Verwey, Haaymann, and Romeijn (*loc. cit.*) of the relation between the particular structure of magnetite and its conducting properties. This compound, as they have shown, is an " inversed " spinel, $Fe^{3+}(Fe^{2+}Fe^{3+})O_4$, and they attribute its very high electronic conductivity to the facility with which an electron can pass, by a series of switches, along those lattice rows containing both Fe^{3+} and Fe^{2+} cations in the crystallographically equivalent positions of 6-fold co-ordination (Verwey and de Boer, *Rec. Trav. chim.*, 1936, **55**, 531). Zinc ferrite and zinc chromite are " normal " spinels, with the octahedrally co-ordinated cation positions occupied exclusively by the tervalent cations. The stoicheiometric compounds have, as our results indicate, at most a very low conductivity. When, by incorporation of a small stoicheiometric excess of oxygen, zinc chromite becomes a positive hole impurity conductor, the raising of some Cr^{3+} cations to a higher valency state realises the condition envisaged by Verwey, with chromium ions of mixed valencies in crystallographically equivalent positions, capable of propagating an electron switch along the [110] lattice rows. In zinc ferrite we may, by analogy, reasonably postulate that the excess electrons, remaining from the loss of a small proportion of oxygen from the crystal lattice, are accommodated by transformation of Fe^{3+} cations to Fe^{2+} cations, again providing the possibility of electron transference by Verwey's mechanism.

FIG. 10.



$MgFe_2O_4$.

FIG. 11.

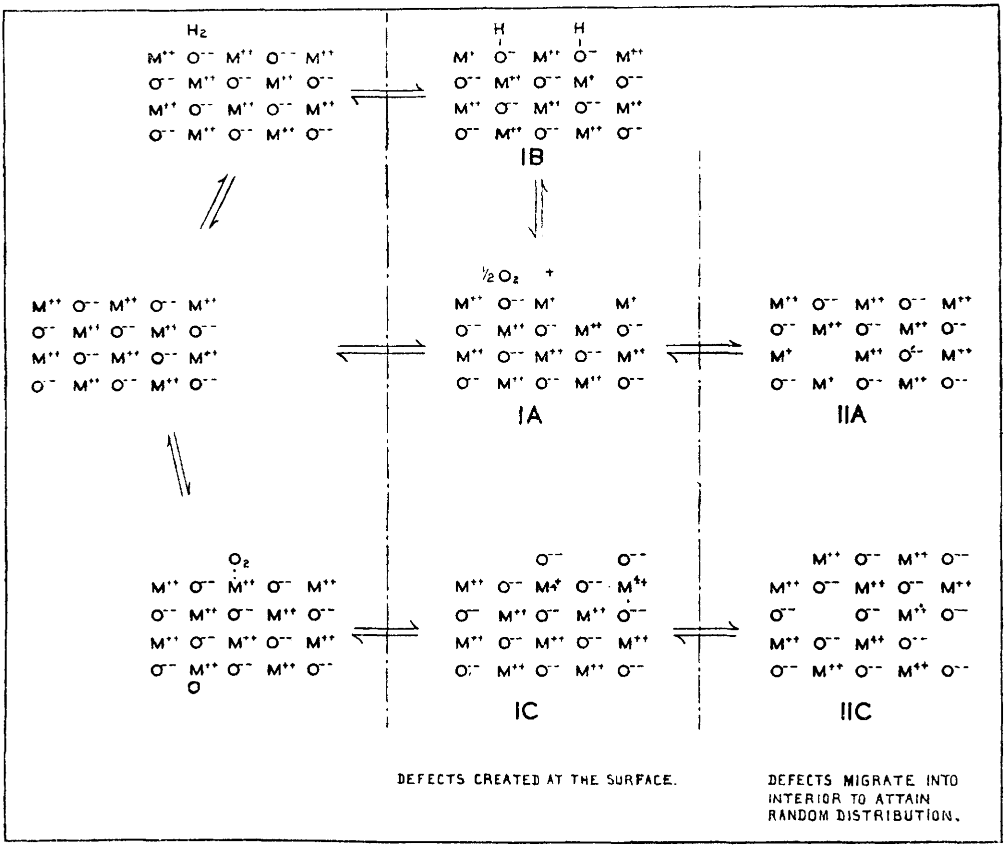


$MgCr_2O_4$.

Conductivity due to the presence of interconvertible cations of mixed valency in the crystallographically equivalent tetrahedral positions is apparently less readily exhibited; possibly the longer spacing between such positions makes the requisite electronic transitions less probable. Thus, zinc chromite shows no sign of excess electron conduction, even in hydrogen at 800° (compare zinc oxide). It may be significant in this connection that we have also found $NiAl_2O_4$ to be a very poor conductor. This is a " normal " spinel (Verwey and Heilmann, *loc. cit.*), with all the Ni^{2+} cations in the tetrahedral positions. By analogy with the oxide, which was shown by Klemm and Hass (*Z. anorg. Chem.*, 1934, **219**, 82) to be non-stoicheiometric, NiO_{1+x}, it might be expected that this nickel spinel would show a marked tendency for positive hole conduction, through the elevation of some of the nickel cations to a higher valency state. However, $NiAl_2O_4$ after being sintered in air at 1000° has a low conductivity at temperatures up to 735°, at least; the conductivity is rather worse in a vacuum than in air.

The observations summarised above have some bearing on a fundamental problem raised by Meyer and Möglich (*Z. Elektrochem.*, 1939, **45**, 68) and Schottky (*ibid.*, p. 69) : that of the temperature range over which the concept of a solid in statistical thermodynamic equilibrium, both internally and with its environment, is of valid application. Attainment of such equilibrium necessarily involves two distinct stages, involving the surface and the interior of the crystal lattice, respectively. These two stages together constitute the fundamental processes in chemical interactions between a gas and a solid phase.

FIG. 12.

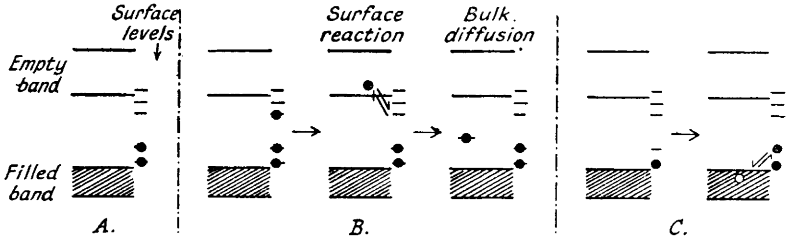


(I) The primary process of interaction involves the surface layers of atoms only, whereby in oxidation and reduction processes lattice defects (in the form of ions of " abnormal " charge) are formed. With oxides behaving as reduction semiconductors (ZnO, $ZnFe_2O_4$, etc.), as is diagrammatically represented in Fig. 12, oxygen may be evaporated directly from the surface of the crystal (I, A) or O^{2-} ions may be converted to OH^- ions through the chemisorption of hydrogen (I, B). In the latter case, subsequent loss of a molecule of water between two adjacent OH^- ions leads to the same ultimate state with one anion site vacant and two additional electrons accommodated on adjacent cations. With oxidation semiconductors (Cr_2O_3, $ZnCr_2O_4$) new anion sites are filled through the chemisorption of oxygen (I, C). The essential feature is that none of these processes depends on the mobility and redistribution of ions or atoms *within* the crystal lattice.

(II) In a state of thermodynamic equilibrium, there will (to a first approximation) be a random distribution of lattice defects throughout the crystal lattice, with a somewhat different must therefore diffuse into the interior of the crystal as in (II, A, II, C) in order that equilibrium may be attained. This step involves place-exchange of either anions or cations, and so can hardly be achieved below the Tammann temperature in the case of nearly stoicheiometric solids, although where marked deviations from stoicheiometric composition occur, self-diffusion may be important at lower temperatures. Hence, as pointed out by Meyer and Möglich, arguments based on attainment of thermodynamic equilibrium are valid only for investigations of semiconductors at sufficiently high temperatures. Meyer and Möglich accordingly distinguished between this high-temperature range ($T > 0{\cdot}5T_m$) and those lower temperatures which are necessarily characterised by frozen or false equilibria.

Our results show clearly that the processes of interaction of oxides with oxygen or hydrogen, leading to large changes in conductivity, occur freely and reversibly at temperatures so low that processes involving lattice diffusion can be excluded from consideration—*e.g.*, the increase in conductivity of zinc oxide in a vacuum at 500°, and the oxidation of zinc chromite at 530°. Further, when the potential leads from a zinc chromite plate were connected to an oscillograph, the changes in conductivity at 760° on alternate evacuation or admission of oxygen or hydrogen were seen to be sensibly instantaneous. The distinction between the immediate change in conductivity and the slower prolonged drift which ensued in hydrogen or carbon monoxide was very clear. Clearly (*a*) an excess or deficit of electrons resulting from changes in the population of the *surface layers* of atoms is sufficient to account for changes in conductivity of the magnitude found, without necessarily involving any change in bulk composition, and (*b*) such changes proceed rapidly and reversibly at temperatures convenient for the study of semiconducting properties. This last point has, unfortunately, been neglected by several recent workers—*e.g.*, in the work of Miller (*loc. cit.*) on zinc oxide, and of Feldman (*Physical Rev.*, **1943**, **64**, **113**) on cuprous oxide—who have attempted to " freeze " the concentration of stoicheiometric lattice defects.

Fig. 13.



Theoretical discussions of impurity semiconductors have been based on the idealised model of impurity levels in an infinite crystal lattice. Möglich and Rompe (*Physikal. Z.*, 1943, **44**, 77), in a paper on the rôle of the surface in the reactivity of solids, have suggested a model that can be extended to interpret the observed relations between surface reactions of the type considered above, and the conductivity of solids. They point out that the permitted energies of electrons at the surface of a crystal are not identical with those of the three-dimensionally periodic lattice as a whole, so that for a finite, stoicheiometric crystal the energy scheme must include filled and unfilled surface levels, in addition to the energy bands of the crystal lattice (Fig. 13, *A*). Excitation of electrons in the surface levels (*e.g.*, photochemically) will be reflected in a change in the Boltzmann distribution of electrons between the filled band, the conduction band, and filled or vacant impurity levels of the crystal lattice. Conversely, the population and energy distribution of electrons in the surface levels—and hence the reactivity and properties of the surface (cf. Garner, *Chem. and Ind.*, 1947, 132)—are profoundly modified by changes in the concentration of impurity levels within the crystal. When oxygen is evaporated out of, or built on to, the surface of an originally stoicheiometric oxide, the net effect is that electrons are added to (Fig. 13, *B*) or removed from (Fig. 13, *C*) the surface levels. Excitation of electrons to the conduction band, or out of the filled valency band, then follows in consequence of the thermal energy of the crystal. If the temperature permits of the necessary ionic mobility, the formation of new impurity centres *within* the crystal, to which a transference of electrons from surface levels takes place, will then ensue. There is thus no paradox involved in the observation that the semiconducting properties may change reversibly and reproducibly as a result of processes which affect only the surface, without attainment of true equilibrium.

There is, as has been stated above, a lower limit of temperature below which equilibration of the surface with the gas phase does not occur with sensible speed. At lower temperatures conducting properties are not reproducible, being entirely dependent on the previous thermal history of each specimen, and showing a drift towards equilibrium values with the onset of surface mobility. Our observations indicate that the condition of reproducibility is achieved above about $0{\cdot}25$—$0{\cdot}3T_m$. Many studies of semiconductors—including nearly all measurements of Hall effect and electronic mean free paths—have been made at temperatures below $0{\cdot}3T_m$; the theoretical significance of such work is very doubtful.

We accordingly recognise three ranges of temperature which determine the properties and reactivity of solid oxides and similar compounds.

(i) Temperatures above about $0{\cdot}5T_m$, at which attainment of true equilibrium is possible. Lattice defects created at the surface can migrate into the crystal lattice, so that a heterogeneous reaction can proceed to completion.

(ii) An intermediate temperature range, roughly $0{\cdot}3T_m$ to $0{\cdot}5T_m$, at which the surface, but not the bulk phase, can interact reversibly with the gaseous atmosphere. Only if the solid has a stoicheiometric range wide enough to produce large changes in the magnitude of the diffusion coefficient can reaction in the ordinary sense proceed. In general, reaction with a gas or with other solids (*e.g.*, spinel formation) can give rise only to surface compounds.

(iii) A low temperature range, below $0{\cdot}3T_m$, in which surface equilibrium is also frozen.

These views accord entirely with those of Garner (*loc. cit.*), based on a different experimental approach. The reversible pick-up of oxygen from, or loss of oxygen to, the gas phase can be regarded as a process of chemisorption or desorption, the rate of which is dependent on the temperature and the activation energy of the sorption process. Attainment of adsorptive equilibrium implies a degree of mobility of the surface atom layers, and it is therefore not fortuitous that the temperature above which the semiconducting properties display reversibility should be close to that at which, in Hüttig's studies of the phenomenology of fritting processes and solid reactions, the change in properties of solids gives evidence of surface diffusion processes.

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