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XLIII. The electrical conductivity of metallic oxides

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Summary of Results.

(1) For rapidly alternating currents a flame containing an alkali-salt vapour behaves like an insulating medium having a high specific inductive capacity.

(2) The conductivity of different alkali-salt vapours in a flame for rapidly alternating currents as measured by the apparent capacity of platinum electrodes immersed in the flame varies as the square root of the conductivity of the same salt vapours for steady currents. This result confirms the view that the negative ions from all salts have the same velocity.

(3) The apparent capacity varies nearly inversely as the square root of the maximum applied P.D.

(4) The apparent capacity is nearly independent of the number of alternations per second.

(5) The apparent capacity is nearly independent of the distance between the electrodes.

(6) The results (1) to (5) are in agreement with the ionic theory of the conductivity of the flame for rapidly alternating currents when the velocity of the positive ions and the inertia and viscous resistance to the motion of the negative ions are neglected in comparison with the effects due to the number of ions per c.c.

(7) The apparent capacity per sq. cm. area of the electrodes is equal, according to the theory just mentioned, to $\sqrt{ne/8\pi V_0}$, where n is the number of positive ions per c.c., e the charge on one ion, and V_0 the maximum applied P.D.

(8) Not more than one molecule in 30 salt molecules is ionized at any instant in the flame, but each molecule is probably ionized and recombines several million times per second.

(9) The steady currents observed through salt vapours in flames are very far from the maximum possible currents corresponding to the number of ions produced per second.

XLIII. The Electrical Conductivity of Metallic Oxides. By F. HORTON, D.Sc., B.A., Fellow of St. John's College, Cambridge.*

THE theory of electrolytic dissociation has furnished a simple explanation of conductivity, in electrolytes, by assuming that the current is carried as a stream of electric charges by the ions into which a certain proportion of the molecules of an electrolyte are dissociated. Conduction in

* Communicated by Prof. J. J. Thomson.

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metals is not due to this cause, for we cannot conceive that a molecule of an elementary substance could be split up into two dissimilar atoms, or groups of atoms, having opposite charges; and experiments have shown that the conduction of electricity through metals is not accompanied by any detectable transportation of matter*.

A theory of metallic conduction not involving the transportation of matter in the atomic state has been put forward by Professor Thomson†. On this theory metallic conductors owe their conductivity to the dissociation of the *atoms* of the metal, the products of dissociation arising from a single atom being an extremely small negatively charged corpuscle and the remaining larger portion of the atom which bears an equal positive charge. These negative corpuscles are identically the same in mass and charge from whatever atom they are produced, and they can move about freely in the mass of the metal. When an electric force acts upon them, they travel in a direction opposite to that of the force, and this convection of charges constitutes the electric current.

The conductivity of compound bodies may belong to either the metallic or the electrolytic class. The distinction between these two classes is generally based on the sign of the temperature coefficient of the conductivity of the conductor in question. If the conductivity decreases with rise of temperature, the conduction is taken to be metallic; if it increases, the conduction is considered to be electrolytic. This, however, cannot be taken as an infallible rule, for, although the conductivity of liquid electrolytes generally increases with the temperature, a series of electrolytic liquids is known which behave in the opposite manner. Such acids as sulphuric and phosphoric, the hydrolytic dissociation of which takes place exothermically, belong to this series. In these cases an increase of temperature decreases the electrolytic dissociation, causing a diminution in the conductivity which more than compensates for the increased mobility of the ions. On the other hand, the conductivity of all the metalloids, which cannot be electrolytic on account of the elementary nature of the conductors, increases with rise of temperature, the increase being probably due to changes in the crystalline structure when heated‡.

It has long been known that many substances which, at the ordinary temperature of the laboratory, may be regarded

* E. Riecke, *Phys. Zeitschr.* ii. p. 639 (1901).

† J. J. Thomson, *Rapports présentés au Congrès International de Physique*, vol. iii. p. 138 (Paris, 1900).

‡ Siemens, *Pogg. Ann.* cliv. p. 117 (1876).

as non-conductors, become conducting when their temperature is raised. The conductivity of such substances was studied by Faraday*, who found that silver sulphide, lead fluoride, corrosive sublimate, and periodide of mercury, all increase very rapidly in conductivity with rise of temperature. Since the time of Faraday this subject has been investigated by many experimenters. It has recently received special attention from Nernst†, who has given it practical application in the Nernst filaments for incandescent lamps. The conduction of electricity through these filaments is considered by Nernst to be electrolytic, but the recent experiments of Streintz‡ and of Guinchant§ have shown that a large number of substances which become conducting at high temperatures give no trace of electrolysis. The conduction in these cases must therefore be metallic, and on Professor Thomson's theory due to the negatively charged corpuscles liberated from the atoms. If this supposition be true, it follows that either the number of free corpuscles within these substances, or the mean free path of these corpuscles, increases very rapidly with rise of temperature. Now Wehnelt|| has studied the emission of corpuscles from the alkaline earths when they are raised to high temperatures, and has found that the rate of emission increases very rapidly with the temperature, and at 1500° C. is quite enormous. At these high temperatures, therefore, there must be a large number of free corpuscles inside the substance, which probably owes its conductivity to their presence. Such an explanation would account for the great increase in conductivity with rise of temperature observed by Faraday, Streintz, and others, and explain the loss of insulating power of quartz and other non-conductors when raised to high temperatures.

The object of the present research was to investigate the variation of electrical conductivity of solid metallic compounds with change of temperature, and to ascertain whether the conduction is carried on electrolytically or metallicity. For this purpose the metallic oxides seemed to be the most

* Faraday, *Exp. Res.* vol. i. § 432 (1833), § 1340 (1838).

† Nernst, *Zeitschr. Elektrochem.* vi. p. 41 (1899); *Gessel. Wiss. Göttingen, Nachr. Math.-Phys.* p. 328 (1900).

‡ Streintz, *Ann. d. Physik*, iii. p. 1 (1900); *Akad. Wiss. Wien. Sitz.-Ber.* iii. 2 a, p. 345 (1902).

§ J. Guinchant, *Comptes Rendus*, cxxxiv. p. 1224 (1902).

|| Wehnelt, *Ann. d. Physik*, xiv. p. 425 (1904); *Phil. Mag.* [6] vol. x. p. 80 (1905).

suitable compounds, especially as the emission of corpuscles from a large number of metallic oxides had been studied by Wehnelt.

The oxides were used in the form of slabs about 1 sq. cm. in area, and from 1 to 2 mms. in thickness. A slab of oxide was placed between two stout platinum plates which were pressed firmly together by means of two porcelain rods 1 cm. in diameter. These rods had a small hole along their axis, and platinum wires from the electrodes passed through them and served to connect to the Wheatstone bridge used for measuring the resistance. The surfaces of the electrodes and of the oxide in contact with them were ground or filed plane so as to make good electrical contact all over.

Two types of electric heating-furnace were used in these experiments. With the more easily fusible oxides it was necessary to watch the oxide to see that the temperature was not raised above the melting-point. The furnace used to heat these oxides consisted of an iron box lined with asbestos cardboard. The porcelain rods passed vertically through the box, the slab of oxide being in the middle. A strip of platinum foil, 5 cms. wide, passed above and below the oxide, and this was heated by an alternating current from a transformer. The oxide could be seen by opening a small door in the side of the furnace. Oxides such as lime, magnesia, and quartz, of high melting-point, were heated in an electric furnace consisting of a coil of No. 20 B.W.G. platinum wire wrapped round a porcelain tube 2.5 cms. in diameter and 13 cms. long. This was placed inside a larger earthenware tube and the space between filled with magnesia. This furnace is shown in section in fig. 1. With both forms of furnace the temperature of the oxide was obtained by means of a thermocouple of wires of platinum and an alloy of platinum with 10 per cent. of rhodium, the junction being close to the oxide.

In order to standardize the thermocouple the melting-point of potassium sulphate was taken as the fixed point, and the galvanometer deflexion corresponding to this temperature (1066° C.) was found. The platinum temperatures given by the galvanometer-readings were corrected to degrees centigrade by means of the curve given by Professor Callendar*. The galvanometer deflexion corresponding to the melting-point of platinum was also found and used for standardizing readings up to 1700° C.

* Callendar, *Phil. Mag.* vol. xlviii. p. 519.

In some cases the resistance of the oxide was obtained by measuring the current passing through it under a known

Fig. 1.—Electric Furnace.

A A are the leads to the heating-coil; B B are the platinum wires from the electrodes; C C the thermocouple wires.

E.M.F. by means of a delicate d'Arsonval galvanometer ; but more generally the resistance was measured directly by a

Wheatstone bridge. With some of the oxides electrolysis was found to accompany the conduction, and with these another method had to be used for obtaining the resistance. Kohlrausch's method of using an alternating current and a telephone indicator does not work well for resistances over 10,000 ohms, and the resistance to be measured was usually greater than this value. The method of using a rotating commutator to reverse the battery and galvanometer circuits together many times a second requires an exceedingly well-made commutator. Unfortunately the one made for the researches which Mr. Fitzpatrick carried out in this laboratory was in use at the time and not available for this work. Other commutators were tried, but none worked satisfactorily.

The method finally adopted was not of great accuracy, but was sufficiently accurate for the object of the present research. It consisted in having the galvanometer permanently connected up to the Wheatstone bridge without a key in circuit, and noticing the direction of its first kick on momentarily closing the battery circuit. The resistance was connected to a reversing key which was reversed after each "make" of the battery circuit, so that successive momentary currents were sent in opposite directions through the electrolyte. This method worked better than I had expected, and, by taking care not to let a continuous current pass through the oxide, results in very good agreement were obtained. There was sometimes a small thermoelectric force developed on heating the oxide, and consequently the resistance in one direction was slightly greater than in the opposite direction. The mean of these resistances was always taken, and the circuit through the oxide was kept open except just when observations were being made. The voltage used on the battery circuit varied, according to the resistance to be measured, from 1 to 500 volts.

The oxides experimented on were lime, baryta, magnesia, bismuth trioxide, plumbic oxide, cupric oxide, sodium peroxide, and quartz. The results obtained will now be given.

Lime.

The piece of lime used was .85 cm. square by .70 mm. thick. Its resistance at the temperature of the laboratory was greater than 100 megohms. The following table contains the resistance, and the conductivity calculated therefrom, at different temperatures :—

Conductivity of Metallic Oxides.

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Temperature Centigrade.	Resistance in ohms.	Conductivity in mhos.
763	70,000,000	1.38×10^{-9}
879	9,125,000	1.06×10^{-8}
930	4,175,000	2.33×10^{-8}
1011	2,000,000	4.85×10^{-8}
1105	600,000	1.62×10^{-7}
1175	245,500	3.96×10^{-7}
1235	104,100	9.33×10^{-7}
1304	35,100	2.77×10^{-6}
1370	2,045	4.75×10^{-5}
1448	122.7	7.90×10^{-4}
1466	91.0	1.035×10^{-3}

Diagram I.—Showing increase of conductivity of *Lime* with temperature.

The relation between the conductivity and the temperature is shown graphically in diagram I. The ordinates give the value of the conductivity, the abscissæ being temperatures in degrees centigrade. In the first curve, starting from the left, each unit of the ordinates represents 10^{-8} mho; in the

ucceeding curves the value of the ordinate is successively multiplied by ten, so that in the second curve each unit is equal to 10^{-7} mho, in the third 10^{-6} mho, in the fourth 10^{-5} mho, and in the last 10^{-4} mho.

These curves are exactly similar to those obtained by Wehnelt* for the relation between the number of corpuscles given out by lime (measured by the saturation current) and the temperature. Wehnelt found that the number of corpuscles emitted from glowing lime obeyed the law found by O. W. Richardson† and by H. A. Wilson‡ to hold for the negative

corpuscles from hot platinum, viz., $n = A\theta^{\frac{1}{2}}e^{-\frac{b}{\theta}}$ where n is the number of corpuscles, θ the absolute temperature, and A and b are constants. If the conduction is carried on by the corpuscles set free in the interior of the oxide at high temperatures, we might expect a similar relation to hold between the conductivity and the temperature.

Diagram II.

In order to test this we may denote the conductivity by c , and write the equation in the form

$$\log_{10} c - \frac{1}{2} \log_{10} \theta = \log_{10} A - 0.434b \theta^{-1},$$

so that on plotting the values of $\log_{10} c - \frac{1}{2} \log_{10} \theta$ against

* Wehnelt, *Ann. d. Phys.* xiv. p. 425 (1904).

† O. W. Richardson, *Phil. Trans. A.* vol. cci. p. 497 (1903).

‡ H. A. Wilson, *Phil. Trans. A.* vol. ccii. p. 243 (1903).

those of θ^{-1} we ought to obtain a straight line. In diagram II. the ordinates are the values of $\log_{10} c - \frac{1}{2} \log_{10} \theta$, the abscissæ being the corresponding values of θ^{-1} .

It will be seen that seven points representing the largest values of θ^{-1} (*i. e.* the lowest temperatures) lie very nearly on a straight line. The fact that the points above 1300° C. do not lie on this line is probably due to disturbing causes which affect the resistance to be measured. At these high temperatures, the lime would probably have some chemical action on the platinum electrodes, causing, possibly, a decrease in the contact resistances. It was, for instance, always found that the lime was fixed to the electrodes after it had been strongly heated, but not when lower temperatures were used. This explanation would account for the fact that the value found for the conductivity at high temperatures was greater than it should be on the present theory. Diagram II. may therefore be taken as showing that the increase of conductivity of lime with temperature follows the same law as the emission of corpuscles from its surface.

When the above series of experiments had been completed, tests were made to see if any polarization could be detected which would show that some part of the conduction through lime was electrolytic. The lime was connected to a battery for a few seconds and a current allowed to pass through it. The battery was then cut out and a delicate d'Arsonval galvanometer substituted. This indicated a small polarization current in the opposite direction to the original current and dying away logarithmically with the time. The polarization current when the lime was at 800° C. was very small, but it increased as the temperature was raised, the increase being no doubt due to the decrease in the resistance of the lime. A battery of 100 volts was next connected up in series with the slab of lime and galvanometer, the latter being shunted for measuring larger currents. The current through the galvanometer gradually decreased, and, if the E.M.F. was left on for a few seconds and the key connected to the lime reversed, a larger deflexion in the opposite direction was obtained which also decreased with time. But if the current was allowed to pass for several minutes in one direction through the lime, the galvanometer deflexion decreased to about a tenth of its original value, and, on reversing the key, the deflexion obtained in the opposite direction was only slightly greater than the small value just before reversing. This increased with time slowly at first, but soon very rapidly, and then more slowly again as a maximum deflexion was reached. the current then decreased with time, at a gradually

decreasing rate until about the same magnitude as the direct current just before reversing. This behaviour may be explained by supposing that a layer of oxygen is formed by electrolysis against the anode, and that this increases the resistance of the circuit in addition to causing the polarization E.M.F. When the circuit is completed for only a short time before the key connected to the lime is reversed, very little gas can have collected at the anode, and this gives a back-E.M.F., but does not greatly increase the resistance. On reversing, therefore, a large deflexion in the opposite direction is obtained. On the other hand, when time is allowed for much gas to collect at the anode, then, on reversing, the deflexion in the opposite direction is slightly larger than the small value just before reversing, owing to the back-E.M.F. This increases as the oxygen recombines with the calcium which is now formed at that electrode, and the oxygen which is being formed at what is now the anode combines with the calcium already liberated there by the direct current. Thus the resistance gradually decreases until all the collected gas is used up; a maximum current then passes and the deflexion afterwards decreases as oxygen collects against the other electrode.

These experiments were carried out at about 1000° C. At higher temperatures the current did not die away to so small a value; and on reversing the key connected to the lime a large deflexion in the opposite direction was obtained which gradually died away, and did not increase even when the direct current had been flowing for a long time. It is probable that this is due to the oxygen escaping more easily from the electrode at the higher temperature and not forming a layer over the anode, and thus increasing the resistance of the circuit as it did in the experiments at 1000° C.

Several specimens of lime were experimented on and gave results practically identical with those described above, both as regards the variation of conductivity with temperature and the electrolytic effects of the current. It thus appears that the conduction of electricity through heated lime is carried on partly by electrolytic ions as in a liquid electrolyte; but the fact that the increase of conductivity with temperature corresponds, so closely, with the increase in the rate of emission of electrons, seems to indicate that most of the conduction is metallic.

Magnesia.

A piece of magnesia $\cdot 84$ cm. $\times$ $\cdot 83$ cm. and $\cdot 090$ cm. thick was used. The resistance of this at the temperature of the laboratory was too large to be measured by the method

used, being over 100 megohms. The values of the resistance at higher temperatures and also of the conductivity calculated from the resistance and dimensions of the slab are given in the following table.

Temperature Centigrade.	Resistance in ohms.	Conductivity in mhos.
471	35,000,000	3.69×10^{-9}
564	3,000,000	4.34×10^{-8}
630	800,000	1.61×10^{-7}
743	215,000	6.00×10^{-7}
828	88,000	1.46×10^{-6}
933	31,000	4.16×10^{-6}
970	22,300	5.79×10^{-6}
1055	12,450	1.04×10^{-5}
1191	4,900	2.63×10^{-5}
1204	6,800	1.90×10^{-5}
1280	12,900	1.00×10^{-5}
1341	290,000	4.45×10^{-7}

Diagram III.—Showing increase of conductivity of MgO with temperature.

In diagram III. the values of the conductivity given in the above table are plotted against the corresponding

temperatures. The curves obtained are similar to those given by lime.

It will be observed, both from the table and diagram, that after 1200°C. the conductivity suddenly altered its behaviour, and began to decrease with increasing temperature. At these temperatures the resistance was not constant, but increased as time went on as well as with increasing temperature. If is, however, well known that the crystalline structure of magnesia alters when heated to high temperatures, the alteration being accompanied by a change in density. Several specimens of magnesia were experimented on and they all behaved in the same manner, giving a minimum resistance at from 1200°C. to 1250°C. It therefore appears probable that this sudden change in the conductivity is due to an alteration of the condition of the oxide into a less conducting state, the resistance continually increasing while the change is going on.

In order to see whether the increase of conductivity with temperature follows the same law as the emission of corpuscles

Diagram IV.

from the surface, the values of $\log_{10} c - \frac{1}{2} \log_{10} \theta$ were plotted against those of θ^{-1} , as in the case of lime. This is done in

diagram IV., which shows that the points lie very nearly indeed on a straight line.

Experiments showed that the conduction of electricity through magnesia was accompanied by a little electrolysis; but all the effects of this were much smaller than in the case of lime.

The results obtained with the other oxides experimented on are very similar to those for calcium and magnesium, the temperature-conductivity curves possessing in all cases precisely the same characteristics as those connecting the emission of corpuscles with the temperature of the oxide when used as the cathode in a discharge-tube. The results obtained with these oxides will therefore be given more briefly.

Baryta.

This was difficult to work with on account of the strong chemical action it has on platinum when heated, and because of the ease with which it absorbs moisture and carbonic-acid gas from the air. Also, if heated above a dull red heat, it takes up more oxygen from the air and forms the dioxide. The numbers given in the following table are therefore not so reliable as those given for lime or magnesia. The dimensions of the piece of barium oxide used were .853 cm. by .843 cm. and .467 cm. thick.

Temperature Centigrade.	Resistance in ohms.	Conductivity in mhos.
307	646,000	1.00×10^{-6}
311	359,000	1.81×10^{-6}
312	274,000	2.37×10^{-6}
320	184,000	3.53×10^{-6}
319	218,000	2.98×10^{-6}
345	78,400	8.29×10^{-6}
355	10,760	6.03×10^{-5}
369	6,892	9.43×10^{-5}
386	602	1.08×10^{-3}
428	35.7	1.82×10^{-2}
450	21.4	3.04×10^{-2}
469	17.6	3.70×10^{-2}
497	14.1	4.61×10^{-2}

When the conductivities in the above table are plotted against the corresponding temperatures, curves similar in type to those given by lime and magnesia are obtained; but

the various readings do not fall so well on the curves as in the former case. This is no doubt due to the causes already mentioned, and especially to the action of the baryta on the platinum electrodes. The effect of this could be seen in the blackening of the oxide through some considerable distance from each surface of contact. Much importance cannot, therefore, be attached to these values of the conductivity of baryta.

Experiments showed that, as with lime and magnesia, some electrolysis was caused by the passing of the current. Some experiments were afterwards made to see whether any evolution of gas at the anode could be detected. These will be described later.

Plumbic Oxide.

Some lead monoxide was melted in an atmosphere of oxygen (to prevent reduction) and cast into a slab. This was filed up to $\cdot 758$ cm. $\times$ $\cdot 733$ cm. and $\cdot 158$ cm. in thickness. The following table contains the values of the conductivity at various temperatures after the resistance had become small enough to be measured.

Temperature Centigrade.	Resistance in ohms.	Conductivity in mhos.
384	7,000,000	$3\cdot86 \times 10^{-8}$
420	2,350,000	$1\cdot15 \times 10^{-7}$
462	650,000	$4\cdot15 \times 10^{-7}$
504	250,000	$1\cdot08 \times 10^{-6}$
539	128,000	$2\cdot11 \times 10^{-6}$
572	72,000	$3\cdot75 \times 10^{-6}$
600	45,000	$6\cdot00 \times 10^{-6}$
646	13,500	$2\cdot00 \times 10^{-5}$
687	4,050	$6\cdot67 \times 10^{-5}$
700	2,870	$9\cdot39 \times 10^{-5}$
757	730	$3\cdot695 \times 10^{-4}$
787	330	$8\cdot175 \times 10^{-4}$

The relation between the conductivity and the temperature is shown graphically in diagram V.

When a current of $\cdot 001$ ampere was sent through this oxide no sign of electrolysis could be detected, either as a liberation of gas or as a polarization E.M.F. This current is much greater than those used in the determinations of the conductivity of the oxide. On sending a current of $\cdot 015$

ampere through the oxide for a short time, and then connecting it up to a delicate galvanometer, a feeble polarization current was indicated ; but this was much smaller than those

Diagram V.—Showing increase of conductivity of *Plumbic Oxide* with temperature.

observed in the experiments with the oxides of the alkaline earths. The temperature of the plumbic oxide during these experiments was 780° C.; the polarization was still smaller at lower temperatures.

Bismuth Trioxide.

Slabs of bismuth trioxide were prepared in a manner similar to that employed with plumbic oxide. Some pure trioxide was melted in a stream of oxygen and cast into a slab which was filed up to the required size. The sample from which the numbers given in the following table were obtained was .77 cm. x .77 cm. and .202 cm. thick.

Temperature Centigrade.	Resistance in ohms.	Conductivity in mhos.
225	80,000,000	4.27×10^{-9}
261	20,000,000	1.71×10^{-8}
315	2,550,000	1.34×10^{-7}
342	800,000	4.27×10^{-7}
376	259,000	1.32×10^{-6}
424	49,000	6.97×10^{-6}
458	22,000	1.55×10^{-5}
487	15,300	2.23×10^{-5}
515	9,500	3.59×10^{-5}
535	7,150	4.77×10^{-5}
566	4,700	7.27×10^{-5}
598	3,400	1.040×10^{-4}
645	2,050	1.664×10^{-4}

The above values of the conductivity are plotted against the corresponding temperatures in diagram VI.

Diagram VI.—Showing increase of conductivity of *Bismuth Trioxide* with temperature.

Electrolysis was more easily detected with this oxide than with plumbic oxide, a small polarization current being obtained even at 200° C.

Cupric Oxide.

Some pure oxide of copper was melted up by means of the oxy-hydrogen flame, and the melted mass ground into shape on a carborundum wheel. Its dimensions were :—1.006 cm. $\times$.994 cm. and 2.179 mms. thick. Two series of experiments were made with this specimen, the first up to 400° C. and the second to over 1000° C. The results obtained in both series are given in the following table :—

Temperature Centigrade.	Resistance in ohms.	Conductivity in mhos.
122	462,400	4.71×10^{-7}
59	91,560	2.38×10^{-6}
66	74,560	2.92×10^{-6}
134	12,360	1.76×10^{-5}
157	5,930	3.67×10^{-5}
268	556.5	3.91×10^{-4}
303	300.8	7.24×10^{-4}
385	96.2	2.26×10^{-3}
463	36.3	6.00×10^{-3}
12	645,100	3.38×10^{-7}
487	27.8	.00784
564	11.13	.02424
618	5.87	.03711
691	2.34	.0931
733	1.455	.1497
786	.845	.258
873	.347	.628
944	.196	1.111
974	.121	1.80
1038	.021	10.37

The resistance of copper oxide at high temperatures is so small, that it was necessary to subtract from the measured resistance the resistance of the platinum leads. The resistance of these at various temperatures was found by a preliminary experiment in which the two electrodes were placed in contact

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and heated up just as in the experiment proper. The values of the conductivity are plotted against the temperatures in diagram VII.

Diagram VII.—Showing increase of conductivity of *Cupric Oxide* with temperature.

No sign of electrolysis could be found when a current was sent through this oxide at the ordinary laboratory temperature. A current of 1.625×10^{-8} ampere was sent through the oxide. This slowly decreased to 1.528×10^{-8} ampere in 10 minutes, but on cutting out the battery no trace of polarization current could be observed. The decrease of current was not due to decomposition such as had been observed in the case of lime; for on reversing the direction of the current through the copper oxide a steady and equal deflexion of the galvanometer in the opposite direction was obtained. Thus we may conclude that the passage of a current of electricity through copper oxide at the ordinary laboratory temperature is not accompanied by electrolysis. At higher temperatures it was

impossible to test for a polarization current because of a thermoelectric effect due to one face of the oxide being slightly warmer than the other. A current of about .25 ampere was sent through the oxide at 700° C. The galvanometer deflexion remained steady except on one occasion when it decreased slightly. In no case did the current fall off as it had done in the experiments with lime, so that we may conclude that at high temperatures, also, the conduction of electricity through copper oxide is not accompanied by electrolysis.

Sodium Peroxide.

The results obtained with this oxide were not very satisfactory on account of the readiness with which it deliquesces when exposed to air. Only a small range of temperature could be used, as the oxide melts at about 300° C. The numbers in the following table refer to a piece of oxide 1 sq. cm. in area and 2 mms. thick.

Temperature Centigrade.	Resistance in ohms.	Conductivity in mhos.
20	5000	4×10^{-5}
59	2500	8×10^{-5}
109	1200	1.67×10^{-4}
198	600	3.3×10^{-4}
244	400	5.0×10^{-4}
284	200	1.0×10^{-3}

Diagram VIII.

The above values of the conductivity are plotted against the corresponding temperatures in diagram VIII.

Quartz.

A rectangular slab of fused quartz was used in these experiments. Its two faces were ground parallel and roughly polished, and the edges were ground square. The area of the slab was $\cdot946 \times \cdot939$ sq. cm. and it was $\cdot1514$ cm. in thickness. The two faces through which the current was to be passed were platinized by means of a colloidal solution of platinum, and thus good contact over the surfaces was assured. The platinized slab was held between the two platinum electrodes in the heating furnace and its resistance at various temperatures measured. The following values were obtained :

Temperature Centigrade.	Resistance in ohms.	Conductivity in mhos.
486	95,000,000	$1\cdot79 \times 10^{-9}$
580	12,000,000	$1\cdot42 \times 10^{-8}$
652	3,500,000	$4\cdot86 \times 10^{-8}$
716	1,570,000	$1\cdot08 \times 10^{-7}$
703	1,980,000	$8\cdot59 \times 10^{-8}$
795	750,000	$2\cdot27 \times 10^{-7}$
869	409,000	$4\cdot16 \times 10^{-7}$
942	250,000	$6\cdot80 \times 10^{-7}$
1013	170,000	$1\cdot00 \times 10^{-6}$
1093	121,000	$1\cdot40 \times 10^{-6}$
1288	65,200	$2\cdot61 \times 10^{-6}$

Diagram IX.—Showing increase of conductivity of *Quartz* with temperature.

The rapid increase of conductivity with rise of temperature is readily seen from diagram IX., in which the above values

of the conductivity are plotted against the corresponding temperatures.

When the experiments already described had been performed, it was thought to be desirable to investigate further the electrolysis which was found to accompany the conduction in the case of some of the oxides, and to apply a more delicate test for it in those cases in which no trace of a polarization current could be detected. The oxides chosen for these experiments were lime, baryta, and cupric oxide; lime and baryta because they were the oxides with which electrolysis had been most easily detected, and the cupric oxide because it behaved as if its conductivity were entirely metallic.

Wehnelt has shown* that if glowing lime (or certain other oxides) be used as a cathode in a discharge-tube, a strong current can be made to pass. If the cathode consists of a strip of platinum covered with lime, the whole of the current must pass through the oxide. If electrolysis takes place, oxygen will be liberated at the free surface of the oxide and calcium next to the platinum strip. The gas pressure in the discharge-tube will thus increase with the passage of the current, and the amount of gas liberated in a given time will be proportional to the current passing. Wehnelt found in his experiments that there was "no notable increase of pressure," which seems to indicate that the passage of the current through the oxide was unaccompanied by electrolysis. In the following experiments much larger cathodes and stronger currents were employed, so that if the conduction of electricity is electrolytic, the amount of oxygen evolved would be quite easily detected.

A strip of platinum foil 2 cms. long and .3 cm. wide, having a thermocouple of fine platinum and platinum-rhodium wires fixed to its middle point, was covered with lime and used as the cathode in a discharge-tube, the anode being a disk of platinum 2 cms. in diameter placed parallel to the strip and about 2 cms. away from it. The discharge-tube was connected to a mercury-pump and McLeod gauge, and the whole apparatus was pumped down to a low pressure. The platinum strip and lime were heated, by means of the alternating current from a small transformer, to a white heat for several hours. The heating was accompanied by a considerable evolution of gas from the oxide. This was pumped out of the apparatus at intervals, and the heating was continued until the pressure remained fairly constant. The transformer

* *Ann. der Physik*, xiv. pp. 425-468 (1904); *Phil. Mag.* vi. pp. 80-90 (1905).

was then removed and the strip was heated to a lower temperature by means of the direct current from a battery of 10 E.P.S. motor cells. The cathode was also connected to the negative pole of a battery of small accumulator-cells, the positive pole of which was connected to the anode through a current-measuring instrument—a Thomson galvanometer for small currents and a milliammeter for larger ones.

In making the experiments, the required temperature of the cathode (indicated by the thermocouple) was first obtained by adjusting the resistance in the heating circuit. The pressure of gas in the apparatus was then measured by the McLeod gauge, and the apparatus left for 15 minutes, after which the pressure was again read and the discharge started through the tube. The current was allowed to pass for 15 minutes. It was measured at intervals during this time and the mean value was calculated. The pressure was then read, and the apparatus was left to itself for another 15 minutes. In this way any liberation of gas due merely to the heating of the cathode could be allowed for, the temperature of the cathode being maintained the same throughout the experiments. It was found that the passage of the discharge slightly increased the temperature of the cathode, and at very high temperatures (1400°C.) the arrangement was unstable, for at the higher temperature the lime gives a larger supply of corpuscles for carrying the current, which is increased, and thus still further increases the temperature of the cathode. In order that the current passing through the tube should not become sufficient to raise the temperature of the cathode above the melting-point of platinum, a small fuse cut from a sheet of thin tin-foil was placed in the circuit.

The results obtained varied with the length of time during which the oxide had been heated before the observations were made. It was found in one case, when there was still a fair amount of gas being given off on merely heating the cathode, that the extra liberation of gas when a current of 2.66×10^{-4} ampere was sent through the tube was within 8 per cent. of that required by Faraday's law on the supposition that the conduction through the lime was entirely electrolytic*. On heating the cathode to about 1400°C. for several hours longer, there was much more gas given off from it, and on pumping this out and repeating the experiment it was found that the evolution of gas had practically ceased, and that on now sending a discharge through the tube the pressure was altered

* It is interesting to note in this connexion that Skinner (Phys. Rev. July 1905) has found that the evolution of hydrogen from a fresh cathode obeys Faraday's Law.

only very slightly, the alteration being in most cases an increase, but in a few cases a decrease. The following numbers serve to illustrate the results obtained :—

Temperature of cathode = 1100° C.

Potential-difference between the electrodes = 40 volts.

Time.	Pressure in mm. of Hg.	Current in amperes.
3:54 P.M.	·0018	
4:3 "	·00185	none
4:21 "	·0021	·03
4:31 "	·00224	none

mm.

Increase of pressure per minute while discharge was passing = ·000014
Mean increase per minute when no discharge was passing .. = ·000010

If the conductivity of the lime was entirely electrolytic, the passage of ·03 ampere would have liberated oxygen at a rate sufficient to increase the pressure of gas in the apparatus by ·0803 mm. per minute. So the actual increase of pressure while the discharge is passing is only $\frac{1}{20,000}$ of what would be expected if the conduction were entirely electrolytic. The experiment may therefore be taken as showing that in the conduction of electricity through heated lime only a very small fraction of the total current is carried by means of electrolytic ions.

A result similar to this was obtained by using barium oxide on the cathode in place of lime. Some experiments were also made with a cupric-oxide cathode, and no increase of gas-pressure in the apparatus could be observed when a discharge was allowed to pass.

Conclusion.

The point of most interest in connexion with the conduction of electricity through the metallic oxides is the method by which the current is carried. Nernst* has given reasons for supposing the conductivity to be electrolytic, the chief of these being (a) that definite traces of electrolysis were found in some cases; the chemical composition at the cathode after the current had been allowed to flow through the oxide for a long time being found to be different from that at the anode; (b) the conductivity of a mixture of oxides was found to be much greater than that of each oxide separately. Nernst states that the products of electrolysis are continually recombining, and so the supply of electrolytic ions is kept up.

* Nernst, *Zeitschr. f. Elektroch.* vi. pp. 41-43 (1899).

The conclusion from the present experiments is just the opposite of this view, and is that the conductivity of the oxides investigated is mainly metallic. It may be that the signs of electrolysis obtained, in some cases, by Nernst correspond to the signs of electrolysis found with some of the oxides in the present experiments. With mixtures of oxides it is probable that signs of electrolysis would be more readily given—for instance, the wandering of colour towards the cathode in the case of mixtures containing coloured oxides (*e. g.* oxide of iron) may be due, as Nernst suggests, to the coloured oxide being in solution in the rest and giving rise to the ordinary phenomena of electrolysis; but I do not think it is justifiable to conclude that because such traces of electrolysis can be detected therefore the whole conductivity is electrolytic.

In the present paper it is shown that some oxides (*e. g.* CuO) show no trace of electrolysis; and I think that if the conduction of electricity through these oxides is carried on by means of electrolytic ions, some evidence of the liberation of the products of electrolysis would have been obtained in the experiment in which a current was passed through oxide of copper whilst it was heated in a vacuum.

The distinction between electrolytic and metallic conductivity is generally based on the sign of the temperature coefficient of the conductivity of the conductor in question. If the conductivity decreases with rise of temperature, the conduction is taken to be metallic; if it increases with rise of temperature, the conduction is considered to be electrolytic. This rule is, however, one with so many exceptions (some of which have already been stated at the commencement of this paper) that it is useless for deciding the question.

The effect of increased temperature on the conductivity of electrolytes has been studied by many observers. For aqueous solutions the experiments over the largest range of temperature are those by Noyes and Coolidge*. These observers have studied the conductivity of solutions of sodium and potassium chloride up to 306° C. They find that for very dilute solutions (·0005 normal) the conductivity increases at a rate closely proportional to the increase of temperature. With more concentrated solutions the conductivity curves rise more slowly and attain a maximum, after which increase of temperature decreases the conductivity. The authors show that this is due to a decrease in the number of dissociated

* Noyes and Coolidge, Proc. Amer. Acad. of Arts & Sci. vol. xxxix. p. 160 (1903-94).

molecules with rise of temperature, which is greater the more concentrated the solution.

Experiments on the conductivity of solutions in other solvents show similar results. Walden and Centnerschwer* have investigated solutions in liquid SO_2 from -76°C. to the critical point, 157°C. In all cases it was found that the conductivity first increases with rise of temperature and then falls off, following roughly a parabolic formula.

An increase of conductivity with rise of temperature is also found in the case of fused salts. The conduction through these is electrolytic, and the amount of the ions liberated by the current has been shown to follow Faraday's law of electrolysis†; but the increase of conductivity of fused salts with temperature is not nearly so great as that obtained in the case of heated metallic oxides. The increase of conductivity with temperature of all the oxides examined in the present paper is much more rapid than in any known case of electrolytic conductivity. On heating a slab of cupric oxide from 12°C. to 385°C. , its conductivity increased 5000 times; and on heating lime from 763°C. to 1466°C. the conductivity increased to nearly 10^6 times its value at the lower temperature.

In cases of electrolytic conductivity the increase of conductivity with rise of temperature is due to the increased mobility of the ions at the higher temperature. As the oxides used in these experiments remained solid throughout the observations, it does not seem reasonable to suppose that the mobility of the current-carriers could have increased by the enormous amounts given above. The only alternative explanation is that the *number* of the carriers is enormously increased, a supposition which is not compatible with the idea that the conductivity is electrolytic; for in cases of electrolytic conductivity increase of temperature decreases the degree of ionization, the decrease being more rapid the more concentrated the solution.

If, on the other hand, we consider the conductivity to be metallic and the current to be carried by the negatively charged corpuscles which are wandering about in the interior of the oxide, formed by the dissociation of the metallic atoms; then the explanation is at once to hand, for Wehnelt's work has shown that the number of these corpuscles emitted by the oxide (and, therefore, probably the number contained by it)

* Walden and Centnerschwer, *Zeitschr. phys. Chem.* xxxix. p. 513 (1902).

† Lorentz, *Zeitschr. f. Elektroch.* vii. p. 277 (1900); p. 753 (1901).

increases rapidly with the temperature. Moreover, in the present paper it has been shown that the conductivity of the oxide increases in the same manner as the rate of emission of corpuscles from its surface.

The fact that mixtures of certain oxides conduct better than either of their constituents, is capable of explanation on the corpuscular theory of metallic conduction. For there is ample proof that the ease with which a corpuscle can escape from an atom depends on its surroundings. In an atom placed by itself and left to its own resources, a corpuscle has nothing to help it to escape except its own velocity; but if it is surrounded by other atoms, the other corpuscles exert forces on it and so help it to escape. A corpuscle, for instance, might escape from an atom in the solid or liquid state when it could not escape in the gaseous state. Liquid mercury is a good conductor of electricity, and if there are the same number of atoms in mercury vapour as in the liquid we should expect a much higher conductivity in the vapour on account of the larger free path of the corpuscles; but neither Maxwell nor Hittorf could find any trace of conductivity through hot mercury vapour. Professor Thomson* found that at high temperatures mercury vapour was a better insulator than air under similar conditions; while Strutt† has shown that up to a full red heat the conductivity of saturated mercury vapour is only about one ten-millionth part of that of the liquid. It seems not improbable, therefore, that there might, in certain cases, be many more free corpuscles in a mixture of two oxides than in either oxide separately. Even neglecting this influence of the surroundings on the freedom of the corpuscles, we should expect to obtain a mixture of better conductivity than either of its constituents by mixing two metallically conducting bodies, one containing a large number of free corpuscles, but in which the mobility of the corpuscles was small, and the other in which the mobility of the corpuscles was very great, but containing only a few. On mixing a little of the first substance with the second a good conducting mixture would be obtained.

I do not, therefore, think that Nernst's reasons for considering the conductivity of heated metallic oxides to be electrolytic are conclusive. The experiments described in this paper seem to show that by far the greater part of the current is carried by negatively charged corpuscles, as in metals. In the case of those oxides or mixtures of oxides in which a

* J. J. Thomson, *Phil. Mag.* [5] xxix. p. 364.

† Hon. R. J. Strutt, *Phil. Mag.* [6] iv. p. 596 (1902).

feeble polarization current or other signs of electrolysis have been observed, we have both metallic and electrolytic conductivity associated in the same substance.

These experiments were carried out at the Cavendish Laboratory, and I gladly take this opportunity of thanking Professor Thomson for his advice and interest during the investigation.

XLIV. *A Note on Talbot's Lines.*

By JAMES WALKER, M.A., *Oxford* *.

IT is sometimes felt that Stokes's explanation of the "polarity" of Talbot's lines is mathematical rather than physical, so that those who are unable to follow the analysis still require an adequate reason for the fact that the retarding plate must be inserted on the one side of the aperture rather than on the other.

Prof. Schuster† has indeed supplied this want by considering the source of light to be due to a succession of impulsive velocities; but there is perhaps still room for an elementary explanation of the phenomenon on the old familiar lines of regarding the light as resolved into a congeries of monochromatic constituents.

1. When a stream of monochromatic light, coming from a distant slit, falls upon the object-glass of a telescope that is limited by a rectangular aperture with its sides parallel to the luminous line, it is easily shown that the diffraction-pattern in the focal plane of the telescope is characterised by a series of dark lines, arranged at equal distances on either side of the geometrical image of the slit. When half the aperture is covered by a retarding plate, the minima of an even order retain their former positions, but those of an odd order are displaced towards the side on which the plate is placed by an amount depending upon the retardation introduced by the plate.

Let us now suppose that the primitive light is white and that its monochromatic constituents have been separated before reaching the aperture by a prism or a grating, so that the different colours occupy different angular positions in the field of view.

The minima of an even order will now disappear; for on account of the dispersion there will be a gradual shift of the

* Communicated by the Physical Society: read February 23, 1906.

† An Introduction to the Theory of Optics, p. 329; Phil. Mag. [6] vol. vii. p. 1 (1904).