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The Electrical Conductivity of Lead Chromate*

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The conductivity of sintered pellets of lead chromate varies with the temperature in accordance with the Boltzmann-type law $\sigma \propto \exp(-1.48\ \mathrm{ev}/kT)$ in the temperature range 700°C to 350°C and with the law $\sigma \propto \exp(-0.60\ \mathrm{ev}/kT)$ at lower temperatures. At constant temperature the conductivity increases with decreasing oxygen pressure, $\sigma \propto P_0^{-1/3.1}$, which indicates that lead chromate probably dissociates in accordance with the equations: $2PbCrO_4 \rightarrow Pb(CrO_2)_2 + Pb^0 + 2O_2$ and $Pb^0 \rightarrow Pb^+ + e$. The energies of these reactions are 5.28 and 1.20 electronvolts, respectively. These same reactions would explain optical and thermal darkening as well as the conductivity, and they indicate along with transport measurements and Seebeck effect measurements that lead chromate is an excess electronic semiconductor.

I. INTRODUCTION

Chrome yellow pigments, which consist essentially of lead chromate, have the unfortunate property of darkening on exposure to light. It was expected that lead chromate is one of that interesting group of photo-sensitive materials, which includes the silver halides and zinc sulfide, that decompose photolytically. With this possibility in view the work of the present paper on the electrical properties of pure lead chromate was undertaken. It was hoped that from this work would come an understanding of the fundamental chemical reactions that produce darkening. In addition to the present paper, studies of the optical and electrical properties of variously treated lead chromate pigments are being carried out at this laboratory, and the results will be published in other papers.

Lead chromate belongs to that group of solids known as semiconductors. The solids classified as semiconductors are those which have "a small electronic conductivity that is negligible at very low temperatures and increases with increasing temperature."[1] The electrical conductivity of a semiconductor is very much a property of the method of measurement. In determining the conductivity of a semiconductor, therefore, certain problems must be considered: the contact with the semiconductor; the effect of impurities and of the mechanical and thermal history on the conductivity; the dependence of the conductivity on voltage, temperature and oxygen pressure; and the determination of the type of conduction. These problems are discussed in the order given in the section on results.

II. PREPARATION OF SAMPLES

Pure lead chromate pigments were prepared for this work by the Krebs Pigment Department of E. I. du Pont de Nemours and Company. They started with C.P. sodium chromate and C.P. lead nitrate and obtained by carefully controlled fractional crystallization very pure salts from which the lead chromate was obtained by precipitation. A spectroscopic analysis made at the du Pont experimental station showed that the samples contained possibly "several parts in 10,000 of Si, Na, and Ca; traces perhaps picked up in analysis of Mg and Ba; and no other metallic impurities." In all of the work carried out here the structure of the material used was restricted to the monoclinic phase which is stable from room temperature to 707°C.

The pigment was pressed into pellets about one-half inch in diameter and one-quarter inch thick with the use of a press made from an eight-ton hydraulic truck jack. Although a die made of hardened tool steel and equipped with two hardened plungers was found satisfactory for making the pellets used in rough measurements, considerable difficulty was encountered because the pigment stuck to the die. In order to reduce this and to eliminate the strains produced when

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* A dissertation in physics presented to the Faculty of the Graduate School in partial fulfillment of the requirements for the degree of doctor of philosophy.

[1] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

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removing the pellet from the die a special divided die was constructed of extremely hard material. About 2 grams of the pigment were used to make each pellet, and the optimum forming pressure employed was 9000 lb./in.^{2}. The density of the pellets thus formed was about 50 percent of the single crystal value. It may be added that natural single crystals from Siberia and Tasmania have a density of 5.92 and 6.00 grams/cm^3, respectively, whereas artificial crystals have a density between 6.1 and 6.3 g/cm^3.[2]

On exposure to the atmosphere the lead chromate pellets were found to absorb up to 0.1 percent of their weight in moisture. This amount of moisture increased the conductivity a hundred-fold. If, however, a current was allowed to pass through the sample for several hours, the conductivity dropped below the value for a carefully dried specimen. Subsequent examination of the sample showed dark areas at the contacts. The conduction increased when these areas were removed. For standardization, all of the pellets used in the final measurements were dried at 105°C for approximately 24 hours.

Contact was made to the sample either with platinum disks which were held against the pellet with a strong spring, or with gold films that were vacuum-evaporated onto the parallel surfaces of the pellet. Platinum disks were usually pressed against the gold layer.

In order to measure the contact resistance some of the samples were formed with probes. Two small flat spirals of 1-mil Nichrome wire were imbedded between three 1-gram sections which were formed into a single pellet. The pellet was pressed in stages, each section being pressed to 2000 lb./in.^{2} before the spiral and next section were placed on it. The entire unit was completed at a pressure of 9000 lb./in.^{2}.

For lead chromate heated 18 hours at 400°C in air the density becomes 5.8 grams/cm^3 or 93 percent of single crystal density. Pellets thus sintered possess the advantage that many of their properties are nearly those of a single crystal. For some measurements the temperature and oxygen pressure during sintering were varied and the sample was quenched to room temperature.

III. APPARATUS AND CIRCUITS

Most of the measurements were made with the current-voltage circuit shown in Fig. 1(a). To prevent puncturing of the sample as a result of Joule heating and the consequent runaway conduction, the ballast tube 6D6 was used as a series resistor with its grid bias adjusted so as to hold the current below 5 milliamperes.

In order to measure the contact resistance, the potentiometer circuit of Fig. 1(b) was added to that of Fig. 1(a). The tube 6F5 is operated as an impedance changer, and was selected because of its large grid resistance and large transconductance. The unknown potential difference appears across the 1 megohm cathode resistor, and is measured with a vacuum tube voltmeter (*VV*).

Two furnaces were used to determine the temperature and oxygen dependence. The high temperature furnace (Fig. 2) is a modification of that described in the thesis of M. Earle.[3] The Alundum tubes (*A*), Glowbar heating elements (*G*), and quartz tube (*Q*) for the vacuum

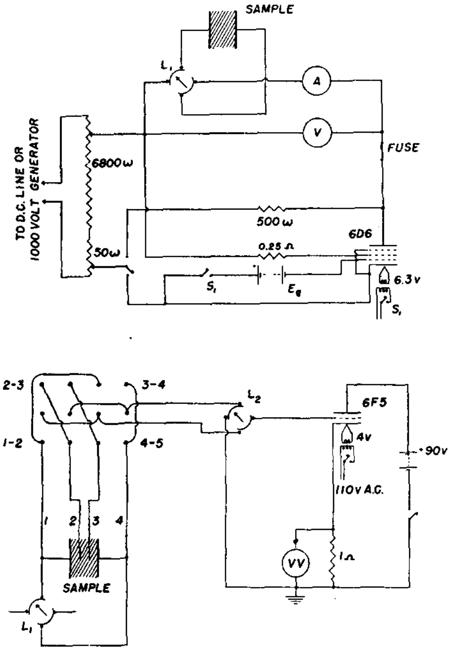

FIG. 1. (a) Upper, circuit for measuring current-voltage characteristics. (b) Lower, circuit for measuring contact potential drop. L_1 and L_2 are two lucite commutator switches coupled so as to keep the grid of the tube 6F5 positive when reversing the current through the sample. Note: ω = ohm, Ω = megohm.

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[2] B. Grossner and F. Mussgnug, Zeits. f. Krist. **75**, 410 (1930).

[3] M. D. Earle, Phys. Rev. **61**, 56 (1942).

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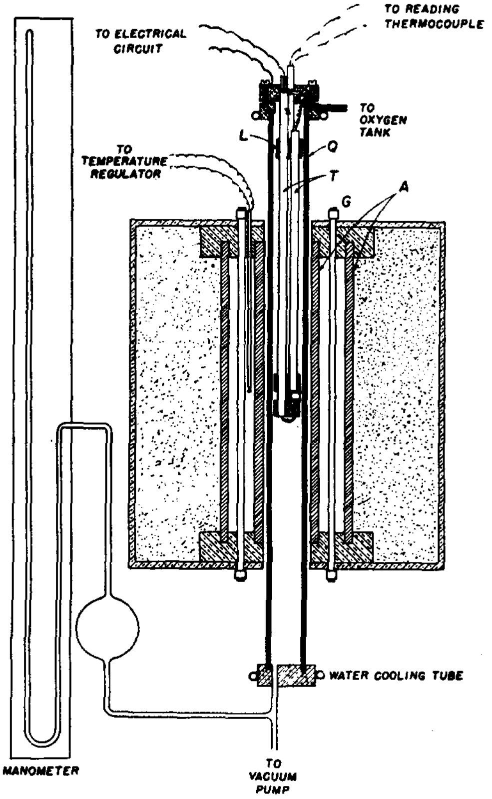

FIG. 2. High temperature furnace.

or oxygen chamber are the same as in his design. Only the reading thermocouple and sample holder are changed. These are inserted through the top end of the quartz tube. A $\frac{3}{8}$-inch diameter thermocouple tube 18 inches long (*T*) is waxed into a tightly fitting hole in the 1-inch thick brass cap. Two lavite blocks (*L*) are sealed to the thermocouple tube with Alundum cement. A third lavite block is sealed to the lower end of a 12 inch tube of the same diameter. This second tube can be moved up and down parallel to the first, during which motion the lavite blocks serve as guides. They also serve as supports for the platinum electrodes. The weight of the 12-inch tube is sufficient to give the mechanical contact. The leads from the sample are taken through the thermocouple tubes. The resistance of both lavite and thermocouple tubing (Alundum) was found to be very high compared with the resistance of the sample at any given temperature.

The second furnace is useful in the temperature range from room temperature to 220°C. Nichrome wire replaces the Glowbar heating element and a Pyrex tube replaces the quartz tube of the foregoing furnace. The electrodes are brass, supported by a stainless steel tube and insulated by Pyrex rods.

IV. RESULTS

A. The Electrical Contacts

As already mentioned, a moist sample through which current is flowing develops on its surface a layer possessing high resistance. The probe method indicates that vacuum-evaporated gold electrodes show no contact resistance when placed on a thoroughly dried sample, whereas vacuum-evaporated aluminum electrodes show a contact resistance. For example, at 105°C the resistance varied from a value equal to three times the volume resistance of the sample at 5 volts to about 5 percent of the volume resistance at 50 volts. On the other hand, at 105°C a contact made mechanically with a platinum electrode has a contact resistance which is independent of the voltage and is 5 times that of the volume resistance of the sample. Mechanical electrodes of lead foil show the same high contact resistance as platinum. The method is not too accurate since the exact position of the probes is difficult to ascertain. Also in these porous unsintered samples the evaporated gold possibly penetrated the surface of the sample. See Table I.

For sintered pellets at 105°C platinum and Nicrome mechanical contacts have about twice the resistance of evaporated gold or lead foil contacts. Aquadag contacts, on the other hand, seem to have half this resistance, perhaps because Aquadag introduces moisture into the

TABLE I. Voltage drop across sections of unsintered sample at 105°C.

	1–2	2–3	3–4	1–4
Pt-Pt	5.5	0.7	3.8	10.0
mechanical	33	3.8	23.1	59.2
	3.7	0.6	3.0	7.0
Au-Au	3.2	3.8	2.9	9.8
evaporated	16.1	18.2	13.8	47.6
Pt-Au mech. evap.	44.5	2.8	1.7	49.1
Al-Al	2.45	0.40	2.40	5.25
evaporated	17.2	14.6	17.1	49.1

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sample. The probe method, which for the set-up used becomes accurate only at higher temperatures (150°C) when the resistance of the sample is sufficiently low, shows that evapoated gold electrodes have no contact resistance. Platinum mechanical electrodes, however, have a high resistance until about 500°C when they become as good as gold electrodes.

B. The Effect of Impurities on the Conductivity

Moisture increases the conductivity, the electrolysis of the water contributing the added conduction.

A series of samples were measured at several temperatures below 200°C. The material from which the samples were made contained metal oxides added after precipitation of the lead chromate. The conductivity of the treated material was found to decrease by as much as a factor of 10,000 and depended directly on the amount and type of oxide added. This behavior is readily explained by assuming that the oxides form layers or coatings of high resistance on the particles of lead chromate. It was found that the light-fastness of these materials in general increased with decreasing conductivity, showing that there is probably a connection between the two properties.

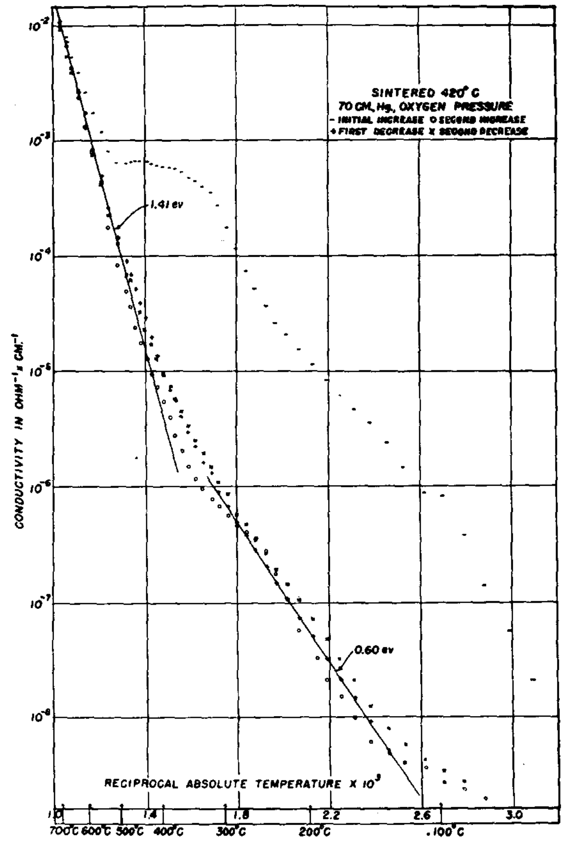

FIG. 3. Conductivity as a function of temperature. The run either up or down took 80 minutes in each case.

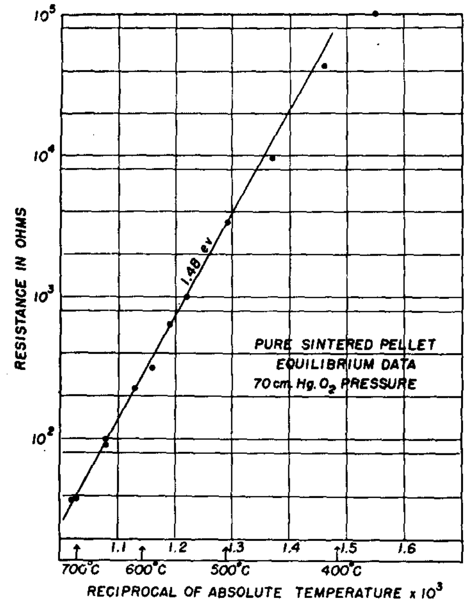

FIG. 4. Resistance-temperature curve for oxygen equilibrium.

C. The Effect of the Thermal History on the Conductivity

An unsintered sample has a conductivity of 1.2×10^{-5} ohm^{-1} cm^{-1} at 105°C. The conductivity of a sintered pellet, on the other hand, also at 105°C, varies with the sintering temperature and oxygen pressure. In fact values that range from 10^{-9} to 10^{-6} ohm^{-1} cm^{-1} have been obtained. The value of 5×10^{-9} ohm^{-1} cm^{-1} found by Kapp[4] for a natural single crystal lies within this range.

D. The Conductivity as a Function of Voltage

The dependence of the conductivity of an unsintered sample on the voltage is related to the contacts, the temperature, and the impurities. Gold electrodes extend the range of Ohm's law

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[4] G. Kapp, Ann. d. Physik 22, 257 (1935).

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to lower voltages and the temperature and impurities have a marked effect on the high voltage end of the range. On the other hand, a carefully prepared sintered pellet shows none of the foregoing behavior, and is closely ohmic over a large range of voltage.

E. The Conductivity as a Function of Temperature

The dependence of the conductivity σ on the absolute temperature T is given for certain temperature ranges by the Boltzmann-type equation

$$\sigma = Ae^{-\epsilon/kT}$$

where k is the Boltzmann constant, ϵ a constant called the activation energy, and A is relatively independent of T. The name "activation energy" will be restricted to k times the slope of the log σ *versus* $1/T$ curve. The significance of the activation energy will be discussed in the next section.

The most significant data concerning temperature dependence have been taken on samples sintered at 700°C. In this case the activation energy is 1.48 ev, as shown in Figs. 3 and 4, in the temperature range from 700°C to about 350°C when the rate of temperature change is sufficiently slow so that oxygen equilibrium is maintained. At lower temperatures the activation energy fluctuates widely about the value 0.60 ev. During very quick runs in which the specimen is taken from 700°C to 375°C in about 4 minutes, the activation energy is 0.65 ev below 20 cm of Hg oxygen pressure and is 0.96 ev in some samples at higher pressures.

As already mentioned, the conductivity at low temperatures depends very much on the temperature and oxygen pressure at sintering. These factors affect the log σ *versus* $1/T$ curves on the initial heating of a quenched specimen from room temperature in the manner shown in Fig. 3. It may be seen that there is a dip, or at least a plateau, in the curve at about 300°C. The precise character of this dip depends upon both the temperature and oxygen pressure at sintering. The low temperature conductivity, despite variations, is in all cases lower after heating than before.

F. The Conductivity as a Function of Oxygen Pressure

There are a few semiconductors in which at higher temperatures there is observed an intrinsic electronic conductivity.[5] It frequently happens, however, that at least part of the conductivity depends on the surrounding gas atmosphere.[6] In such cases the conductivity is related to the presence of a stoichiometric excess of one of the constituent atoms. This concentration of stoichiometric-excess atoms in the semiconductor is proportional to some power of the partial pressure of one of the constituents of the semiconductor in the surrounding atmosphere. In excess semiconductors in which there is conduction by electrons this is a negative power, whereas in defect semiconductors in which holes conduct it is a positive power. The particular law which applies in a given case gives a hint concerning the chemical reaction which produces the conducting units in the semiconductor. In zinc oxide, for example, the conductivity varies inversely as the fourth root of the oxygen pressure. This indicates that zinc atoms are formed and oxygen molecules released. In the case of zinc oxide, however, it is not possible to tell immediately whether nearly all or only a few of the zinc atoms lose their electrons to the conduction band, since both possibilities lead to the one-fourth law.[7]

The case of lead chromate is more complicated than the usual case of the metallic oxide, because a chromate radical replaces the simpler oxygen ion. However, the steps used to compute the oxygen dependence associated with an assumed reaction are the same as in the simpler cases. As we shall see, there is reason for assuming that a small number of lead chromate molecules dissociate according to the reaction:

$$2PbCrO_4 \rightarrow Pb(CrO_2)_2 + Pb^0 + 2O_2$$

or

$$Pb^{++} + 2CrO_4^{--} \rightarrow 2CrO_2^{-} + Pb^0 + 2O_2.$$

There are formed in this way n_b neutral lead

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[5] H. Dünwald, H. H. von Baumbach, and C. Wagner, Zeits. f. physik. Chemie **B22**, 226 (1933).

[6] K. Baedacker, Ann. d. Physik **22**, 749 (1907); **29**, 566 (1909); Baedacker, Physik. Zeits. **9**, 431 (1908); **13**, 1080 (1912); C. Wagner, Physik. Zeits. **36**, 721 (1935); B. Gudden, Ergeb. d. exact. Naturwiss. **13**, 223 (1934).

[7] P. H. Miller, Phys. Rev. **60**, 890 (1941).

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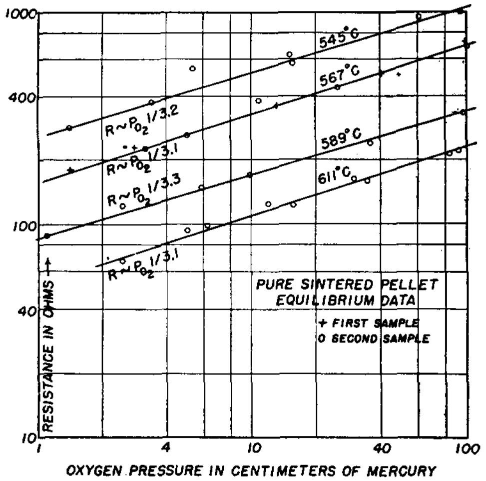

FIG. 5. Resistance-pressure curves.

atoms which probably occupy interstitial positions. n_b may be calculated as follows.

We make the assumption that the crystal is in thermodynamic equilibrium at the temperature T. This requires that the free energy shall be a minimum. The free energy A is made up of the following terms: (1) the energy required to produce the above reaction; (2) the free energy of the vacancies in the positive ion lattice; (3) the free energy associated with the chromite, CrO_2^-, ions; and (4) the free energy of the oxygen molecules. Thus

$$A = n_b\epsilon_b + kTn_b \ln (n_b/N) + 2kTn_b \ln (2n_b/N) + kT(N_0+2n_b) \ln N_0+2n_b/C,$$

where ϵ_b is the energy of the foregoing chemical reaction, N is the number of molecules of lead chromate composing the lattice, N_0 is the number of molecules of oxygen in the gas surrounding the crystal, and C is a constant.[8] It follows that for the free energy to be a minimum n_b must satisfy the following condition

$$n_b \propto N_0^{-\frac{2}{3}} \exp (-\epsilon_b/3kT) \propto P_0^{-\frac{2}{3}} \exp (\epsilon_b/3kT)$$

since N_0 is proportional to the partial pressure of the oxygen and provided that $n_b \ll N_0$.

At a particular temperature, n_f of these n_b lead atoms will be ionized:

$$Pb^0 \rightarrow Pb^+ + e.$$

The number n_f of free electrons thus produced may be calculated with the assumption of thermodynamic equilibrium following the procedure outlined above. This leads to the condition

$$n_f \propto n_b^{\frac{1}{2}} \exp (-\epsilon_f/2kT)$$

provided $n_f \ll n_b$. Therefore, since the conductivity σ is proportional to n_f,

$$\sigma \propto P_0^{-\frac{1}{3}} e^{-\epsilon/kT}$$

where $\epsilon = \epsilon_f/2 + \epsilon_b/6$.

We now see the significance of the activation energies of the previous section. They consist of two terms. One arises from the energy necessary to produce the chemical reaction and the other comes from the energy necessary to produce the ionization reaction. Both of these terms enter when the rate of temperature change is such as to maintain oxygen equilibrium, so that we must set $\epsilon_f/2+\epsilon_b/6$ equal to 1.48 ev. When the temperature is changed very rapidly, however, the slower chemical reaction is suppressed to a great extent, so that the activation energy depends mainly on the ionization reaction. Therefore $\frac{1}{2}\epsilon_f$ lies between 0.96 and 0.65 ev. In the opinion of the writer the lower value is the most reliable. This is indicated by the fact that at low temperatures where the chemical reaction is almost completely suppressed the activation energy is about 0.60 ev (Fig. 3). Using 0.60 ev for $\frac{1}{2}\epsilon_f$ it follows that ϵ_f is 1.20 ev and ϵ_b is 5.28 ev.

If the assumption that lead chromate dissociates according to the equations given above is valid, we should expect lead chromate to be an excess electronic conductor and should therefore expect that the conductivity would decrease with increasing oxygen pressure. This in fact is found to be the case. Measurements of the oxygen dependence of the conductivity were made around 600°C. The results are shown in Fig. 5. It is found that the conductivity obeys the law:

$$\sigma \propto P_0^{-1/3.1}$$

which is very close to the foregoing theoretical law, namely:

$$\sigma \propto P_0^{-\frac{1}{3}}.$$

The reaction which leads to this theoretical law was chosen from a number of possible reactions as being the most likely. It should be noted that

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[8] C is approximated by $(2\pi mkT)^{\frac{3}{2}}V/h^3$ where m, k, T, and h have the usual meaning and V is the volume of the containing vessel; see F. Seitz, reference 1, p. 462.

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lead chromate becomes green on being heated in the absence of oxygen. This color must be assumed to come from trivalent chromium, which supports the preceding reaction.

It is of interest to note that if most of the interstitial lead atoms are ionized, thermodynamic considerations would predict

$$\sigma \propto P_0^{-\frac{1}{2}}.$$

G. The Ionic or Electronic Nature of the Conducting Carriers

The foregoing discussion indicates that lead chromate is a normal electronic conductor. Transport measurements of the type employed by Tubandt[9] have been made to test this directly. The results indicate that the ionic conduction must be less than 1 percent of the total conduction. It must be admitted that there is a slight possibility that blocking layers between the pellets or between the individual grains prevented the ions from migrating to the electrodes. This seems very unlikely, however, since Tubandt's methods have proved successful in so many cases.[10]

Hall effect measurements have also been attempted. However, the results to date have not been reliable because of the high resistance of the samples.

Seebeck effect measurements, on the other hand, indicate clearly that lead chromate is an excess semiconductor. From qualitative measurements the Seebeck e.m.f. per degree is in the neighborhood of 3 millivolts at 50°C. The hotter electrode was positive, so that the conductors are electrons. As a check, the effect was measured in Cu_2O, which is known to be a hole conductor, and it was found that the hotter electrode was negative as it should be. It is interesting to note that the free electron model preducts that the Seebeck e.m.f. should be equal to $\frac{1}{2}\epsilon_f/T$. This gives for the Seebeck e.m.f. at 50°C the value $\frac{1}{2}(1.20/325)$ or about 2 millivolts which is in rough agreement with the measured value.

H. Summary of Results

In the measurement of the electrical conductivity of lead chromate the best results have been obtained with the use of sintered pellets possessing gold electrodes that were evaporated on in vacuum. (1) Such samples have a negligible contact resistance and obey Ohm's law over a large range of voltage and temperature. (2) The conductivity has been found to vary with the temperature in the range from 700°C to 350°C in accordance with the Boltzmann-type law $\sigma \propto \exp(-1.48ev/kT)$, whereas the conductivity obeys the law $\sigma \propto \exp(-0.60ev/kT)$ at lower temperatures. (3) At constant temperature the conductivity increases with decreasing oxygen pressure in accordance with the relation $\sigma \propto P_0^{-1/3.1}$. This relation indicates that lead chromate dissociates in accordance with the equations:

$$2PbCrO_4 \rightarrow Pb(CrO_2)_2 + Pb^0 + 2O_2$$
$$Pb^0 \rightarrow Pb^+ + e.$$

The activation energies for these reactions are probably 5.28 and 1.20 electron volts, respectively. These same reactions may explain the optical darkening process with the optical excitation replacing thermal excitation in producing the darkening substance. (4) Hall effect measurements on sintered pellets have not been reliable; however, transport measurements show that ionic conduction is probably less than 1 percent and Seebeck effect measurements indicate conduction by electrons with a Seebeck e.m.f. of about 3 millivolts per degree. (5) It is concluded that lead chromate is an excess electronic semiconductor.

In conclusion I wish to thank Professor F. Seitz, Dr. P. H. Miller, and Dr. A. W. Lawson for suggesting this problem and for their helpful advice and criticism. I am also indebted to W. Feldman and members of Works Progress Administration Project 25792 for assistance in observation and the Krebs Pigment Department of E. I. du Pont de Nemours and Company for financial assistance.

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[9] C. Tubandt, *Handbuch der Experimentalphysik* (1932), Vol. 12, p. 396.

[10] In support of the conclusions drawn here is the recently published article by Selma B. Brody in J. Chem. Phys. **10**, 650 (1942) in which it is concluded from x-ray investigations that lead chromate has a close packed structure and therefore ionic migration is unlikely.

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