bronzes ($NaWO_3$) can lose sodium according to the reversible reaction $NaW^{V}O_3 \rightleftarrows Na^0 + W^{VI}O_3$.

The tungstic oxide dissolves in the remaining sample with formation of anionic substitutional solid solutions. The cubic bronzes can contain up to 80% tungstic oxide. The lattice constants *versus* tungstic oxide-content are shown in Fig. 3.

The properties of pure sodium metatungstate and those of the solid solutions are described. The tetragonal blue bronzes contain 80–90% tungstic oxide. Their color is more greenish. Compounds with 92–96.4% tungstic oxide were green. For samples with still higher tungstic oxide concentration see above.

ROLLA, MO. RECEIVED JANUARY 19, 1948

The Sodium Tungsten Bronzes. II. The Electrical Conductivity of the Bronzes

BY M. E. STRAUMANIS[1] AND A. DRAVNIEKS[2]

Introduction.—The high electrical conductivity of tungsten bronzes was reported first by Hägg[3] who observed a large increase in conductivity with increase in temperature. He suggested that the increase was the result of progressive sintering.

More recent investigations made by the authors, however, show that the conductivity effect is much more complex in nature. The purpose of the present paper is to establish the factors responsible for these changes in conductivity.

The General Behavior of Sintered Yellow Bronzes.—The specimens were prepared from either a pure yellow powder of sodium tungsten bronze or from a corresponding mixture of tungsten powder, tungsten trioxide and sodium tungstate (composition given on page 684). The powder was pressed into small cylinders by means of a steel pellet press and the specimens were then sintered at 700–750° in high vacuum for one to two hours and cooled under vacuum. The specimens were 10–15 mm. long, about 6 mm. in diameter, hard and brittle. The color was yellow to orange. The ends of the specimens were ground parallel, polished and coated with graphite. To measure the electrical resistance, the specimens were fastened in a jig (Fig. 2b) supplied with suitable leads. The resistance was measured with a good technical ohmmeter.

Generally, the resistance of freshly prepared specimens was 0.2–0.6 ohm, depending on the composition. However, the resistance increased continuously,[4] reaching values of 10,000 ohms and even higher (Fig. 1). The reproducibility of the resistance *vs.* time curves was poor. Sections of the curve can be described by an equation of the form

$$r = r_0\,(1 + \alpha\sqrt{t})$$

where r_0 = initial resistance, t = time and α = coefficient which changes slowly with time. The weight of a specimen increased by 0.08–0.2% during a run.

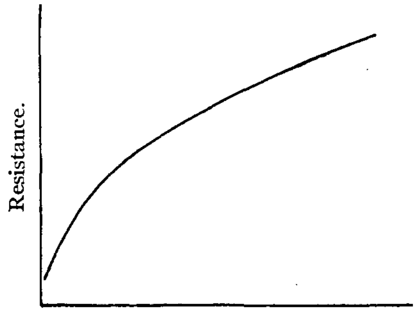

Fig. 1.—Increase of electrical resistance with time of a briquette of yellow bronze exposed to air.

The resistance of a specimen did not change when it was kept in vacuum, or in hydrogen, nitrogen, hydrogen sulfide, dry oxygen or pure water vapor, or when the specimen was protected from air by rubber tubing. When the atmospheric air was admitted, the resistance started to increase immediately. A particularly rapid and irregular increase in resistance was caused by oxygen saturated with moisture or moist air. The change due to moist air is shown in Table I.

TABLE I

RESISTANCE CHANGES OF TWO SPECIMENS OF BRONZE SPECIMEN B_2 IS YELLOW BRONZE, 10.3% WO_3; SPECIMEN F_1 IS RED-BROWN BRONZE, 12% WO_3; AIR SATURATED WITH WATER VAPOR AT 20°

Specimen B_2			Specimen F_1	
Time, min.	Resistance, ohm	Remarks	Time, min.	Resistance, ohm
0	0.45	High	0	0.54
90	.46	vacuum	60	.55
100	.62	Water	70	.58
120	.67	vapor	210	.64
130	.70	pure	245	.68
140	6.3	Air	250	3.3
150	23.0	and	260	18
160	55	water	270	53
170	101	vapor	280	115
180	160		290	220
330	620		300	330
360	640		320	600
			350	1100

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(2) Illinois Institute of Technology, Chemistry Department, Corrosion Research Laboratory.

(3) Hägg, *Z. physik. Chem.*, **B29**, 201 (1935).

(4) Observed first by Dr. G. Münch, State Institute of Metal Chemistry, Marburg a. Lahn.

At resistances over 1000 ohms polarization effects were observed. This polarization was never observed when only small amounts of moisture were allowed to make contact with the specimens.

The lost conductivity can be easily restored to an appreciable extent by drying the specimen over phosphorus pentoxide or by placing it in a vacuum; *e. g.*

50 ohms	(moist air)	120 ohms
120 hms	(P_2O_5)	60 ohms
60 ohms	(moist air)	850 ohms
850 ohms	(P_2O_5)	200 ohms

Full restoration is achieved only by sintering the sample in vacuum. Mild warming in air restores the conductivity in part, but the resistance increases again upon cooling, since renewed adsorption of oxygen and water vapor takes place. Table II shows the course of an experiment in air and in vacuum.

TABLE II

THE DECREASE OF RESISTANCE OF A SPECIMEN OF YELLOW BRONZE IN AIR AND IN VACUUM AT ELEVATED TEMPERATURES

In air			In vacuum			
Time, min.	Temp., °C.	Resistance, ohm	Time, min.	Temp., °C.	Resistance, ohm	Press., mm.
0	22	> 12000	0	20	12000	0
25	70	9200	20	280	2000	0
38	80	1090	30	290	620	0.2 (?)
50	90	450	40	310	390	0.2
65	100	120	80	390	36	0.2
100	105	56	90	410	13	0.2
153	105	41	110	550	1.9	0.2
161	100	41	170	580	1.2	1.5
178	90	44	200	680	1.0	2.0
181	80	45	215	730	0.9	2.2
184	72	46	230	790	0.82	2.5
186	65	47	240	800	0.78	2.5

The pressure developed in vacuum is due to adsorbed gases evolved from the specimen.

The conductivity can also be restored if the specimen is heated by passing a strong electric current through it.

Consequently, it may be stated that the increase in resistance of sintered porous specimens of tungsten bronzes is caused by the simultaneous adsorption of oxygen and water vapor. The presence of both is necessary.

The small amounts of adsorbed oxygen and moisture (several tenths of a per cent.) causing the changes and easy desorption indicate that the formation of sodium tungstate is not the process responsible for the effects described. However, it is known that the conductivity of pure elements can be appreciably decreased by intercrystalline layers of poorly conducting surfaces. A typical example is boron.[5]

Sodium bronze ($NaWO_3$) decomposes at high temperatures; tungsten, sodium tungstate and other compounds are formed.[6] Sodium tungstate acts as an intercrystalline cement holding the grains of pure bronze (see sintering, page 686). But only the metallic tungsten could be expected to form unstable, poorly conducting adsorption compounds with water and oxygen.[7]

Investigations on very pure tungsten bronzes were conducted to eliminate the effects caused by the intercrystalline substance.

The Conductivity of Pure Sodium Tungsten Bronzes.—The apparatus as shown in Figs. 2a and b was employed to measure the conductivity, temperature coefficients and change of conductivity under the influence of different agents. The specimen was placed in the glass tube between the two well-fitted steel pistons of the jig (Fig. 2b). The screw was tightened until the measured resistance attained a constant value. Then the jig was placed in the apparatus shown in Fig. 2a. The resistance of the leads was subtracted from the total measured resistance. The device could also be employed for measuring the resistance of powders.

The procedure used for removing the tungsten and sodium tungstate particles from the specimens is described in the previous article.

The data measured on powders of two tungsten bronzes are shown in Table III.

TABLE III

THE SPECIFIC RESISTANCES (σ) AND CONDUCTIVITIES (κ) OF THE TWO PUREST SODIUM TUNGSTEN BRONZES IN VACUUM AT DIFFERENT TEMPERATURES, IN WATER VAPOR, AND IN WATER VAPOR WITH AIR

$NaWO_3$, almost 100%, fine crystalline				$NaWO_4 \cdot WO_3$ (11.6% WO_3), reddish, coarsely crystalline			
Time, min.	Temp., °C.	σ ohm.	κ ohm^{-1}	Time, min.	Temp., °C.	σ ohm.	κ ohm^{-1}
0	450	0.0059	170	0	450	0.036	28
20	300	.0029	350	25	400	.033	30
65	20	.0029	350	30	350	.031	32
Water vapor, 14 mm.				35	300	.02	50
80	20	.0029	350	90	20	.0026	385
110	20	.0029	350	1290	20	.0026	385
Air admitted, 90 mm.				Water vapor with air			
140	20	.0029	350	1310	20	.0026	385
				1390	20	.0026	385

The agreement in values obtained at 20° (350–385 ohm^{-1}) is satisfactory in view of the low reproducibility of such measurements.

The measurements on pressed and sintered specimens of yellow bronze are shown in Table IV. They possess lower conductivity, and the conductivity does not change in dry air, but decreases rapidly in moist air.

The negative temperature coefficient indicates a metallic (electronic) type of conductivity.[8]

The fact that some authors[3] have found a positive temperature coefficient of conductivity may be explained by the presence of moisture and oxy-

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[5] Henninger, *Ann. Physik*, **28**, 245 (1937).

[6] Straumanis, THIS JOURNAL, **71**, 679 (1949).

[7] If tungsten is replaced by metallic silver (mixture of silver Na_2WO_4 and $NaWO_3$) no change in resistance could be observed (see p. 686).

[8] Meyer, *Z. Elektrochem.*, **50**, 276 (1944).

TABLE IV

THE SPECIFIC RESISTANCES (σ) AND CONDUCTIVITIES (κ) OF TWO SINTERED BRONZE SPECIMENS OF DIFFERENT COMPOSITION IN VACUUM, HYDROGEN AND DRY AIR AT DIFFERENT TEMPERATURES

Specimen A with 4.4% WO$_3$				Specimen C$_2$ with 10.6% WO$_3$			
Time, min.	Temp., °C.	σ, ohm.	κ, ohm^{-1}	Time, min.	Temp., °C.	σ, ohm.	κ, ohm^{-1}
0	18	0.18[a]	5.6	0	20	0.21[a]	4.8
30	250	.13[a]	7.7	40	400	.12[a]	8.3
40	350	.03[a]	33	50	450	.08[a]	12.5
80	430	.024[a]	42	60	470	.053[a]	18.8
Hydrogen admitted				75	475	.044[a]	23
130	430	.018	55	95	485	.04[a]	25
185	430	.013	77	105	400	.028	36
Hydrogen exhausted, vacuum				115	300	.02	50
200	300	.013	77	130	200	.017	59
210	200	.011	91	155	20	.015	67
225	50	.0098	102	195	20	.015	67
2800	15	.0072	139	Dry air admitted			
2860	15	.0072	139	285	20	.015	67
				2835	20	.015	67

[a] The specimens contained adsorbed oxygen and water vapor.

gen in the nitrogen employed to blanket the specimens in earlier work. The present paper shows that water and oxygen are again adsorbed upon lowering the temperature. In this way a positive temperature coefficient is obtained due to reaction which is not germane to pure NaWO$_3$ (bronze) or to NaWO$_3$ containing tungsten trioxide.

The conductivities and temperature coefficients of bronzes with higher tungsten trioxide content are shown in Table V.

TABLE V

THE CONDUCTIVITIES AND TEMPERATURE COEFFICIENTS OF CONDUCTIVITY OF SODIUM-TUNGSTEN BRONZES WITH HIGHER TUNGSTEN TRIOXIDE CONTENT (ALL SOLID SOLUTIONS)

Specimen	WO$_3$, %	κ in ohm^{-1} at °C. 20	400	430	450	500	$\frac{1}{\kappa_0} \times \frac{d\kappa}{dT} \times 10^3$
III	0	350	..	..	170	..	−1.2
A	4.4	189	73	..	...	..	−1.6
A	4.4	139[a]	..	77	...	..	−1.1
E$_1$	7.9	51[a]	38	..	...	..	−0.67
E$_2$	7.9	26	16	..	...	..	−1.0
$_1$E$_2$	10.3	44	..	13	...	..	−1.7
B$_2$	10.3	44	..	..	...	10	−1.6
C$_2$	10.6	99	14[c]	..	...	..	−2.6
C$_2$	10.6	67	..	..	...	25[d]	−1.3
F$_1$	12.0	21[b]	19	..	...	..	−0.25

[a] 15°. [b] 25°. [c] 350°. [d] 485°.

Here large differences in conductivity of different specimens were observed, even in parallel experiments. Generally, the conductivity decreases with increasing tungsten trioxide content. The temperature coefficient is negative throughout and its values lie within 1:10 ratio.

The specimens with still higher tungsten trioxide content are very brittle and collapse under pressure applied in the jig. Since for specimens with more than 35% tungsten trioxide the resistance was not affected by moist air, a simpler apparatus was employed.

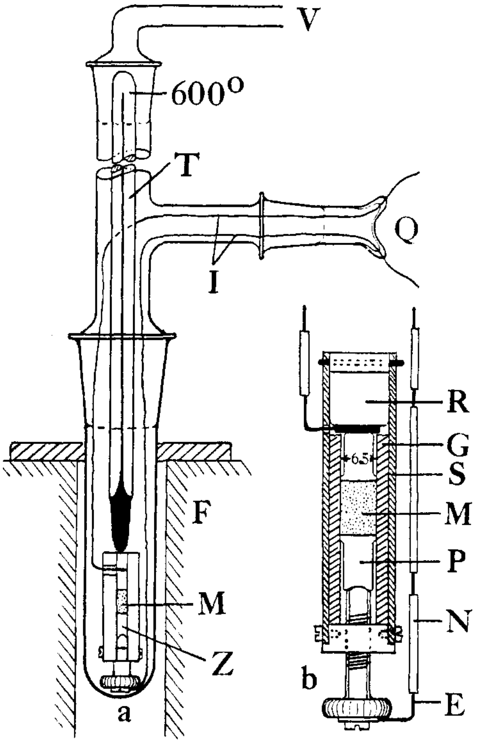

Fig. 2.—Apparatus for the measurement of resistance of sintered samples or powders in vacuum or in the presence of different gases at different temperatures: a, the complete apparatus; b, the jig; E, lead; F, furnace; G, glass tube; I, insulated leads; M, specimen; N, insulation; P, steel piston; Q, to ohmmeter; R, porcelain; S, slitted iron tube; T, thermometer; V, to vacuum pump; Z, slit.

TABLE VI

THE SPECIFIC RESISTANCE OF SODIUM TUNGSTEN BRONZES WITH HIGH TUNGSTEN TRIOXIDE CONTENT. THE COLORS OF BRONZES, SEE PAGE 683, ROOM TEMPERATURE

Specimen	WO$_3$, %	σ, ohm	Specimen	WO$_3$, %	σ, ohm
G$_1$	38.8	0.00166	116	93.6	980
146	46.5	52	117	94.8	360
150	51	135	118	95.6	155
155	65	3.2	120	96.9	8300
104	69.6	4.5	121	97.3	2800
156	70	6.3	122	97.8	16300
105	73	67	123	98.2	13700
107	79	65	125	98.9	29000
109	86.5	23	126	99.1	31500
114	91	24	127	99.3	17000
115	92	70	WO$_3$[a]	100	200000

[a] Heated in vacuum at 920°

The violet specimen G$_1$ with 38.8% tungsten trioxide had the highest conductivity in the whole series, 600 ohm^{-1}.[9] With higher tungsten trioxide contents the resistance increases rapidly but the results fluctuate. The addition of small amounts of $NaWO_3$ decreases the resistance of tungsten trioxide very effectively. Tungsten trioxide is a semiconductor of the excess type.[10,11,12]

Reasons for Resistance Changes in Sintered Specimens.—The measurements reported above demonstrate that the pure sodium tungsten bronzes possess constant conductivity at constant temperature. Therefore, the changes in resistance of sintered specimens of bronze are caused by an intercrystalline phenomenon and due to an intercrystalline substance.

If the metallic tungsten is assumed to take part in the effect, the behavior of a mixture of tungsten and sodium tungstate should be similar to that of the bronze specimens. Accordingly, an identical study was made with specimens of a tungstate and tungsten powder mixtures. These were pressed in the same way as the bronze specimens, with subsequent heating at 600° in vacuum. The resistances were as shown in Table VII.

TABLE VII

SPECIFIC RESISTANCE OF Na_2WO_4 WITH DIFFERENT AMOUNTS OF TUNGSTEN ADDED

Wt. % W	13	20	30	40	50	55
Resist. ohm	17000	12000	11400	334	0.29	0.067

The specimen with 50% tungsten was dark gray and its behavior studied in the apparatus of Fig. 2. The resistance in atmospheric air began to increase during the first day. The specimen showed the same behavior as the bronzes. At very high moisture contents the specimen became white and the changes in resistance were then irreversible, apparently due to the formation of sodium tungstate from the tungsten.

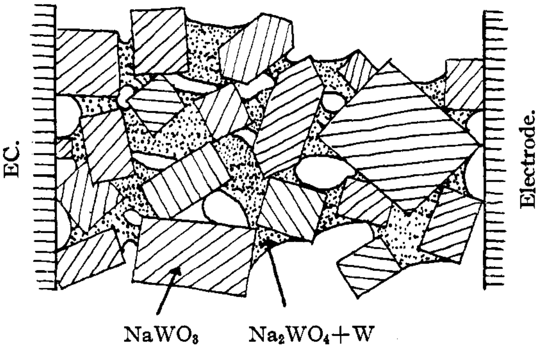

Fig. 3.—Structure of a sintered sodium tungsten bronze specimen: sodium tungstate cements the bronze grains, the black dots represent tungsten, the pores are white. The bronze crystals are shown smaller than they actually are in comparison with the intercrystalline tungstate–tungsten mass.

Similar specimens prepared from sodium tungstate with 30% silver powder added had 0.32 ohm resistance, but this value did not change in moist air. No changes of resistance were observed in pressed tungsten powders.

Consequently, it may be concluded that the resistance changes of sintered bronzes are caused by elementary tungsten in combination with sodium tungstate or similar products. The presence of elementary tungsten in sintered bronzes was also detected by X-ray diffraction patterns. Free tungsten and sodium tungstate are not found if the bronze specimens contain more than about 35% tungsten trioxide. Such specimens are therefore brittle and insensitive to moist air.

The Structure of Sintered Bronze Specimens.—The schematic structure of sintered specimens is suggested by the foregoing observations as shown in Fig. 3.

The conductivity of the aggregate is caused by tungsten particles which form conducting bridges in the mass of sodium tungstate. The latter also cements the grains of the bronze. In moist air the formation of adsorption compounds begins on the surface of the tungsten particles with a simultaneous binding of oxygen and water. As a result many bridges are ruptured and the resistance of the whole aggregate increases. The diffusion of moist oxygen proceeds deeper and deeper through the pores. Upon placing in vacuum or heating, the adsorption compound is decomposed and the conductivity improves. However, not all of the interrupted bridges can be regenerated. In many places the reaction may proceed to form sodium tungstate, a non-conductor. Also, $NaWO_3$ is slowly oxidized to tungstate. The volume increases and cracks are formed. The degree of destruction depends upon the duration of contact with moist oxygen and the amount of moisture. The regeneration is not complete in vacuum or by gentle heating as sodium tungstate does not decompose and is not reduced at low temperatures in hydrogen. Upon heating to 700° in vacuum the bronze decomposes partly to tungsten and sodium tungstate and new tungsten bridges are formed. In this way the effects observed concerning the conductivity behavior of tungsten bronzes are easily and completely explained.

Adsorption Compound on the Surface of Tunsgten.—The concept of the adsorption compound which is used as an explanation for the change of the conductivity of a tungsten–tungstate mass needs further elaboration. Although it is well known that at high temperatures tungsten easily forms oxide films,[13,14,15] this does not occur under ordinary conditions. The surface of a tungsten grain is probably in a particularly active state, as a result of being embedded in the sodium tung-

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(9) Perhaps the bronzes of transition composition, THIS JOURNAL, **71**, 679 (1949), possess still higher conductivity.

(10) Friedrich, *Z. Physik*, **31**, 813 (1925).

(11) Friedrich, *ibid.*, **34**, 637 (1925).

(12) Meyer, *ibid.*, **85**, 278 (1933).

(13) Langmuir, *Physik Z.*, **15**, 529 (1914).

(14) Kingsdom, *Phys. Rev.*, **24**, 510 (1924).

(15) Donal, *ibid.*, **36**, 1172 (1930).

state.[16] In this active state tungsten is able to react with oxygen and water forming an unstable adsorption compound. This view is supported by the following experiment: The purest yellow bronze was mixed with anhydrous sodium tungstate and tungsten powder and pressed. Specimens of this mixture behaved in the same way as the sintered bronze specimens.

Acknowledgment.—The above-mentioned work was performed in the State Institute for Metal Chemistry, Marburg a. d. Lahn, Germany. One of the authors (A. Dravnieks) would like to extend his gratitude to Dr. R. Schenck, director, for permission to use the Institute facilities for this investigation.

Summary

The specific conductivity of pure yellow sodium tungsten bronze is about 400 ohm^{-1} and the temperature coefficient is negative. The conductivity is electronic.

The temperature coefficient is definitely negative also for bronzes with up to 20% of tungsten trioxide (in solid solution). The highest specific conductivity (600 ohm^{-1}) is shown by the violet bronze with 38.8% of tungsten trioxide. At higher trioxide contents the resistance of the powder increases.

In the preparation of sintered specimens of sodium tungsten bronzes the $NaWO_3$ decomposes partly upon heating in vacuum, and tungsten, sodium tungstate and similar products are formed. These products cement the powder to a hard, brittle, porous specimen. Tungsten particles form conducting bridges between the crystals of actual bronze. The bridges are interrupted reversibly to some extent by moist oxygen. In this way the peculiar electrical behavior of sintered specimens can be completely explained.

Specimens with more than 35% of trioxide do not contain any free tungsten; therefore, the increase in resistance in moist air does not occur.

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[16] Anhydrous sodium tungstate is quasicubic and the lattice constant is ~5.57 kX.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE ARGONNE NATIONAL LABORATORY]

The Oxidation States of Neptunium in Aqueous Solution[1,2]

BY J. C. HINDMAN, L. B. MAGNUSSON[3] AND T. J. LACHAPELLE[3a]

The preliminary investigation in 1940 by the discoverers of element 93 (neptunium), McMillan and Abelson,[4] led these authors to the conclusion that there were lower and upper oxidation states of neptunium analogous to the +4 and +6 oxidation states of uranium. These and other experiments,[5] including those by Voigt, Sleight, Hein and Wright,[6] which suggested the possible existence of a +5 oxidation state, were performed by tracer methods using the 2.3 day beta emitting isotope Np^{239}. By use of the long-lived alpha emitting Np^{237} discovered in 1942 by Wahl and Seaborg,[7] it is possible to study neptunium with weighable amounts of material and in July, 1944, Magnusson and LaChapelle[8] succeeded in isolating the first pure compounds of neptunium using as the source of the Np^{237} uranium irradiated with cyclotron neutrons. At this time these investigators definitely established the existence of the +4 and +6 oxidation states by the preparation of microgram quantities of the solid compounds, neptunium(IV) dioxide, NpO_2, and sodium neptunium(VI) dioxytriacetate, $Na_2NpO_2(OOCCH_3)_3$. Zachariasen[9] was able to show by X-ray diffraction studies that these compounds were isomorphous with the analogous compounds of uranium and plutonium.

The isolation and purification of milligram quantities of Np^{237} made possible a more extensive investigation of the chemistry of this element. The first few milligrams were isolated as the result of special runs in the chemical extraction plant of the Clinton Laboratories (now the Oak Ridge National Laboratory) in Tennessee. The Np^{237} from this source was concentrated and isolated in pure form by a group from the Metallurgical Laboratory. This group was headed by J. J. Katz and consisted of Magnusson, LaChapelle, J. R. Gilbreath and W. C. Beard. Larger quanti-

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[1] This work was carried out during 1945 at the Metallurgical Laboratory of the University of Chicago under Contract No. W-7401-eng-37.

[2] Presented in part before the Division of Physical and Inorganic Chemistry at the Chicago Meeting of the American Chemical Society in April, 1948.

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[3a] Present address: Department of Chemistry, University of California at Los Angeles, Los Angeles, California.

[4] E. M. McMillan and P. H. Abelson, *Phys. Rev.*, **57**, 1185 (1940).

[5] G. T. Seaborg and A. C. Wahl, THIS JOURNAL, **70**, 1128 (1948).

[6] A. F. Voigt, N. R. Sleight, R. E. Hein and J. M. Wright, Manhattan Project report CN-1979, Oct. 10, 1944. To appear as paper No. 15.9 of Vol. 14B, Plutonium Project Record of the National Nuclear Energy Series.

[7] G. T. Seaborg and A. C. Wahl, to be published as paper No. 1.5, Vol. 14B, Plutonium Project Record of the National Nuclear Energy Series, *Phys. Rev.*, **73**, 940 (1948) (written on April 14, 1942).

[8] L. B. Magnusson and T. J. LaChapelle, Manhattan Project CN-2088, Sept. 1, 1944, THIS JOURNAL, **70**, 3534 (1948).

[9] W. H. Zachariasen, Manhattan Project report CN-2091, Sept. 4 (1944). To appear as papers Nos. 20.7, 20.8, Plutonium Project Record of the National Nuclear Energy Series; Symposium on Chemistry of Transuranium Elements, 1948 Spring Meeting, Am. Chem. Soc., Chicago, Ill., *Phys. Rev.*, **73**, 1104 (1948).