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The Sodium Tungsten Bronzes. I. Chemical Properties and Structure

BY M. E. STRAUMANIS

Introduction

The tungsten bronzes were discovered by F. Wöhler in 1824.[1] Since they have metallic properties, the name "tungsten bronzes" was applied, although they are neither alloys nor intermetallic compounds.

Later the "bronzes" were investigated by Brunner,[2] Spitzin[3] and others. W. F. de Jong found that the bronzes have the perovskite ($CaTiO_3$) type of structure and that the formula of the yellow bronze must be $NaWO_3$.[4] G. Hägg confirmed this statement and showed (1) that tungsten in the yellow bronze is pentavalent, (2) that sodium metatungstate and tungstic oxide form solid solutions with lattice contraction and change of color (from yellow through red and violet to dark blue) and (3) that the bronzes are very good electric conductors.[5]

The intention of this present work is to describe the still unknown qualities of tungsten bronzes and to find the end of the solid solution series.

Preparation of the Bronzes

Because of the limited amount of the required high purity starting material (sodium tungstate, tungsten and tungstic oxide) available, the quantities of the bronzes obtained were insufficient for precise chemical analyses. In fact, chemical analyses are not necessary because the absorption of tungstic oxide by the bronze is accompanied by shrinkage of its lattice. This property was used to determine the composition of the resulting bronzes. The lattice constants were found by the powder method, applying the author's technique.[6] Although the work was not done in thermostats, the precision was sufficient to determine the tungstic oxide content of the bronzes with an accuracy of 0.1% by weight. The presence of other reaction products in the samples has also been confirmed by X-rays.

The purest yellow bronzes (without any excess tungstic oxide) have the highest lattice constants and they must be prepared first. It can be shown that these compounds become brighter when treated with sodium vapor. The reduction was carried out in small iron tubes (0.5 × 2 cm.); on the bottom of the tube there was a piece of sodium approximately 1 mm. in diameter; the rest of the tube was filled with bronze (*e. g.*, the blue); the tube was closed loosely with an iron stopper and then slipped into a slightly larger tube of "supremax" or quartz glass, which finally was evacuated, annealed and sealed off. On heating in a furnace at 700–800° the reaction was completed in half an hour. The reaction began at about 400°. The sodium vapor reacted to produce sodium tungstate and tungsten in the iron tube. On the top of these products were grains of yellow bronze, followed by grains of darker colored bronze. Powder diagrams of the bright yellow grains showed that the highest lattice constants obtained by Hägg[5] (a = 3.850 kX) could be attained easily and even surpassed (see Table I).

TABLE I

HIGHEST LATTICE CONSTANTS OF THE YELLOW BRONZE, AFTER TREATMENT WITH LITHIUM OR SODIUM VAPOR, OR TUNGSTEN POWDER (UNDER FUSED $NaWO_4$)

Sample	Reductant	a in kX	Color
81	Li	3.8479	Golden
76	Na	3.8479	yellow
183	W	3.8494	Brighter golden yellow
62	Na	3.8502	Bright
69	Na	3.8504	yellow
70	Na	3.8504	Bright
61	Na	3.8508	yellow
182	W	3.8520	Bright
182a	W	3.8518	yellow

In the presence of tungsten under molten sodium tungstate the reaction evidently comes to equilibrium and an essentially purer bronze results. It is probable that sample 182 contains only a very small excess of WO_3.

This sample was prepared according to the reaction

$$3Na_2WO_4 + 2WO_3 + W = 6NaWO_3{}^{7}$$

The best results were obtained when the reaction took place under a cover of excess sodium tungstate:

W	0.60 g.
WO_3	1.52
Na_2WO_4	2.88 + 3 g. (anhydrous)
	8.0 g.

The dry mixture was slowly heated in vacuum up to 950° and then during the course of four hours uniformly cooled down to 700°. Then the current was turned off. The bronze crystals were completely under solid sodium tungstate, which could be removed with boiling water. On the sur-

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(1) Wöhler, *Pogg. Ann.*, **2**, 350 (1824).

(2) Brunner, "Beitrage zur Kenntnis der Wolframbronzen," dissertation, Zürich, 1903.

(3) Spitzin, *Z. anorg. allgem. Chem.*, **148**, 69 (1925); Spitzin and Kaschtanoff, *ibid.*, **157**, 141 (1926); *Z. anal. Chem.*, **75**, 440 (1928).

(4) de Jong, *Z. Krist.*, **81**, 314 (1932); de Jong and Stek, *ibid.*, **83**, 496 (1932). See also Glemser and Sauter, *Z. anorg. allgem. Chem.*, **252**, 156, 159 (1943).

(5) Hägg, *Z. physik. Chem.*, **B29**, 192 (1935).

(6) Straumanis and Ievinš, "Die Präzisionsbestimmung von Gitterkonstanten nach der asymmetrischen Methode." Springer, Berlin. 1940; Edwards. Ann Arbor. Mich., 1948.

(7) Worked out by Dr. G. Münch in the Institute for Metal Chemistry in Marburg.

face of the very nice cubic crystals of bronze, there still adhered sodium tungstate and fine tungsten powder (greenish appearance). These were easily removed with warm sodium hydroxide solution containing some sodium peroxide. Of course, the crystals then appeared slightly corroded (Fig. 1a). At higher temperatures larger crystals are obtained, but they were defective as evidently the bronze begins to decompose at 1000° (Fig. 1b). The sodium tungstate in excess obviously furthers the growth of the crystals; the bronze does not dissolve in it even at higher temperatures.

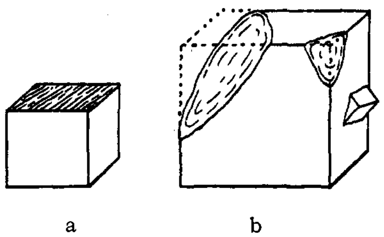

Fig. 1.—Crystal diagrams: a, cubic crystal slightly stripped; b, a larger and defective crystal with intergrowth.

For preparation of any deeper colored bronze the exact stoichiometric reaction (in vacuum, one-half—one hour, 700–800°) $NaWO_3 + xWO_3 \rightarrow$ deeper colored bronze was used.

Properties of Pure $NaWO_3$.—A sketch of two crystals is shown (Fig. 1). The crystals are shiny, brittle and have weak cleavage parallel to 100. The cleavage planes also have a strong metallic luster.[8] The crystals are good electric conductors. The conductivity ($\sim$ 400 Ω^{-1}/cm.$^{-1}$) is comparable with that of graphite.[9]

Under oxygen-free water the compound keeps its luster for several months and no appreciable solubility was detected. However, dissolution was observed in oxygen-rich water

$$2NaWO_3 + {}^1/_2O_2 \longrightarrow Na_2W_2O_7 \text{ (very slowly)}$$

The presence of $Na_2W_2O_7$ was proven beyond doubt by power photographs. An addition of hydrogen peroxide considerably increased the velocity of the reaction.

Strong bases dissolve sodium metatungstate only in the presence of oxidizing agents

$$2NaWO_3 + 2NaOH + {}^1/_2\ O_2 \text{ (air)} \longrightarrow 2Na_2WO_4 + H_2O \text{ (very slowly)}$$

$$2NaWO_3 + Na_2O_2 \longrightarrow 2Na_2WO_4 \text{ (quickly)}$$

The deeper colored bronzes dissolve in bases more readily the more tungstic oxide the compounds contain. The reaction is retarded by the pentavalent tungsten, it must be first oxidized to soluble tungstates.

The high resistance of sodium metatungstate to acids can be explained by the development of insoluble surface films containing tungstic acid. A mixture of nitric and hydrofluoric acids destroys the yellow bronze rather quickly. A greenish precipitate results which sometimes turns yellow (tungstic acid) and sometimes white.

The phenomena observed during heating of the bronze can be explained as follows: In the bronze crystals there is an equilibrium that is in accordance with the statements of Hägg[5] on the structure of $NaWO_3$

$$Na^+W^VO_3 \rightleftharpoons W^{VI}O_3 + Na^0 \qquad (1)$$

A rise in temperature promotes this oxidation–reduction reaction to the right. Sodium ion acts as oxidizing agent, converting W^{5+} into W^{6+}

$$W^VO^-{}_3 \longrightarrow W^{VI}O_3 + e$$
$$Na^+ + e \longrightarrow Na^0 \qquad (2)$$

The electron has only to pass from W^{5+} to sodium ion and the reaction is finished. The bronze must therefore have good electric conductivity[10] and the sodium ion must be very mobile. The mobility of sodium ion follows also from the structure of sodium metatungstate (see Fig. 2).

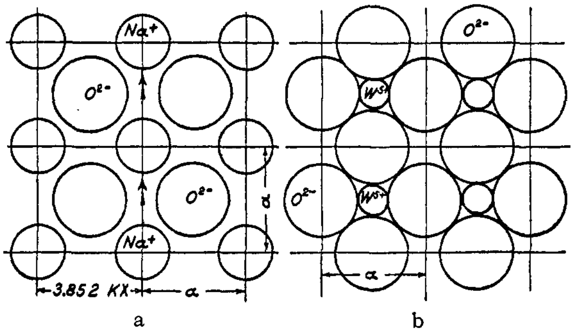

Fig. 2.—Structure of $NaWO_3$ (according to Hägg), showing positions: Na^+ 000, W^{5+} $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $3O^{2-}$ $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$; a, first layer; b, second layer; the third is identical with the first.

The sodium ion squeezes from one 000-site to another, especially at higher temperatures. If tungstic oxide is only slightly in excess there will be many empty 000-sites in the crystals.

On heating the yellow bronze in air, it begins to cake and turns blue-black. According to (1), sodium oxidizes on the surface and the tungstic oxide distributes in the crystal

$$NaWO_3 + xWO_3 = \underset{\text{deeper colored bronze}}{NaWO_3(W^{VI}O_3)_x} \qquad (3)$$

Simultaneously on the surface occurs

$$2NaWO_3 + {}^1/_2O_2 \longrightarrow Na_2W_2O_7, \text{ and}$$
$$Na_2O + WO_3 \longrightarrow Na_2WO_4 \qquad (4)$$

On heating sodium metatungstate above 700–800° *in vacuo*, reaction (1) becomes noticeable and the sodium vapor reduces the sodium metatungstate. Tungsten, sodium tungstate and some not

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[8] The polished, ground crystal is reddish and becomes yellow after few days. Moisture instantly causes the yellow color; however, it disappears soon.

[9] See the article of Straumanis and Dravnieks. THIS JOURNAL, **71**, 683 (1949).

[10] Friedrich, *Z. Physik*, **31**, 813 (1925); **34**, 637 (1925); see also Meyer, *Z. Elektrochem.*, **50**, 274 (1944).

yet identified products result. The latter cause the caking of the sodium metatungstate crystals (m. p. of sodium tungstate is $\sim 700°$). A part of the sodium vapor reacts with the glass or porcelain; the color of the resulting bronze then becomes deeper.

These reduction reactions can be completely suppressed, if there is present in the tube a sodium acceptor (*e. g.*, iodine in an evacuated tube at 700° *ca.* one hour)

$$\begin{aligned} NaWO_3 &\rightleftharpoons Na + WO_3 \\ Na + I &\longrightarrow NaI \qquad (5) \\ NaWO_3 + xWO_3 &\longrightarrow NaW^{V}O_3(W^{VI}O_3)_x \end{aligned}$$

With the help of iodine the sodium of the sodium metatungstate can be extracted almost completely; a few tenths of one per cent. remain in the resulting tungstic oxide which is then green.

A very good sodium acceptor is tungstic oxide itself (700°, vacuum); the bronze reacting according to (2) and (3) and the tungstic oxide with sodium according to (1), from right to left. A homogeneous composition finally results. The sodium metatungstate extracts the tungstic oxide even from a (Na_2WO_4 + WO_3)-melt.[11]

It follows from this that a deeper colored bronze must absorb the sodium from a brighter one until the sodium pressure is equal. Even 1-mm. crystals of the yellow bronze, embedded in an excess of the red bronze and heated under vacuum become red or in a similar fashion blue if embedded in a blue bronze (this corresponds to "mimicry" in the living world). However, they do not lose their single crystal properties.

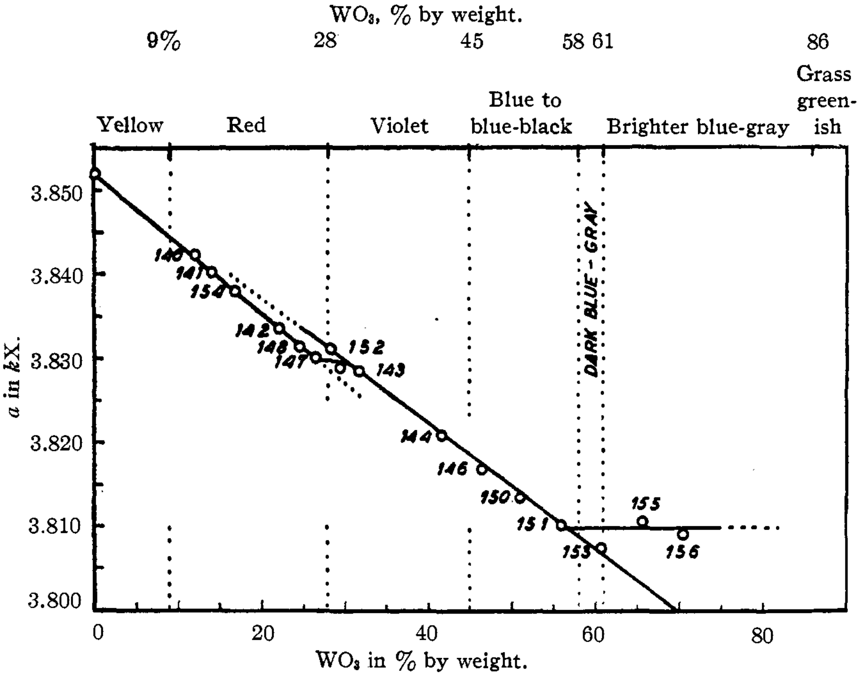

Fig. 3.—The solubility of tungstic oxide in cubic sodium metatungstate is between 56–57% by weight of tungstic oxide, using reaction (3) and 800°.

By increasing the sodium vapor pressure, reaction (1) can be directed from right to left, the vacant 000-sites will be filled while the corresponding amount of W(VI) passes into W(V) and the bronze becomes brighter (Table I).

The Solubility Limit of Tungstic Oxide in Sodium Metatungstate.—For determination of this limit the reaction (3) and the reaction

$$NaWO_3 + xI \rightleftharpoons Na_{(1-x)}(W^{V}O_3)_{1-x}\,(W^{VI}O_3)_x + xNaI \; (x < 1) \qquad (6)$$

were used. All experiments were carried out at 800° in evacuated fused tubes. The results are summarized in Fig. 3. Between 27 and 30% tungstic oxide there is a transition zone; the red bronze absorbs tungstic oxide without changing the lattice. This phenomenon was proven by repeated experiments on different samples. Thus the succeeding violet and blue bronzes must have a slightly different structure although the difference is not visible from the X-ray diagram.[12] At the above-mentioned point the bronzes have the highest electric conductivity.[9]

The lattice contraction follows from the fact that the W(VI) has a smaller ionic radius than W(V). The deviation of the measured lattice constants from the calculated points is shown in Table II.

Up to 52% tungstic oxide the lines are sharp, then the background begins to darken. At 57% tungstic oxide new lines appear. The limit is between 56 and 57% tungstic oxide (at 800°, rapid cooling, see Fig. 3). The cubic bronze cannot absorb more than 57% tungstic oxide without changing its structure. This statement is only partially correct as it depends on the method of preparing the tungstic oxide rich sample.

If the sodium is extracted from the sodium metatungstate using reaction (6), one can obtain compounds with considerably higher tungstic oxide content without breaking down the old cubic lattice:

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(11) If the yellow bronze and tungstic oxide in two adjacent dishes are heated under vacuum, the tungstic oxide becomes blue, violet or even red, because the bronze evaporates sodium and the tungstic oxide absorbes it readily.

(12) See v. Laue, "Röntgenstrahl-Interferenzen," Leipzig, 1940, p. 179b, or 1948, p. 193.

$$(W^{V}O_6)^{7-} \rightleftharpoons (W^{VI}O_6)^{6-} + e$$
$$e + Na \longrightarrow Na$$

and outside of the crystals

$$Na + I \longrightarrow NaI$$

The old structure remains in perfect order (sharp lines); only the lattice shrinks, while in the first case (reaction 3), a new lattice must be built up from the triclinic tungstic oxide. Extracting the sodium with iodine, a sample with a lattice constant a = 3.7913 kX, corresponding to 81.9% tungstic oxide, was obtained. However, weak new lines were already on the film.

TABLE II

THE DEVIATION OF THE MEASURED POINTS FROM LINEARITY

The first 6 points: $a = 3.8519 - 0.000829.WO_3\%$; the last 7 points: $a = 3.85\ 9 - 0.000743.WO_3\%$.

No.	Wt. WO_3, %	a meas. in kX	a calcd. in kX	Diff.	Diff. in %
140	12.08	3.8422	3.8419	+0.0003	+0.0078
141	13.96	3.8403	3.8403	± .0000	± .000
154	16.88	3.8380	3.8379	+ .0001	+ .0026
142	21.88	3.8335	3.8338	− .0003	− .0078
148	24.5	3.8312	3.8314	− .0002	− .0026
147	26.48	3.8303	3.8300	+ .0003	+ .0078
152	28.42	3.8311	3.8308	+ .0003	+ .0078
143	31.60	3.8285	3.8284	+ .0001	+ .0026
144	41.90	3.8208	3.8208	± .0000	± .000
146	46.5	3.8167	3.8174	− .0007	− .018
150	51.0	3.8134	3.8140	− .0006	− .016
151	56.0	3.8103	3.8103	± .0000	± .000
153	60.8	3.8075	3.8068	+ .0007	+ .018

The change in color of the samples with the contraction of the lattice (increasing tungstic oxide content) can also be seen from Fig. 3. Of course, the change is not sudden but gradual.

The Nature of the Cubic Bronzes

From the description given it is evident that all the cubic tungsten bronzes from yellow to dark blue belong to the same series of anionic substitutional mixed crystals: the complexes $(W^{V}O_6)^{7-}$ of the sodium metatungstate are replaced at random by the slightly smaller $(W^{VI}O_6)^{6-}$ complexes (the corners of the octahedra are common); the sodium sites remain open. The ready replacement can be explained by the statement of Brakken that in tungstic oxide the $(W^{VI}O_6)^{6-}$ complexes are already present.[13]

The formation of solid solutions is therefore possible, even if the components belong to different crystal systems (here cubic and triclinic). The conditions are: (1) the dimensions of the replaceable structure units cannot differ more than 5% in any direction[14] and (2) the sum of the charges must be zero. This occurs frequently when the components have a similar chemical formula and a similar lattice structure with similar lattice constants (Grimm).

The samples of the bronzes also confirm the rule that compounds containing an element in two valencies are intensely colored.

Compounds with a Higher Tungstic Oxide Content.—Extracting sodium from the blue bronze (~ 80% tungstic oxide) by help of iodine, gives a blue-greenish sample that begins to sublime at 850°. In the sample there are thin, long, blue needles with a greenish lustre. Rotating crystal diagrams showed that these belong to the previously described tetragonal bronze (lattice constants: a = 12.47 kX; c = 3.819; c/a = 0.306).[15] This diagram is similar to that of the cubic blue bronze.

With further loss of sodium (or tungstic oxide absorption) the samples become brighter and more greenish. The tetragonal cell contracts and new lines appear. At 92–96.4% tungstic oxide by weight a greenish-gray sample results. The diagrams have very many sharp lines and have a certain similarity with the tetragonal bronzes.

When the sodium is extracted still more, olive-green samples, brighter than the above-mentioned, can be obtained. The X-ray films are very rich with lines and show transition to the pure tungstic oxide patterns. In the region of 96.4–98.2% tungstic oxide the diagram of pure tungstic oxide can clearly be observed.

If the bronze contains more than 98.6% tungstic oxide, the powder photographs cannot be distinguished from pure tungstic oxide but the lines are, strange to say, sharper than the lines of the pure compound. Samples up to 99.3% tungstic oxide were prepared; their color is bright greenish-gray, they sublime to form thick, very brittle, slightly translucent crystals (not needles).

There are also some other compounds in the reaction tubes, especially when they are heated above 1000°. Even traces of sodium metatungstate give the tungstic oxide a greenish color.

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Summary

It has been proven that the sodium tungsten

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[13] Brakken, *Z. Krist.*, **78**, 487 (1931): tungstic oxide consists of octahedra also (with common oxygen corners). But these are oblique, because the symmetry of the lattice is triclinic or pseudo rhombic. The oblique octahedra evidently change into regular when absorbed by the bronze.

[14] Straumanis and Stahl, *Z. physik. Chem.*, **194**, 130 (1944).

[15] de Jong and Stek, ref. 4, found a = 17.5 Å. (in the direction of the diagonal of the base 12.4Å); $\bar{c}$ = 3.8; c/a = 0.217. Hägg, ref. 5, found a = 12.13 and c = 3.77 Å.

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.

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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.

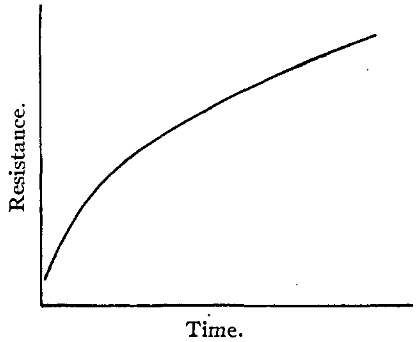

Fig. 1.—Increase of electrical resistance with time of a briquette of yellow bronze exposed to air.

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 Time, min.	Specimen B_2 Resistance, ohm	Remarks	Specimen F_1 Time, min.	Specimen F_1 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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(1) University of Missouri, School of Mines & Metallurgy, Department of Metallurgy, Rolla, Mo.

(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.