Deviations will also be observed if any processes occur where part of the enriched N^{15} is picked up at the rear in a form which does not exchange, but which does redeposit at the front edge of the band. For example, if there is carbonate in the sodium hydroxide, this might react with ammonia to give ammonium carbamate. If the carbamate hydrolyzes only slowly as it is swept across the adsorbed ammonium band, it may transport enriched N^{15} from the rear to the front of the band without permitting equilibration. Acid conditions at the front boundary could bring about hydrolysis, redeposition and contamination of the N^{14} at this point.

Deviations may also occur if the driving solution contains any nitrogenous impurities, or if the hydrogen-form resin bed contains nitrogen in a form which can yield ammonia. The latter case apparently occurs in our experiments and sets a lower limit for the N^{15}–N^{14} ratio in the leading plates of the band. Any ammonia in the sulfuric acid or water used to recondition the resin will introduce ammonia into the resin stream and prevent the attainment of low N^{15}–N^{14} ratios. An even more serious possible mechanism for resin contamination is that a small amount of the ammonia might react with the resin (perhaps with the sulfonic acid group) to give a compound which does not exchange rapidly or break down completely in cold caustic or the sulfuric acid regenerant solution. Such a compound might be broken down fairly completely by the heat generated by the reaction of the NH_4OH with hydrogen-form resin at the front edge of the band during the next cycle of elution. Such an effect can be minimized by passing hot caustic over the resin after the band has passed. Analysis of hot caustic strip solution used for this purpose has shown traces of ammonia enriched in N^{15} left behind on the resin. This effect is small and is not observed when the isotopic ratio at the front edge is high. The effect does become important, however, where the N^{15}–N^{14} ratio to be measured is low, particularly, if the compound causing the trouble was formed sometime previously when the N^{15}–N^{14} ratio was high.

Finally, deviations from linearity at very low and very high isotopic ratios may arise from analytical errors in the mass spectrograph as a result of background or air contamination of the gas samples.

D. Continuous Operation with a System of Fixed Bed Ion-exchange Columns (in collaboration with J. Capellen, D. M. Provow and H. Burkholder).—The theory of continuous operation with a system of fixed bed ion-exchange columns was discussed previously. The value of ϵ given in Section II-B indicated that a total of 39 moles of band displacement would be required to resolve each mole of nitrogen (added as ammonium hydroxide) into the individual nitrogen isotopes. Calculation showed that each 4-inch by 5-foot column of Dowex 50-X12, 100–200 mesh resin had an exchange capacity of about 32 equivalents. If an addition of ammonia were made once each cycle of ten columns, a total of 320 equivalents of resin would be traversed between injections. Consequently, 8.2 equivalents of ammonia should be added per cycle.

In order to test the validity of these calculations, a series of ten 4-inch diameter columns five feet long was prepared.

The original adsorbed band consisted of 3.5 liters of 15 *N* ammonium hydroxide (diluted 30-fold for loading). The band was eluted down 30 columns with 0.6 *N* NaOH at a flow rate of 400 ml. per minute before any additional ammonia was added or any N^{14}-rich product was withdrawn. Thereafter, 550 ml. of 15 *N* ammonium hydroxide in 15 liters of solution was added each cycle and a corresponding amount of N^{14} product was withdrawn. No enriched N^{15} product was removed, except when profiles of the adsorbed band were taken to determine its condition. Injections were initially made nine inches ahead of the tail-end of the band, but as the N^{15} concentration in the rear part of the band increased, it became necessary to gradually move the point of injection forward in order to stay on the normal plateau. The injection point was 16 inches from the tail-end of the band by the 500th column.

The depleted product being withdrawn early in the experiment had a N^{15}–N^{14} ratio of about 0.00012, but the ratio tended to increase gradually. When the N^{15}–N^{14} ratio of the depleted product exceeded 0.00050, the length of the band was increased by making an addition but no withdrawal. In all, two such increases were made so that the band was about 100 inches long by column number 550 and contained the equivalent of 4.6 liters of 15 *N* ammonia or 69 moles. Figure 4 is a profile of the band taken as the band passed from the 598th to the 599th column just before an injection and withdrawal were made. Profiles were also taken at the bottoms of columns 599 and 609 just after additions and withdrawals were made. The fact that the data for profiles 599 and 609, exactly one cycle apart, fall on the same curve demonstrates that a more or less steady state had been achieved for this semi-continuous method of operation.

It is planned to operate these semi-continuously fed columns under conditions where 99.99% N^{14} is withdrawn at the front and greater than 99% N^{15} is bled slowly from the rear edge of the band. Before this can be done, however, sufficient N^{15} will have to be accumulated in the band to fill the necessary N^{15}-rich plates. It would, of course, be possible to begin withdrawing highly purified N^{15} from the present band, if it were eluted for a few cycles at a reduced flow rate with a lower concentration of NaOH. This would shorten the HETP and, thereby, decrease the amount of total N^{15} required to fill the number of plates required to attain a mole fraction of N^{15} equal to 0.99. This would not be especially desirable, since the decreased hold-up of N^{15} would hardly justify the decreased rate of production caused by the slower rate of elution.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CONNECTICUT]

The Preparation of a Strontium–Niobium Bronze with the Perovskite Structure[1]

BY DANA RIDGLEY AND ROLAND WARD

RECEIVED APRIL 27, 1955

A study of the ternary oxide system of strontium and niobium has revealed the existence of a cubic phase of the Perovskite type which possesses the characteristics of the tungsten bronzes. The approximate limits of composition of this phase are $Sr_{0.7}NbO_3$ (a_0 = 3.981 Å.) to $Sr_{0.95}NbO_3$ (a_0 = 4.016 Å.). The color changes from deep blue to red with increasing strontium content. The compressed powder possesses a high electrical conductivity. Phases giving rise to complex X-ray patterns exist between the limits $Sr_{0.5}NbO_3$ (white) and $Sr_{0.65}NbO_3$ (black). With strontium content higher than $Sr_{0.95}NbO_3$, a blue phase which may be tetragonal was found. Evidence was obtained for the existence of similar phases in the ternary oxide systems of barium–niobium and barium–tantalum.

Only a few metallic oxide systems are metallic conductors. Most of these are the lower oxides of some of the transition metals which are usually considered to be in the same class as nitrides and carbides. The others appear to be confined to the tungsten bronzes which have the general formula M_xWO_3 where M is an alkali metal and x is less than unity. The sodium and lithium tungsten bronzes have the cubic perovskite structure when the value of x lies between 0.35 and 0.9 for sodium and 0.3 and 0.57 for lithium.[2] The lattice con-

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(1) Taken in Part from the Doctoral Dissertation of Dana Ridgley. 1955.

(2) M. E. Straumanis and S. S. Hsu, THIS JOURNAL, **72**, 4027 (1950); Arne Magnéli and R. Nilson, *Acta Chem. Scand.*, **4**, 398 (1950).

stant varies directly with increasing proportions of alkali metal.[2,3] When the alkali metal concentration falls below these limits, a tetragonal structure is adopted[2,4] which is thought to be similar to that of the potassium tungsten bronzes[5] in which the values of x lie between 0.475 and 0.57. The limiting composition for this structure is $K_{0.6}WO_3$. The larger alkali metal cations give rise to a hexagonal structure[6] for which x lies between 0.27 and 0.32, the upper limit being 0.33. According to Magnéli[4–6] the tetragonal and hexagonal structures are, like the perovskite structure, dependent upon the sharing of all the oxygen atoms between two tungsten atoms which are in octahedral coördination with the oxygen atoms. The limiting capacity of the structures for alkali metal ions is set by the available cavities in the framework of WO_6 octahedra. Straumanis, on the other hand, has treated these systems as solid solutions of WO_3 in the metatungstates MWO_3 although this composition is apparently never quite reached with sodium and is even more remote from the upper limit of the lithium bronze. This approach suggests that there is present in the crystal both pentavalent and hexavalent tungsten.

The studies which have been made of the electrical conductivity[7] and magnetic susceptibility[8] of the tungsten bronzes strongly support the view that these phases should be regarded as solid solutions of alkali metal cation and a more or less free electron in the crystal lattice. These quantitative studies have been confined to the sodium and lithium tungsten bronzes but qualitative tests indicate that the hexagonal rubidium and cesium bronzes have comparable conductivity.[6] The bronzes which have been prepared so far all appear to have these properties in common: (1) high electrical conductivity, (2) a more or less wide variation in composition in which the lattice dimensions vary directly with the concentration of the alkali metal cation, (3) characteristic colors which may range from blue to red or yellow-brass, (4) all of the structures are based on WO_6 octahedra sharing corners. Many attempts to prepare similar phases in which molybdenum replaces tungsten have proved to be fruitless because of the high oxidizing power of the molybdenum(VI) oxide.[9]

It appeared to us that there was a reasonable possibility that bronze-like phases should exist with the group V elements niobium and tantalum. Both of these elements form perovskite-like oxides $MNbO_3$ and $MTaO_3$ with sodium and potassium. By substitution of an alkaline earth metal for the alkali metal a defect perovskite such as $M^{II}_{0.5}Nb^{V}O_3$ should be possible. An increase in the alkaline earth metal concentration should then lead to a phase analogous to the sodium tungsten bronze. This paper describes the preparation and characterization of such a phase in the strontium–niobium oxide system. Some evidence also was obtained for the existence of similar phases in the barium–niobium system and in analogous systems using tantalum.

Experimental

The niobium(V) oxide used in these experiments was 96.64% Nb_2O_5 the principal impurity being tantalum(V) oxide. A small amount of titanium(IV) oxide is probably also present. Niobium(IV) oxide was prepared from this material by reduction with hydrogen at 1200° for 36 hours. The X-ray diagram checked very closely with that reported by Brauer[10] and the ignition of the reduced oxide in air gave the theoretical weight gain within experimental error. The presence of tantalum as an impurity was unfortunate but this was the best sample of niobium(V) oxide available to us. In view of the readiness with which tantalum and niobium compounds form solid solutions it is to be expected that the products obtained contain the same proportion of tantalum as our source material which is about 1.75 atomic %. It seems unlikely that this would be a structure-determining factor in the type of crystal encountered in this work.

Reagent grade strontium carbonate was heated in a stream of hydrogen at 1100° for 36 hours to obtain the anhydrous oxide. Analysis of the product showed 97.7% SrO. The remainder was assumed to be adsorbed moisture and carbonate formed on exposure to the atmosphere during the preparation of samples. The barium carbonate and calcium carbonate were reagent grade quality. Only a few experiments were made with tantalum oxide which was listed as certified product grade. It was not analyzed.

A mixture of calcium carbonate and niobium(V) oxide, upon heating in hydrogen for 48 hours at 1150° showed no reduction. Mixtures of tantalum(V) oxide and barium carbonate ranging from $BaCO_3:Ta_2O_5$ to $4BaCO_3:Ta_2O_5$ gave heterogeneous mixtures of a blue and a white product upon prolonged heating at 1170 to 1200° in hydrogen. Under the same circumstances, however, the barium carbonate–niobium(V) oxide and strontium carbonate–niobium(V) oxide gave mainly dark blue products. In some of these, ruby red crystals were visible under the microscope.

Mixtures of ratio $BaCO_3:Nb_2O_5$ from 1 to 2.2 yielded a dark blue product with a very complex X-ray diffraction pattern. The mixture having the highest ratio, upon heating in hydrogen at 900° for 8 hours and at 1100° for 36 hours, formed a mass of dark blue needles. This result could not be duplicated. The X-ray pattern of red and bronze colored phases, which were separated mechanically from one of the products, indicated a cubic structure (a_0 = 4.09 Å.). In nearly all cases, the products were heterogeneous and attempts to achieve uniformity by grinding and reheating the mixtures were on the whole unsuccessful. The evidence pointed to the volatilization of one of the components. Consequently a method with sealed containers was used.

Assuming that the general formula for the bronze series could be represented by the formula $M^{II}_{0.5+x}NbO_3$, a series of mixtures were made in the following way. An appropriate mixture of strontium carbonate and niobium(V) oxide was heated in air to 1200° until all the carbonate was decomposed. The product of this reaction was intimately mixed with the theoretical amount of granulated niobium metal to give the required formula. This mixture was sealed under vacuum in a silica capsule and heated for 24 to 124 hours at 1150 to 1200°. The samples were usually removed for regrinding every 24 hours. The reaction is assumed to occur according to the equation

$$(0.5 + x)MO + 0.4xNb + (0.5–0.2x)\ Nb_2O_5 \longrightarrow M_{0.5+x}\ NbO_3$$

When no niobium metal was used, the samples were merely heated in air. They were white and gave a very complex X-ray diffraction pattern which did not correspond to either reactant or to any hitherto reported niobate. The barium–niobium system gave black products with complex X-ray diffraction patterns when x was 0.25 and 0.4, but with x = 0.5 a heterogeneous product consisting of red and black phases was formed. The diffraction pattern indicated a cubic structure but some extra lines were present. Higher proportions of barium carbonate were tried. At a composition corresponding to $Ba_{1.50}NbO_{3.5}$ a red cubic phase was formed. No further investigation of the barium system

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(3) M. E. Straumanis, THIS JOURNAL, **71**, 679 (1949).

(4) Arne Magnéli, *Structure Reports*, **12**, 294 (1949).

(5) Arne Magnéli, *ibid.*, **12**, 292 (1949).

(6) Arne Magnéli, *Acta Chem. Scand.*, **5**, 372 (1951); **7**, 315 (1953).

(7) B. W. Brown and E. Banks, *Phys. Rev.*, **84**, 609 (1951).

(8) F. Kupka and M. J. Sienko, *J. Chem. Phys.*, **18**, 1296 (1950).

(9) M. E. Straumanis and K. K. Irani, THIS JOURNAL, **74**, 2114 (1952).

(10) G. Brauer, *Z. anorg. allgem. Chem.*, **248**, 1 (1941).

TABLE I

CHARACTERIZATION OF PHASES PRODUCED BY HEATING STRONTIUM OXIDE WITH NIOBIUM(V) AND NIOBIUM(IV) OXIDES *in vacuo*

Compn. of mixture	Anal. compn. of product	Temp., °C.	Time, hr.	Color	Structure
$Sr_{.5}NbO_3$	....	1200	14	White	Complex
$Sr_{.65}NbO_3$	$Sr_{.585}NbO_{3.00}$	1100	48	Black	Complex
$Sr_{.7}NbO_3$	$Sr_{.675}NbO_{3.04}$	1100	48	Blue-black	Extra lines Cubic $a_0 = 3.981$
$Sr_{.75}NbO_3$	$Sr_{.737}NbO_{3.06}$	1050 1100	48 24	Dark blue	Cubic $a_0 = 3.986$
$Sr_{.80}NnO_3$	$Sr_{.762}NbO_{3.04}$	1050 1100	48 24	Dark blue	Cubic $a_0 = 3.992$
$Sr_{.85}NbO_3$	$Sr_{.816}NbO_{3.06}$	1050 1100	48 24	Purple	Cubic $a_0 = 4.000$
$Sr_{.85}NbO_3{}^b$	$Sr_{.820}NbO_{2.96}$	1025	38	Purple	Cubic $a_0 = 4.009$
$Sr_{.95}NbO_3{}^b$	....	1150	67	Red	Cubic $a_0 = 4.016$
$Sr_{1.00}NbO_3{}^b$	....	1025	38	Red + blue (trace)	Extra lines Cubic $a_0 = 4.024$
$Sr_{1.15}NbO_3{}^b$	....	1025	48	Blue + red (trace)	Tetragonal (?)
$Sr_{1.20}NbO_3$	....	1200	48	Light blue	Tetragonal (?)

[a] Precision of measurements of lattice constant ±0.001 Å. [b] Samples prepared from pellet wrapped in tantalum foil.

was made because the results with the strontium–niobium system were of more immediate interest. A cubic phase was observed with mixtures corresponding to values of x from 0.25 to 1.0. The color changed from blue-black to purple to red with increasing strontium content. Also a slight lattice expansion was noticeable between the low and high strontium products. A mixture at $x = 0.15$ gave a black product with a complex X-ray pattern which showed some similarities to the cubic pattern.

There were certain inherent disadvantages in this procedure. First, the difficulty of bringing all the coarsely powdered metal into reaction and secondly the pre-ignition of the alkaline earth carbonate and niobium pentoxide of the mixture left some doubt as to the precise composition of the mixture. Completely homogeneous products were not usually obtained.

The following procedure was found to be satisfactory. Mixtures of strontium oxide, niobium(IV) oxide and niobium(V) oxide were prepared by grinding the powders together. The compositions were according to the equation

$$(0.5 + x)SrO + 2xNbO_2 + (0.5 - x)Nb_2O_5 \longrightarrow Sr_{(0.5+x)}Nb^{IV}_{2x}Nb^{V}_{1-2x}O_3.$$

The mixtures were compressed into pellets to limit the reaction with the container, sealed in evacuated silica capsules and heated at temperatures from 1100 to 1200°. The most uniform products were obtained at 1100° and this temperature was used for most of the preparations. It was found that better results followed a short ignition of the pellet in the capsule under vacuum prior to sealing. This pre-ignition should be only of short duration (about 45 seconds) lest a serious loss of strontium occur. In this way a series of products were obtained which were in most instances homogeneous so far as could be judged from X-ray diffraction patterns and by examination under the microscope. The data concerning these preparations are listed in Table I.

Products which appeared to be completely homogeneous were analyzed for strontium and niobium. No good procedure could be found for the determination of strontium and niobium from the same sample. The strontium analysis was based on a procedure devised by Atkinson, Steigman and Hiskey[11] in which niobium, tantalum and titanium are removed by heating the sample in a stream of dry hydrogen chloride and chlorine saturated with carbon tetrachloride vapor. The temperature (about 500°) was sufficiently high to remove the pentachlorides and also the oxytrichlorides of niobium or tantalum. The residue of strontium chloride was dissolved in water and titrated with disodium Versenate solution. The method is based on the procedure for magnesium by Cheng, Kurtz and Bray,[12] modified according to the suggestions of Cheng.[13] The procedure gave satisfactory results with known mixtures of strontium carbonate and niobium(V) oxide.

Niobium was determined by the method of Knowles and Lundell.[14] The sample was ignited in air to give a white product which was fused with potassium pyrosulfate and dissolved in concentrated sulfuric acid. By careful dilution the strontium sulfate settled out rapidly and was removed by filtration. The niobium solution was run through a Jones reductor column into an excess of ferric ammonium sulfate solution. The only modification in the Knowles and Lundell procedure was in the dilution of the concentrated sulfuric acid solution. This was necessary because of the presence of strontium. A correction of the total niobium determined had to be made for the presence of 3% tantalum in the original niobium(V) oxide.

The gain in weight of a sample upon ignition in air was taken as a means of estimating the amount of strontium metal or niobium(IV) in the sample. The oxygen content of the sample was arrived at by taking the amount commensurate with the proportion of Sr^{+2}, Sr and Nb^{+5} found by these analyses. This is not a very satisfactory procedure, but it was the best we were able to devise.

From Table I it can be seen that the proportion of strontium found by analysis was consistently lower than that used in the original mixture by about 3 to 5% in most cases. This is much greater than the estimated experimental error which is about 0.5%, and it is thought that some of the strontium may be volatilized from the sample during the prolonged heating *in vacuo* necessary to give uniform samples. In the preparation of some of the samples, the pelleted powder mixture was wrapped tightly in tantalum foil before being sealed in the evacuated silica tube. This appeared to prevent the loss of strontium to some extent, but the method could be used only with the samples containing relatively high proportions of strontium oxide. The samples prepared in this way are marked with an superscript *b* in Table I.

The X-ray powder diffraction data for the products from samples of original composition $Sr_{0.5}NbO_3$, $Sr_{0.65}NbO_3$, $Sr_{0.82}NbO_3$ and $Sr_{1.15}NbO_3$ were obtained from Cu Kα radiation using a camera of radius 215 mm. Long exposures, 40 hours or more, were made in most cases to bring out the weak lines of the pattern. The data for only one cubic phase ($Sr_{0.82}NbO_3$) are given in Table II. The structures of the other phases could not be deduced from the powder patterns. The data for these are available through ADI.[15]

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[11] R. H. Atkinson, J. Steigman and C. F. Hiskey, *Anal. Chem.*, **24**, 477 (1952).

[12] K. L. Cheng, T. Kurtz and R. H. Bray, *ibid.*, **24**, 1640 (1952).

[13] Private communication.

[14] H. B. Knowles and G. E. F. Lundell, *J. Research Natl. Bur. Standards*, **42**, 405 (1949).

[15] Material supplementary has been deposited as Document number 4640 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

The lattice constants given in Table I for the cubic phases were derived using the extrapolation technique of Taylor and Sinclair.[16] In all the X-ray diagrams representing the cubic phase, some weak and very weak extra lines were present. It was not possible to determine whether these lines were due to the presence of some impurity or were indications of a superlattice. They did not correspond to any known oxide of niobium or to any likely strontium compound, nor did they match any of the principal lines of the phases with lower strontium content. The lines representing the cubic phase were sharp.

The pattern of the product obtained from the mixture of composition $Sr_{0.65}NbO_3$ contains a large number of strong lines among which can be found those corresponding to a cubic cell with a lattice constant of about 3.981 Å. It is possible that this places the lower limit of the composition of the cubic phase at $Sr_{0.7}NbO_3$ and that this sample is heterogeneous consisting of the cubic phase and other phases of lower strontium content. This part of the system requires further study.

The cubic structure represented by the stronger lines in the patterns obtained with samples in the composition range $Sr_{0.7}NbO_3$ to $Sr_{0.95}NbO_3$ is of the perovskite type. The calculated intensities are in good agreement with those observed. The observed intensities given in Table II were obtained from a spectrometer tracing using the relative areas under the curve as indicative of intensity. No correction was made for absorption. This measurement has been made for one preparation only. No indications of the faint reflections were found in the measurements made with the spectrometer.

TABLE II

X-RAY POWDER DIFFRACTION PATTERN OF $Sr_{0.82}NbO_3$

Cu Kα Radiation, 35 kv., 17 ma., North American Philips Spectrometer.

$h^2 + k^2 + l^2$	Intensity Obsd.	Intensity Calcd.	d, Å. Obsd.	d, Å. Calcd.
1	10.7	9.5	3.997	4.0020
2	100	100	2.830	2.8298
3	1.2	1.7	2.306	2.3106
4	44.5	39.0	2.000	2.0010
5	4.8	2.9	1.789	1.7898
6	44.7	40.7	1.6336	1.6338
8	23.9	17.5	1.4143	1.4149
9	1.5	1.3	1.3335	1.3340
10	19.2	17.5	1.2648	1.2655
11	0	0.1	....	1.2066
12	7.1	7.7	1.1551	1.1553
13	1.1	0.6	1.1088	1.1100
14	23.3	23.8	1.0694	1.0696
16	3.5	4.4	1.0002	1.0005
17	0.9	1.0	0.9698	0.9706
18	15.4	16.8	.9432	.9433
19	0	0.02	....	.9181
20	14.8	10.3	.8949	.8949
21	1.1	1.3	.8732	.8733
22	9.5	14.0	.8532	.8532
24	19.0	27.8	.8169	.8169
25	1.2	1.3	.8001	.8004
26	76.6	98.4	.7850	.7849

Indexed as cubic perovskite-type cell, $a = 4.002_0 \pm 0.001$ Å.

The plot of lattice constant *vs.* x in the formula $Sr_{0.5+x}NbO_3$ is shown in Fig. 1. The open circles represent the analytical values while the half-shaded circles represent the starting composition of the mixtures. There appears to be a Vegard's Law dependence throughout the cubic range within the precision of the measurements. The points corresponding to $a_0 = 4.009$ deviate considerably.

From the analytical data, it seems likely that the strontium content is somewhat less than the initial composition of the mixture. The true composition–lattice constant curve is probably more nearly represented by the dashed line in Fig. 1. The lower limit of composition for the cubic phase is near $Sr_{0.7}NbO_3$. The upper limit is likely to be less than $SrNbO_3$. The mixture with this composition gave a heterogeneous product consisting of a ruby-red phase and a small amount of a blue phase. The mixture of highest strontium content which gave a pure red phase corresponds to $Sr_{0.95}NbO_3$. This sample was made using a tantalum foil envelope.

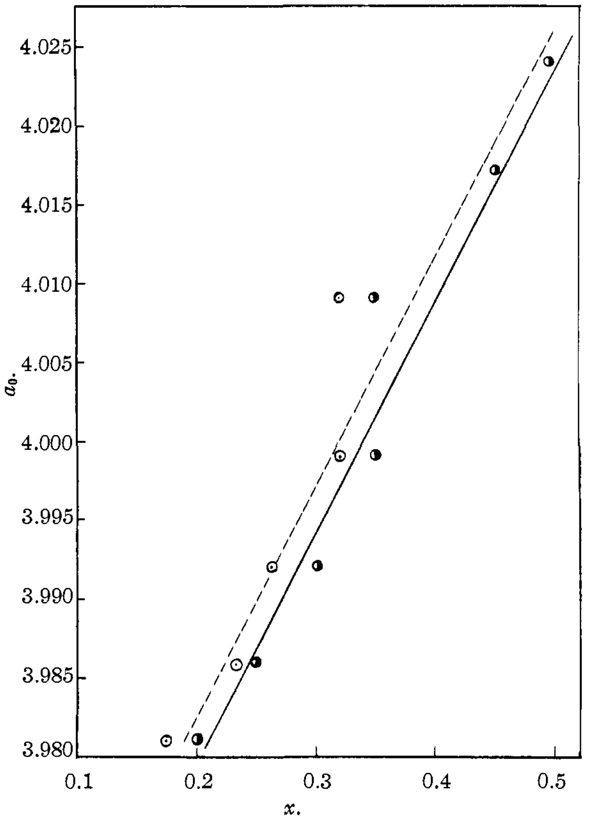

Fig. 1.—The variation of lattice constant with strontium content in the cubic perovskite phase $Sr_{0.5+x}NbO_3$.

An unusual feature of this system is the abrupt change in color from red to blue when the strontium content rises above the limit tolerated by the cubic structure. This blue phase coexists with the red cubic phase in products made from mixtures with initial composition $Sr_{1.00}NbO_3$ to $Sr_{1.15}NbO_3$. When this was increased to $Sr_{1.2}NbO_3$ a pure blue phase was formed. A preliminary study of the X-ray data for this preparation indicated that the structure may possess tetragonal symmetry. The actual composition of this product is not known. It is possible that it lies in the range $Sr_{0.95}NbO_3$ to $SrNbO_3$.

All of these products, which resemble the tungsten bronzes in the properties just described also possess the characteristic inertness toward strong oxidizing acids such as aqua regia and hot concentrated perchloric acid but are readily decomposed by fusion with alkali or with potassium pyrosulfate under oxidizing conditions.

The magnetic properties were not examined critically and only a crude estimate of electrical conductivity was made. A powdered sample of composition $Sr_{0.8}NbO_3$ was compressed into a hole six mm. in diameter and 1 cm. long in a lucite block. The resistance of this powder under compression was measured with an electronic voltmeter. The resistance varied somewhat with the pressure exerted on the sample and the minimum value obtained was about 6.5 ohms from which it would appear that the specific conductivity is of the order of 0.5 ohm.$^{-1}$ This is somewhat less than that of the sodium tungsten bronzes. The temperature coefficient of conductivity was not studied.

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[16] A. Taylor and H. B. Sinclair, *Proc. Phys. Soc.*, **57**, 126 (1945).

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STORRS, CONN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF TORONTO]

Rates of Copper Dissolution in Aqueous Ammonium Hydroxide Solutions[1]

BY BENJAMIN C.-Y. LU AND W. F. GRAYDON

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The rates of dissolution of polycrystalline metallic copper in aqueous ammonium hydroxide solutions have been determined under various experimental conditions. Over a considerable range of conditions the dissolution has been found to be autocatalytic. The autocatalytic dissolution is well represented by a half-order rate equation. An empirical equation is presented which represents the autocatalytic rate data with an average deviation of $\pm 4\%$. The rate equation is discussed in terms of a mechanism which assumes that the rate controlling process is the removal of cuprous ion species from the copper solution interface by diffusion. Data are also given for an essentially zero-order rate of dissolution observed when the dissolving medium was concentrated with respect to oxygen or very dilute with respect to cupric ion species.

Introduction

There have been four previous investigations of the dissolution of copper in aqueous ammonia solutions.[2-5]

The earliest work by Yamasaki[2] was done using air-saturated solutions. Evidence was found for autocatalysis and for an initial rate which was independent of ammonia concentration. Lane and McDonald[3] more recently investigated the dissolution of copper in oxygen-saturated ammonia solutions. Under these quite different experimental conditions they found no evidence for autocatalysis and reported a first-order dependence on ammonia concentration. Rather surprisingly, they stated that their results seemed to disprove the conclusions of Yamasaki. The data of these two early contributions are considered by Halpern[5] to be discrepant and to provide conflicting information. Halpern reported data for the corrosion of copper in aqueous ammonia solutions saturated with oxygen at pressures up to about eight atmospheres. He found no evidence for autocatalysis and reported a first order dependence on $[NH_3]$ and $[NH_4^+]$.

It is apparent that the experimental conditions and the data given by Halpern are similar to those reported by Lane and McDonald. It is also evident that the experimental conditions and the data reported by Yamasaki are very different from those reported in the two later contributions. It would seem reasonable to consider the possibility that no conflict or inconsistency exists, but rather that all the data are valid for the conditions specified.

Experimental

The apparatus used was essentially the same as previously described.[6] It consisted of a covered Pyrex beaker in which a cylinder of copper was rotated. The copper cylinder (1.8 cm. diameter) was rotated by means of an axially mounted lucite rod. The ends of the copper cylinder were protected from the corroding medium by lucite washers. The solution in the beaker was kept saturated with air or oxygen by bubbling the appropriate gas through the solution. The gas was passed through one wash bottle containing dilute sodium hydroxide solution and two containing ammonium hydroxide solution before introduction into the dissolving medium. The copper samples used in this work were machined from refinery copper rod (99.95+% copper) which was supplied by the Anaconda American Brass Ltd. The samples were polished with 3/0 emery paper. Rate determinations were done by solution analysis. Samples of the copper solution were withdrawn periodically, evaporated to dryness, made up with dilute hydrochloric acid and the copper content was determined polarographically.

Results and Discussion

Rate Dependence on Copper Concentration.—The primary point to be established is whether the dissolution of copper in aqueous ammonium hydroxide solutions is or is not an autocatalytic reaction. As shown in Fig. 1 we have found an essentially zero-order rate for the dissolution of copper in 0.76 N aqueous ammonium hydroxide solution saturated with oxygen at one atmosphere. Thus under these conditions there is little evidence for autocatalysis. This conclusion agrees with those of Lane and McDonald and of Halpern who used oxygen-saturated solutions. However, the data which we have obtained for the dissolution in air-saturated ammonium hydroxide solutions, Fig. 2, are convincing evidence for the existence of an autocatalytic reaction under conditions similar to those employed by Yamasaki. Thus we find no conflict or discrepancy between the data of Yamasaki and those of Lane and McDonald. It is apparent that the mechanism of the dissolution is not the same for both sets of experimental conditions.

The major conclusions reached by Lane and McDonald for high oxygen pressure have been verified by Halpern. We have not extended the investigation of copper dissolution under these conditions. However, some additional work has been done on the dissolution of copper in air-saturated solutions under the conditions which result in an autocatalysis.

All the data which have been obtained in this Laboratory for the autocatalytic dissolution of copper have given linear half-order plots as shown in

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