TABLE V

THERMODYNAMIC FUNCTIONS FOR FORMATION OF MgD_2

T, °K.	ΔF^0, cal./mole	ΔS^0, cal./mole-deg.	ΔH^0, cal./mole	$\Delta C_p{}^0$, cal./mole-deg.
800	8620	−33.7	−18,350	
298	−7800	−32.5	−17,480	0
298	−8240	−32.5	−17,350	(−2)

If the data for MgD_2 are treated in a similar manner, and the additional assumption made that the variation of ln N_D *vs.* $1/T$ has the same slope as was found for ln N_H *vs.* $1/T$, the values shown in Table V are obtained. The uncertainties should be larger in this case than for MgH_2 because fewer experiments were done.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, NEW YORK]

Some Solid State Studies of Silver-doped WO_3[1]

BY M. J. SIENKO AND B. R. MAZUMDER

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A material corresponding to $Ag_{0.010}WO_3$ has been isolated from the thermal equilibration of WO_3 with various sources of silver. Single crystal studies indicate that it is orthorhombic (a = 7.35, b = 3.73 and c = 3.85 A.) and that it conducts as a metal between 25 and 600° (specific resistivity increases linearly from 0.072 ohm-cm. at 25° to 0.155 ohm-cm. at 600°). The electron mobility at 25° is 0.44 cm.^{2}/volt sec., which is approximately the same as that previously observed in thallium tungsten bronze. It is proposed that $Ag_{0.010}WO_3$ represents a defect structure in which a 5 d conduction band of WO_3 is populated by electrons from the silver atoms and in which a more symmetric structure of WO_3 has been stabilized by configurational entropy.

In a continuing program of preparing and characterizing new solid state defect structures, we have tried to grow single crystals of the silver tungsten bronze, $Ag_{0.4}WO_3$, tentatively reported previously by Conroy and Sienko.[2] Instead of $Ag_{0.4}WO_3$, we have found repeatedly as the equilibrium phase a material corresponding to $Ag_{0.01}WO_3$, which has interesting properties bearing on the problem of metal tungsten bronze formation and properties. This communication describes the preparation, characterization and interpretation of this "doped" WO_3 which can be considered a dilute analog of the well-known tungsten bronzes.[3]

Preparation.—All three of the conventional methods of bronze formation—thermal, vapor phase and electrolytic—which successfully produced thallium tungsten bronze[4] also produced the material $Ag_{0.01}WO_3$. However, the electrolytic method using platinum electrodes on a molten mixture of Ag_2WO_4 and WO_3 produced essentially no $Ag_{0.01}WO_3$ but large amounts of metallic silver instead; with a tungsten anode, on the other hand, though the product was not homogeneous, there was good yield of $Ag_{0.01}WO_3$. (We take this as supporting evidence that bronze formation by electrolysis is not a simple deposition of M_xWO_3 but involves a secondary reaction in which either a primary cathode product, possibly M, or a primary anode product, possibly WO_2, reduces the melt. In the case of silver, in contrast to thallium and the alkali metals, the activity of the primary cathode product is apparently too low to give much reaction). Actually the thermal method gave the best product, consistently yielding the same type of crystals of $Ag_{0.01}WO_3$ no matter which of the following mixtures was heated: Ag + WO_3, Ag_2WO_4 + WO_3 + W, Ag_2WO_4 + WO_3, Ag_2WO_4 + Ag + WO_3, Ag_2CO_3 + WO_3. Apparently what is required is WO_3 and Ag, the Ag coming either from pure metal or from the thermal decomposition of an oxysalt. The equilibration was carried out both in vacuum and under argon at 950° for times ranging up to 160 hr. The best product was obtained from 3 Ag_2WO_4: 4 WO_3:W after heating for 24 hr. under argon and then cooling at about 0.5° per min. The black shiny crystals of $Ag_{0.01}WO_3$ were isolated by leaching the cooled mass in aqueous NaCN for about 5 days. Spent leach solution containing the brown $W(CN)_8{}^{-4}$ was decanted every 24 hr. and replaced with fresh NaCN solution. When no more brown color was formed, the product was successively washed with water, boiled with concentrated HNO_3 and leached with 48% HF overnight. The product $Ag_{0.01}WO_3$ seems to be as inert as the tungsten bronzes to acid reagents. Furthermore, the material is only slowly attacked by NaCN. In fact, the basis of our separation is that $Ag_{0.01}WO_3$ is essentially unaffected by CN^- whereas WO_3 and the normal tungstates are reduced by H_2O in the presence of CN^-.

Analysis.—Like the tungsten bronzes, $Ag_{0.01}WO_3$ could be brought into solution by fusion with a Na_2CO_3–$NaNO_3$ mixture followed by treatment with water. Addition of HNO_3 to the solution gave a precipitate of tungstic acid which could be filtered off to allow electrodeposition-analysis for silver. Subsequent addition of cinchonine hydrochloride gave on digestion a bit more tungstic acid which was combined with the first portion. Burning produced WO_3. Analysis of 12 samples, including those from different preparations, gave 99.27 ± 0.2% WO_3 and 0.48 ± 0.04% Ag, corresponding to $Ag_{0.010}WO_3$.

Densities.—Densities were determined pycnometrically using water as the immersion liquid. Crystals from the different preparations gave the same density within the precision of the experiment and, except for the electrolytic product, there was no appreciable difference between the coarse and fine crystals. The most probable value of the density is 7.28 ± 0.07 g. per cc. This compares to 7.33 g. per cc. calculated from the X-ray parameters given below, assuming two $Ag_{0.01}WO_3$ units per unit cell.

X-Ray Measurements.—Powder diffraction photographs were taken with both 57.3 and 114.6 mm. cameras, using CuKα radiation. Because of difficulty in assigning indices to the various reflections, due to numerous extinctions, oscillating single crystal photographs also were taken using molybdenum radiation. On the basis of these, the structure has been assigned to the orthorhombic system with lattice parameters a = 7.35, b = 3.73 and c = 3.85 Å.

Electrical Resistivity Studies.—Three apparently single crystals up to 4 mm. in the longest dimension were mounted in a four-probe device similar to the one described previously for the thallium tungsten bronzes.[4] Two tungsten probes

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[1] This research was supported by the United States Air Force under Contract No. AF 49(638)-191 and was monitored by the Air Force Office of Scientific Research and Development Command through its Directorate of Solid State Sciences.

[2] L. E. Conroy and M. J. Sienko, THIS JOURNAL, **79**, 4048 (1957).

[3] See, for example, the excellent review by R. P. Ozerov, *Uspekhi Khimii*, **24**, 951 (1955).

were pressure clamped to the long face of a crystal and served to measure the *IR* drop along the crystal as current was passed between the other two probes, which were pressure clamped to the ends of the crystal. In this way contact resistances could be avoided. Periodic reversal of the current direction was without effect on the *IR* drop indicating absence of thermoelectric effects. Current through the crystal was monitored by measuring the *IR* drop in a standard resistor in series with the crystal.

The temperature variation of resistivity was determined by mounting the crystal in its holder along with an associated chromel–alumel junction in a Vycor tube which could be evacuated or filled with argon. An electric furnace of the combustion-tube-type controlled the temperature. Two hours was allowed for thermal equilibration at each measured point. Both rising and cooling sweeps were carried out for each crystal. As shown in Fig. 1, the resistivity varied from 0.072 ohm-cm. at 25° to 0.155 ohm-cm. at 600°, being essentially linear with temperature over the whole range.

A fourth crystal, represented by the dashed line in the figure showed a reversible decrease in resistivity from 25 to 300°, and this portion could be retraced several times. However, once the crystal was heated above 350°, the resistivity increased and followed identically the "normal" curve. On subsequent cooling to room temperature, the anomalous dotted portion was not reproduced but the resistivity followed the normal pattern. We believe that in this one case we may have had a metastable form of $Ag_{0.01}WO_3$ which went over to the more usual form above 350°. This would not be too surprising since WO_3 itself undergoes a phase transition at 330° and, from observations we have made on the Tammann temperature in Ag_2WO_4, Ag^+ ions apparently become mobile near 400°.

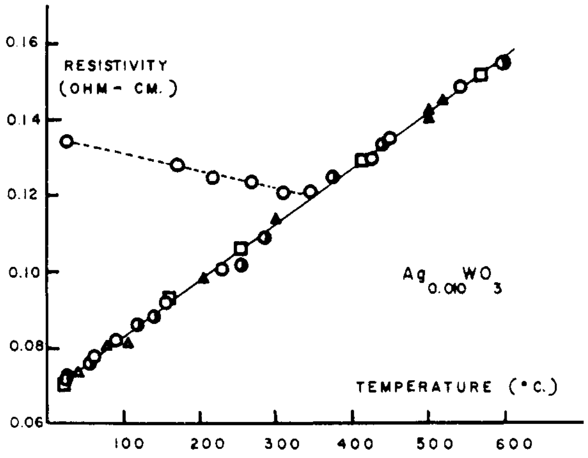

Fig. 1.—Specific resistance *vs.* temperature for several crystals of $Ag_{0.010}WO_3$. The dotted portion represents the anomalous behavior of crystal 4, data for which are given as open circles. The dotted portion was not reproducible once the crystal had been heated above 350° and is attributed to a metastable form.

Discussion

The apparently metallic behavior of $Ag_{0.01}WO_3$, as indicated by the linear rise of resistivity with temperature, is at first sight surprising, but it can be accounted for on the basis of the model proposed for thallium tungsten bronze, Tl_xWO_3, and other bronzes.[4] Excitation of the valence electrons from the relatively few silver atom impurities present into a conduction band of WO_3 would give an almost empty conduction band. If the number of carriers in the band did not change much with temperature—this would be true if ionization of the guest atoms were complete—then behavior would be metallic and resistivity would increase with heating because of thermally reduced mobility of the carriers. As postulated for the thallium tungsten bronzes, the conduction band in WO_3 is probably a 5 *d* band resulting from overlap of the d_ϵ orbitals of the tungsten atom. Evidence for believing that the same band is involved in $Ag_{0.01}WO_3$ as in the tungsten bronzes comes from a comparison of the electron mobility in $Ag_{0.01}WO_3$ with that in $Tl_{0.20}WO_3$. Assuming in each case that the atom added to WO_3 is completely dissociated with respect to one electron, we can calculate from the observed conductivity $\sigma = ne\mu$ (σ, the specific conductance; n, the number of charge carriers per cc.; e, the charge of the carrier; μ, the mobility) that the electron mobility in $Ag_{0.01}WO_3$ is 0.44 cm.^{2}/volt sec. and in $Tl_{0.20}WO_3$, 0.31 cm.^{2}/volt sec. This assumes that only electron carriers are involved.

Mobilities of this order of magnitude are what one might expect from comparison with other *d*-banded materials. For example, in TiO, where conduction is believed to be through a 3 *d* band, the electron mobility is 0.36 cm.^{2}/volt sec.[5] As contrast, in ZnO, where conduction is believed to be through the 2 *p* band of the oxygens, the mobility is considerably higher—of the order of 100–200 cm.^{2}/volt sec.[6] Also, in Fe_2O_3, where overlap of the *d* functions is supposed to be so small that banding does not occur and conduction goes through an activated "hopping" process, the electron mobility is considerably lower—of the order of 0.01 cm.^{2}/volt sec.[7] Presumably, in these doped WO_3 systems banding is more favored than in Fe_2O_3 because the 5 *d* wave function would stick out considerably further than the 3 *d*. The overlap of the 5 d_ϵ orbitals would still be small and the resulting band would be narrow, but this is precisely what we need for mobilities of the order of 1 cm.^{2}/volt sec.

The other interesting aspect of $Ag_{0.01}WO_3$ is the crystal structure and its close relation to that of WO_3. As reported by Andersson,[8] WO_3 at room temperature is monoclinic with a = 7.285, b = 7.517, c = 3.835 Å. and β = 90.9°. Rosen, Banks and Post,[9] in their X-ray investigation of the high temperature forms of WO_3, found that there is a phase change at 330° to an orthogonal structure which they indicate as probably orthorhombic. In going from monoclinic to orthorhombic the a and c spacings increased and the b remained essentially unchanged. It is possible that the present $Ag_{0.01}WO_3$ is derived directly from this high temperature form of WO_3. Compared to stoichiometric WO_3, our structure for $Ag_{0.01}WO_3$ shows an increase in the a spacing (from 7.285 to 7.35 Å.), a shortening of the b spacing with a halving of the repeat distance (from 7.517 to 3.73 Å.), and essentially no change in the c spacing.

A possible mechanism for the formation of $Ag_{0.01}WO_3$ is that at the temperature of equilibration the rather mobile silver atoms migrate into the rela-

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[4] M. J. Sienko, THIS JOURNAL, **81**, 5556 (1959).

[5] F. J. Morin, *Bell System Technical Journal*, **37**, 1047 (1958).

[6] E. E. Hahn, B. R. Russell and P. H. Miller, *Phys. Rev.*, **75**, 1631 (1949).

[7] F. J. Morin, *ibid.*, **83**, 1005 (1951).

[8] G. Andersson, *Acta Chem. Scand.*, **7**, 154 (1953).

[9] C. Rosen, E. Banks and B. Post, *Acta Cryst.*, **9**, 475 (1956).

tively large cavities of the WO_3 structure. On cooling, the WO_3 lattice need not revert to its original monoclinic structure because there would now be an increased entropy contribution from the mixing of empty cavities and cavities occupied by silver atoms. If the enthalpy change between the monoclinic and rhombic varieties of WO_3 is small (and it is probably no more than a hundred calories or so) and if the doping with Ag produces no significant decrease in the vibrational entropy contribution for the WO_3 structure, then the configurational entropy, though only of the order of 0.09 e.u., may be sufficient to stabilize the orthorhombic crystal structure at room temperature.

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A Calorimetric Determination of the Values of ΔH^0 for Mercury(II)–Halide Complex Ion Reactions and the Derived Values of ΔS^0 [1,2a,b]

BY PATRICK K. GALLAGHER AND EDWARD L. KING

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The values of ΔH^0 for the reactions $HgCl_{n-1}^{+3-n} + Cl^- = HgCl_n^{+2-n}$ (n = 1 to 4) and $Hg^{+2} + 4X^- = HgX_4^=$ ($X^- = Br^-$ and I^-) in solutions of ionic strength = 0.5 M determined by calorimetric measurements are −5.9, −6.9, −2.2, +0.1 −27.7 and −44.3 kcal., respectively. Coupled with the equilibrium quotient values obtained by Sillen and co-workers, and by Marcus, this study permits the evaluation of the entropy changes accompanying these reactions. The abnormally positive value of the entropy change in the fourth stepwise mercury(II)–chloride reaction suggests that a decrease in coördination number of mercury(II) occurs in this reaction. With some of the data obtained here in combination with data on mercury(II)–bromide reactions reported by Scaife and Tyrrell, one can demonstrate the validity of the Latimer and Jolly method of calculating the "replacement" contribution to value of ΔS^0.

Although it is often assumed that the coördination number of a metal ion remains constant in its complex ion formation reactions, there are certainly some systems in which this is not the case. That the mercury(II)–chloride complex ion system, with the reactions

$$HgCl_{n-1}^{+3-n} + Cl^- = HgCl_n^{+2-n}$$

where n = 1 to 4, may be an example was suggested by van Panthaleon van Eck on the basis of X-ray diffraction of aqueous solutions containing mercury(II) ion and chloride ion.[3] These data[3] were interpreted in terms of a coördination number of six for mercury(II) in the species with zero,[4] one and two chloride ions, and a coördination number of four for mercury(II) in the species with four chloride ions; a coördination number of five was suggested by van Panthaleon van Eck for the species with three chloride ions, although this was admitted to be uncertain.[3b] There are theoretical arguments for a distorted ~~octahedral~~ configuration of ligands about mercury(II).[5]

The present paper deals primarily with calorimetric experiments which establish the values of ΔH^0 for the mercury(II)–chloride complex ion formation reactions in aqueous solution at 25°. The ionic strength of the final solutions was 0.5 M, with the principal cationic contributor being hydrogen ion. In all solutions except those in which the tetrahalide species formed to a significant extent, the principal anionic species present was perchlorate ion. In the interpretation of these calorimetric studies, it was assumed that the value of each relevant quotient of activity coefficients was constant and had the same value as is appropriate for solutions of ionic strength equal to 0.5 M in which the principal cationic species was sodium ion; this was the medium in which Sillen[6a] and Marcus[6b] established the values of the equilibrium quotients. The mercury(II) concentration in the present work was less than 0.05 M; it is assumed that further dilution of the mercury(II) species would result in no heat effect. The standard state for the solute species in this study is a hypothetical one molar solution in which the ionic strength is 0.5 M. The zero superscript when used with ΔF, ΔH and ΔS pertain to the standard changes in these quantities referred to this standard state.

The ΔS^0 values can be derived from the combination of the ΔH^0 values obtained in this work and the ΔF^0 values established by Sillen[6a] and Marcus.[6b] It is anticipated that any reaction in which a change in the coördination number occurs will have associated with it a standard entropy change which is abnormal compared to the values associated with reactions in which there is no such change. The big problem is deciding what a normal ΔS^0 value would be. The standard entropy changes for a series of complex ion formation reactions without coördination number change, after appropriate correction for the symmetry number factor, may, perhaps, be expected to conform to the equation[7]

$$\Delta S^0_{\text{cor}} = a - b\Delta Z^2 \qquad (1)$$

where ΔZ^2 is the sum of the squares of the charges

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[1] This work was supported in part by grants from the United States Atomic Energy Commission (Contract No. AT(11-1)-64, Project No. 3), and the Research Committee of the Graduate School, University of Wisconsin.

[2] (a) Presented in part at the 135th National meeting of the American Chemical Society, Boston, Massachusetts, April, 1959. (b) Taken in part from the Ph.D. thesis of Patrick K. Gallagher, University of Wisconsin, 1959.

[3] (a) C. L. van Panthaleon van Eck, H. B. M. Wolters and W. J. M. Jaspers, *Rec. trav. chim.*, **75**, 802 (1956); (b) C. L. van Panthaleon van Eck, Thesis, Leiden (1958).

[4] (a) In hexagonal mercury(II) oxide, each mercury(II) is surrounded by a distorted octahedron of oxygen atoms; K. Aurivillius and I. B. Carlsson, *Acta Chem. Scand.*, **12**, 1297 (1958). (b) Aquozinc (II) ion in aqueous solution has been shown to be $Zn(OH_2)_6^{+2}$; F. A. Cotton and H. P. Hansen, *J. Chem. Phys.*, **28**, 83 (1958).

[5] L. E. Orgel, *J. Chem. Soc.*, 4186 (1958).

[6] (a) L. G. Sillen, *Acta Chem. Scand.*, **3**, 539 (1949); (b) Y. Marcus, *ibid.*, **11**, 599 (1957).

[7] (a) E. L. King, *J. Phys. Chem.*, **63**, 1070 (1959); (b) E. L. King and P. K. Gallagher, *ibid.*, **63**, 1073 (1959).