nal ingredients tends to fix the arsenic to some extent. Hence, the mixture, when introduced into the firing chamber, contains magnesium arsenates of various compositions (depending upon initial ratios added) plus magnesium carbonate and stannic oxide.

The new compound may be considered as having the composition $2(2MgO \cdot SnO_2) \cdot (3MgO \cdot As_2O_5)$. When these preformed compounds are added in the proper ratio and fired, a good pattern of the compound is obtained, although with slight traces of impurity because of some loss of As_2O_5. Once formed, however, the compound is as stable as $6MgO \cdot As_2O_5$; that is, the pattern line intensities show no change after firing for 4 hr. at 1200°.

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[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY, LOS ALAMOS, NEW MEXICO, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW MEXICO, ALBUQUERQUE, NEW MEXICO]

The Magnesium–Hydrogen System[1-3]

BY J. F. STAMPFER, JR., C. E. HOLLEY, JR., AND J. F. SUTTLE

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The decomposition pressure of magnesium hydride was measured under conditions such that the precision and accuracy of the temperature and pressure measurements could be estimated and the composition of the solid phases determined. The diffusion of hydrogen through the walls of the apparatus and the solubility of hydrogen in the walls was considered. The apparatus and the method of making the measurements are described. The decomposition pressures were converted to fugacities by use of the Beattie–Bridgeman equation of state for hydrogen and fitted to straight lines to give $R \ln f_{H_2} = (-17{,}785 \pm 76)/T + 32.28 \pm 0.45$ and $R \ln f_{D_2} = (-17{,}480 \pm 110)/T + 32.48 \pm 0.17$. Magnesium hydride, MgH_2, was found to be a stoichiometric compound within the limits of error of the measurements. The solubility of hydrogen in magnesium was found to increase from 2 atom % at 440° to 10 atom % at 560°. From these measurements thermodynamic functions for the formation of magnesium hydride and magnesium deuteride were estimated.

Introduction

The preparation and some physical properties of magnesium hydride have been described.[4-7] However, the reported equilibrium decomposition pressures were not adequate for the calculation of thermodynamic data. This system was, therefore, reinvestigated under conditions such that the precision and accuracy of the temperature and pressure measurements could be estimated and the composition of the solid phase or phases determined. In addition, some measurements were made on the magnesium–deuterium system.

Experimental

Apparatus.—Since previous work had shown the necessity of making measurements of pressures up to several hundred atmospheres and temperatures up to several hundred degrees, the apparatus was designed for a maximum pressure of 350 atm. and a maximum temperature of 600°. The reactor vessels were made from 347 stainless steel bar stock. The one used for the pressure measurements was a cylinder $3^1/_2$ in. long × 2 in. o.d. with a $2^3/_4$ × $^1/_2$ in. hole bored into it. Diffusion from this reactor was too fast for accurate measurement of quantities of hydrogen present in the gas phase at the higher temperatures, so the composition measurements were made in a heavier walled reactor 7 in. long × 5 in. o.d. with a 2 × $^1/_2$ in. hole. Since no mechanical closure was found to be satisfactory through a temperature cycle, the vessels were closed by welding to pressure tubing which could then be attached to the measuring apparatus. Pressure tubing and pressure valves and fittings were used throughout the measuring system.

Pressures were measured by means of Heise gauges, either 8 or 16 in. in diameter, graduated up to 5000 psi. with 5 lb. graduation marks. The 16 in. gauge was calibrated with a dead-weight tester and the 8 in. gauge was calibrated by comparison with the larger gauge. The principal uncertainty in the pressure readings was the 5 psi. uncertainty in the reproducibility of the gauge readings themselves.

The temperatures of the reactors were maintained by means of a surrounding furnace which could be held constant within 1° at any temperature from room temperature up to 600°. With the smaller reactor a $^5/_8$ in. thick copper liner was used in the furnace to even out temperature fluctuation. With the larger reactor there was no room for the copper liner, but the larger mass of stainless steel effectively served the same purpose. Control of the furnace was by means of a Wheelco temperature controller operating from a chromel-alumel thermocouple in the furnace, which controlled a portion of the heating current.

The volumes of the reactor and the other pertinent parts of the measuring system were measured, using helium, by comparing with a known volume which had been calibrated by weighing it with and without water in it.

Materials.—The magnesium was supplied by the Dow Chemical Co., Midland, Mich., and was doubly distilled metal which had a purity of 99.98%, the chief impurities being iron, 100 p.p.m., copper 60 p.p.m. and zinc 50 p.p.m. Turnings were prepared from an ingot of this material immediately before they were loaded into the reactor; thus the oxygen content could be assumed to be low. No analysis was made for non-metallic elements. The magnesium hydride was supplied by Metal Hydrides, Inc., Beverly, Mass. It contained 88.8% MgH_2, 7.5% Mg metal and 3.7% MgO. The MgO may have formed during handling and shipment since the material was reported to be 93% MgH_2. The hydrogen was from the National Cylinder Gas Co., Denver, Colorado, and was >99.94% H_2, <0.05% air and <0.01% H_2O. The deuterium was from the Stuart Oxygen Co., San Francisco, Calif., and contained 99.20% D_2, 0.72% H_2 and 0.08% N_2.

Procedure.—For the measurements of the decomposition pressures the smaller reactor was cleaned, loaded with the desired amount of fine magnesium turnings, welded to the pressure tubing and attached to the line. The system was outgassed under vacuum at 500° for several hours, after which hydrogen was admitted at 200–300 atm. pressure at the same temperature to convert the major part of the mag-

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[1] This work was done, in part, under the auspices of the U. S. Atomic Energy Commission.

[2] Taken in part from the dissertation submitted by J. F. Stampfer, Jr., in partial fulfillment of the requirements for the Ph.D. degree, Chemistry Department, University of New Mexico.

[3] Presented at the XVII International Congress of Pure and Applied Chemistry, Munich, Germany, August 31, 1959.

[4] E. Wiberg, H. Goeltzer and R. Bauer, *Z. Naturforsch.*, **6b**, 394 (1951).

[5] E. Wiberg and R. Bauer, *Chem. Ber.*, **85**, 593 (1952).

[6] F. H. Ellinger, *et al.*, THIS JOURNAL, **77**, 2647 (1955).

[7] W. Freundlich and B. Claudel, *Bull. soc. chim. France*, 967 (1956).

nesium to magnesium hydride. The decomposition pressures in the region of two solid phases then were determined by noting the constant pressure reached at any given temperature for various over-all compositions. Measurements were made with temperature increases and temperature decreases to ensure that equilibrium pressures were being observed. In this manner 129 values of the decomposition pressure were measured at various temperatures from 314 to 576°. Commercial magnesium hydride, instead of the metal, was used as the starting material for some of the measurements, and no significant difference was observed in the dissociation pressures.

It was not possible to determine pressure–composition isotherms with the small reactor because of the loss of hydrogen by diffusion. With the large reactor the rate of diffusion was small enough so that corrections for it could be made and measurements of composition were possible. The amount of hydrogen in the gas phase was calculated from the known volume of the reactor, the pressure, the temperature and the equation of state of hydrogen. Measured amounts of hydrogen could be withdrawn from the reactor by means of an auxiliary calibrated volume. In determining an isotherm the experiment was started at a pressure well above the decomposition pressure and small aliquots of hydrogen were withdrawn and measured in a calibrated volume. Any resulting loss of hydrogen by the gas phase in the reactor was calculated from the change in pressure to determine whether any hydrogen was evolved from the solid phase or phases. It was assumed that at hydrogen pressures much greater than the decomposition pressure, the solid consisted of unreacted magnesium metal and stoichiometric magnesium hydride. This assumption is based on two observations. First, every sample of magnesium hydride which the authors have examined either visually with a microscope, or by X-rays, has contained magnesium metal. Secondly, the hydrogen removed from the reactor at pressures above the decomposition pressure comes mostly from the gas phase (the amount removed from the solid phase is about $^1/_2$% of the total amount in the solid phase). Therefore, the total amount of hydrogen removed from the solid phases when the isotherm was completed was assumed to be equivalent to the amount of MgH_2 present originally. The amount of hydrogen in the solid phase or phases then could be calculated for each point of the isotherm.

Isotherms also were measured using commercial magnesium hydride as the starting material.

In order to obtain a graphical equation of state for the hydrogen at the high temperatures, blank runs were made with the reactor. The ideal gas law was used for the gas in the reactor and a correction factor was calculated which included effects due to deviations from the ideal gas law, solubility of hydrogen in the reactor walls and change of reactor volume with temperature. In addition, the rate of diffusion of hydrogen through the walls had to be measured at the various temperatures and pressures and appropriate corrections made. For the hydrogen measurements in the calibrated volume at room temperature use was made of compressibility factors available in the literature.[8,9]

The attainment of equilibrium in the region of two solid phases was verified by approaching the pressures from both directions. In the one phase region, equilibrium was considered to have been attained when the rate of pressure change became constant, the change then being due only to diffusion. This means that there is uncertainty as to whether or not the measurements were made at equilibrium in this region, particularly at the lower temperatures. Of course, strictly speaking, equilibrium was never attained, because of the hydrogen loss by diffusion.

Results

The isotherms determined at 440, 470, 510 and 560° are plotted in Fig. 1. An isotherm for MgD_2 is also shown which will be discussed later. As can be seen, the main portion of each isotherm is essentially horizontal, indicative of two solid phases having the compositions at the two ends of the horizontal portion of the curve. (Actually the "horizontal" has a slight slope, the pressure at the high hydrogen composition end being about 2% higher than at the low composition end. This is hardly more than the experimental error, but we believe it is real although we have no explanation for it.) The composition at the upper end is $MgH_{1.99\pm0.01}$ over the range of temperature investigated. The compositions at the lower ends of the isotherms vary with the temperature and indicate a solid solution of hydrogen in magnesium.

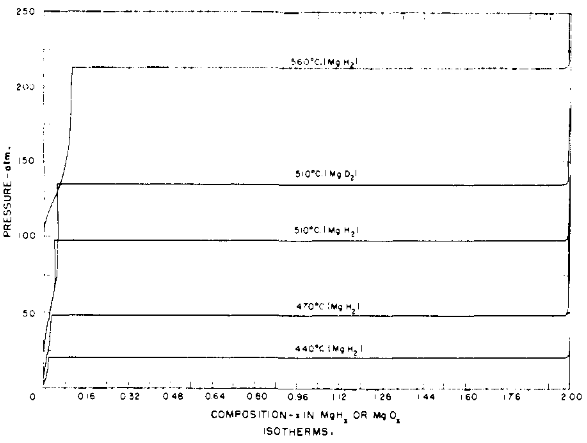

Fig. 1.

In Table I are listed the experimentally determined decomposition pressures at equilibrium for magnesium hydride in the region of two solid phases at temperatures from 314 to 576°. These pressures were converted to fugacities by the use of the Beattie–Bridgeman equation,[10] and the resulting fugacities, as a function of temperature, were fitted by means of least squares to the equation $R \ln f_{H_2} = (\Delta H_0/T) + I$. The values determined for the constants were $\Delta H_0 = -17{,}785 \pm 76$ cal./mole and $I = 32.28 \pm 0.45$ cal./°C., where R is the gas constant, f_{H_2} is the fugacity of hydrogen and T is the absolute temperature, and the uncertainty given is at the 95% confidence level. With these values of the constants the standard deviation of the fit of the points to the straight line was 0.063 cal./°C. When the points were fitted to an equation containing additional terms such as $A \ln T$, BT and CT^2 or D/T^2, the uncertainty intervals found for A, B and C or D in each case were larger in magnitude than the terms themselves and the fit was not significantly better than with the straight line.[11] Figure 2 shows a plot of $R \ln f$ *vs.* $1/T$.

The compositions at the lower ends of the isotherms at the various temperatures are listed in Table II. The uncertainty in these mole fractions is estimated to be of the order of 0.007. These values were fitted to the equation $\ln N_H = 4.67 \pm 2.6 - 6{,}225 \pm 2{,}000/T$. Solving for

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(8) J. Hilsenrath, *et al.*, "Tables of Thermal Properties of Gases," National Bureau of Standards, Circ. 564, U. S. Government Printing Office, Washington, D. C., 1955, p. 254 ff.

(9) H. W. Wooley, R. B. Scott and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **41**, 379 (1948).

(10) C. E. Holley, Jr., W. J. Worlton and R. K. Zeigler, "Compressibility Factors and Fugacity Coefficients Calculated from the Beattie–Bridgeman Equation of State for Hydrogen, Nitrogen, Oxygen, Carbon Dioxide, Ammonia, Methane and Helium," Los Alamos Scientific Laboratory Report LA-2271 (1958).

(11) The authors are indebted to Keith Zeigler and Aaron Goldman, of the Theoretical Division of this Laboratory, for help in the statistical treatment of the data.

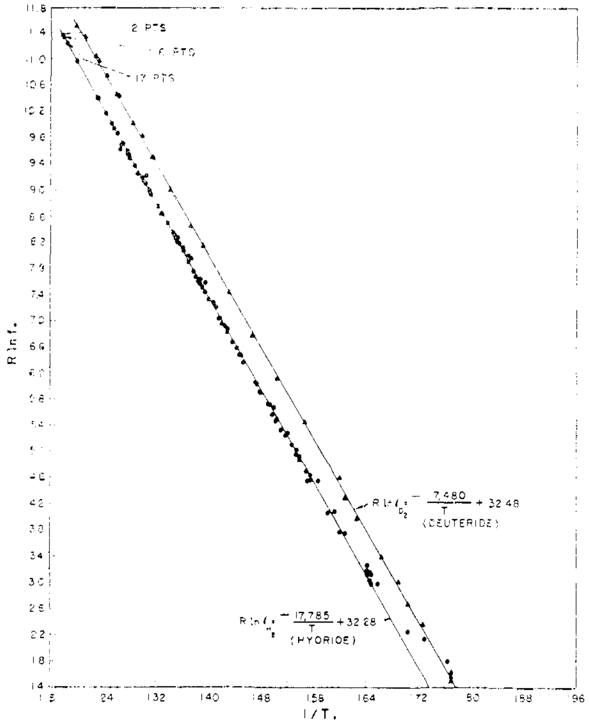

Fig. 2.

N_H, $N_H = 107\ e^{-6,225/T}$. Although the choice of a straight line for this relation is somewhat arbitrary, the accuracy of the data is not sufficient to justify any particular assumed curvature. And, to the first approximation at least, the solubility would be expected to follow a relation of the form chosen.

Quantitative conversion of magnesium to magnesium hydride was not achieved. In the best run the product contained 93.1% MgH_2, 3.0% MgO and 3.9% Mg metal. Usually the hydride content was slightly less, and there was always free magnesium metal.

Magnesium–Deuterium.—The main purpose in making MgD_2 was to determine the deuterium positions in the crystal lattice by means of neutron diffraction.[12] This system was not investigated as completely as the magnesium–hydrogen system, but enough data were taken to indicate the similarities and differences. The measurements were made in the large reactor used for the pressure–composition isotherms. Thirty-one measurements of decomposition pressure were made at temperatures from 279 to 561°. These are given in Table III.

According to the data of Michels and Goudeket[13] the differences between the compressibility factors for hydrogen and deuterium are less than 0.1% even at the highest pressures encountered in the present investigation. Therefore, the deuterium pressures were converted to fugacities by the aid of the same tables as were used for hydrogen.[10] The data then were fitted, as in the case of the hydride, to a straight line, $R \ln f = (\Delta H_0/T) + I$, and the constants were found to be $\Delta H_0 = -17{,}480 \pm 110$ cal./mole and $I = 32.48 \pm 0.17$ cal./°C. The standard deviation of the fit was 0.26 cal./°C. The poorer fit and larger uncertainty interval in the case of deuterium are believed to be due to the smaller number of points used. This equation is plotted in Fig. 2.

After the decomposition pressures were determined, the magnesium was allowed to react with D_2 at 420° and 2400 psi. in order to convert as much of the magnesium as possible to the deuteride. It then was removed and analyzed and found to be 85.7% MgD_2, 3.1% MgH_2, 4.6% MgO and 6.6% Mg. No MgH_2 phase was detected by X-ray examination; hence, it is probable that the hydrogen was distributed throughout the MgD_2 lattice. The presence of the hydrogen means that the de-

TABLE I

DECOMPOSITION PRESSURES OF MAGNESIUM HYDRIDE

587	2.31	676	18.51	739	60.22	793	136.58
603	3.67	677	18.71	739	62.13	796	142.02
607	3.67	679	19.94	741	62.13	799	146.72
607	4.01	680	20.14	742	63.08	804	158.67
608	3.81	688	23.41	742	63.22	813	177.47
608	4.08	690	24.91	743	64.65	813	177.95
609	4.15	691	24.05	748	69.07	834	233.07
609	4.36	693	26.27	752	74.45	844	265.27
609	4.01	696	27.56	753	74.45	844	265.80
622	5.78	700	30.62	756	78.67	844	265.87
625	5.85	700	30.08	762	86.67	844	265.67
628	7.01	702	31.37	763	87.24	844	265.74
632	6.87	704	32.05	764	88.19	844	265.53
638	9.05	706	33.21	764	90.98	844	266.08
643	9.12	706	33.21	764	88.87	844	266.69
643	9.53	708	36.34	764	89.27	844	266.62
645	9.05	710	37.70	766	100.17	844	266.28
646	9.80	714	38.52	767	93.30	844	265.12
650	10.82	717	40.97	768	95.34	844	265.19
650	10.96	717	43.96	770	98.33	844	264.85
652	11.70	719	42.33	774	103.30	844	265.47
652	11.23	721	43.55	777	107.31	844	265.05
655	12.18	721	45.05	777	107.66	844	264.71
658	13.34	722	44.57	777	107.52	844	265.27
659	13.13	724	46.00	781	113.58	845	265.12
662	13.68	726	47.81	782	116.37	848	279.28
665	14.97	728	53.22	783	117.05	848	279.75
666	14.77	730	53.90	784	119.22	848	279.96
667	16.47	730	51.45	788	126.37	848	278.80
668	15.58	734	56.21	788	126.98	848	279.41
670	16.88	735	57.57	789	125.08	848	278.32
671	16.94	738	59.27	790	121.54	849	280.50
						849	280.71

TABLE II

CONCENTRATIONS OF HYDROGEN IN MAGNESIUM SATURATED WITH HYDROGEN

T, °K.	Mole fraction H(N_H)	Mole fraction Mg(N_{Mg})
713	0.020	0.980
743	.031	.969
778	.026	.974
783	.024	.976
783	.040	.960
783	.034	.966
783	.036	.964
833	.093	.907

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(12) W. H. Zachariasen, J. F. Stampfer, Jr., and C. E. Holley, Jr., *Acta Cryst.*, to be published.

(13) A. Michels and M. Goudeket, *Physica*, **8**, 353 (1941).

TABLE III

DECOMPOSITION DEUTERIUM PRESSURES OVER MAGNESIUM DEUTERIDE

T, °K.	P (atm.)	T, °K.	P (atm.)
552	1.63	682	29.67
565	2.11	699	41.17
565	2.18	719	58.72
565	2.25	729	67.98
567	2.45	745	89.21
578	2.93	760	112.34
579	3.27	761	113.30
587	3.81	770	132.49
592	4.49	778	145.69
601	5.44	791	176.65
615	7.35	793	178.69
622	8.64	803	204.48
625	10.00	811	228.23
647	15.38	814	236.94
665	21.43	825	271.64
		834	301.72

TABLE IV

THERMODYNAMIC FUNCTIONS FOR FORMATION OF MgH_2

T, °K.	ΔF^0, cal./mole	ΔS^0, cal./mole-deg.	ΔH^0, cal./mole	ΔC_p^0, cal./mole-deg.
800	8000 ± 120	−31.47 ± 0.88	−18,350 ± 390	5.8 ± 8.8
600	1580 ± 80	−32.21 ± 0.48	−17,830 ± 80	0.7 ± 1.4
298	−8170	−32.3	−17,790	0
298	−7600 to −8300	−30.4 to −31.2	−16,900 to −17,350	(−2)

composition pressures reported for MgD_2 are somewhat in error.

Only one isotherm was run on the magnesium–deuterium system, at 510°. This isotherm is plotted in Fig. 1. Unfortunately, the deuterium in this run was contaminated with about 10% hydrogen. As in the case of the magnesium–hydrogen system, the upper limit of the region of two solid phases was the stoichiometric di-deuteride within the limits of error of the measurement. At the lower end, the composition was $MgD_{0.05\pm0.01}$, compared with an average value for 4 isotherms of $MgH_{0.034\pm0.007}$ for the hydrogen case at the same temperature. A quantitative comparison is not warranted because of the appreciable amount of hydrogen in the deuterium, but it is probably justifiable to conclude that at 510° deuterium may be about 30% more soluble in magnesium than is hydrogen.

Thermodynamics.—The equilibrium studied, in the magnesium–hydrogen case, may be represented as Mg(s, satd. with hydrogen, equil. P) + H_2(g, equil. P) = MgH_2(s, equil. P), the MgH_2 being considered a stoichiometric compound. For this equilibrium the equilibrium constant would be

$$K = \frac{a_{MgH_2}}{a_{Mg}a_{H_2}}$$

and the standard free energy change would be

$$\Delta F^0 = -RT\ln K = RT\ln a_{H_2} + RT\ln a_{Mg} - RT\ln a_{MgH_2}$$

The standard states for magnesium and for magnesium hydride are taken as the pure solid materials under 1 atm. pressure and the standard state for hydrogen as the pure gas at unit fugacity. Raoult's law is assumed to hold for the magnesium with hydrogen dissolved in it. On making the appropriate substitutions one obtains

$$\Delta F^0 = RT\ln f_{H_2} + RT\ln N_{Mg} + (\bar{V}_{Mg} - \bar{V}_{MgH_2})(P\text{ equil.} - 1)$$

where the last term takes account of the variation of activity with pressure for the magnesium and magnesium hydride. This last term varies from about 0 at room temperature to about 24 cal. at the highest temperature at which pressure measurements were made. It is therefore negligible compared to the uncertainties in the other terms and is neglected in the following treatment of the data. Substituting the analytical expression for $R\ln f_{H_2}$ and noting that $N_{Mg} = 1 - N_H$, we have

$$\Delta F^0 = -17{,}785 + 32.28T + 1.98\,T\ln(1 - N_H)$$

Taking $N_H = 107\,e^{-6{,}225}/T$ and differentiating in the standard manner, we have

$$\Delta S^0 = -\frac{\partial\Delta F}{\partial T} = -32.28 - 1.98\ln(1 - N_H) - \frac{12{,}300}{T}\,\frac{N_H}{1 - N_H}$$

$$\Delta H^0 = -T^2\,\frac{\partial\Delta F/T}{\partial T} = -17{,}785 - \frac{12{,}300\,N_H}{1 - N_H}$$

$$\Delta C_p{}^0 = \frac{\partial\Delta H^0}{\partial T} = \frac{7.7\times10^7}{T^2}\,\frac{N_H}{(1 - N_H)^2}$$

The quantities ΔF^0, ΔS^0 and ΔH^0 all get their principal contribution from measurements of the decomposition pressure and only minor contributions from the solubility measurements. Consequently, although the uncertainty in N_H is large compared to its magnitude, it does not contribute a large uncertainty to the total magnitude of these quantities. For $\Delta C_p{}^0$, however, the total contribution comes from the solubility measurements and the uncertainty is large.

Values for these thermodynamic quantities are shown in Table IV. The uncertainty intervals attached were obtained by the method of propagation of errors. The value at 298° was obtained by extrapolating the straight line relations for ln f_H *vs.* $1/T$ and ln N_H *vs.* $1/T$.

It seems unlikely that $\Delta C_p{}^0$ should be zero at room temperature. A value of −2 could be estimated by Kopp's Rule. If this value is used to estimate the values for the other functions at room temperature, the values shown in the last line of Table IV are obtained. These latter values were calculated from the equations $\Delta C_p{}^0 = -2$; $\Delta H^0 = \Delta H_0{}^0 - 2T$; $\Delta F^0 = \Delta H_0{}^0 + 2T\ln T + IT$; and $\Delta S^0 = -2\ln T - 2 - I$. The constants $\Delta H_0{}^0$ and I were determined from the values of ΔF^0 and ΔH^0 at 800 and 600° and found to be $-16{,}300 > \Delta H_0{}^0 > -16{,}750$ and $17.0 < I < 17.8$. The correct value for these thermodynamic functions at 298° doubtless lies in the neighborhood of the numbers given. Not enough information is known to permit estimation of a meaningful uncertainty interval.

TABLE V

THERMODYNAMIC FUNCTIONS FOR FORMATION OF MgD_2

T, °K.	ΔF^0, cal./mole	ΔS^0, cal./mole-deg.	ΔH^0, cal./mole	ΔC_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.

Acknowledgments.—The authors wish to acknowledge the helpful advice and criticism of J. F. Lemons, Group Leader, Los Alamos Scientific Laboratory. In addition R. M. Douglass, F. H. Ellinger, R. D. Gardner, E. L. Head, E. D. Loughran and E. VanKooten of the Los Alamos Scientific Laboratory gave valuable assistance in the analytical work.

[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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[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).