over the range of concentrations studied. This indicates that as we reduce the methanol concentration, the equilibrium gradually shifts from I to IV and that in pure chloroform solution the sitting-atop complex probably exists in the form of a dimer, Fe_2Cl_6–SA$(PP)_2$. A probable structure of this dimeric complex is depicted in Fig. 5.

TABLE III

EQUILIBRIUM MEASUREMENTS IN CHLOROFORM SOLUTIONS CONTAINING 1.0% BY VOLUME OF METHANOL

[Sitting-atop complex] (mM)	[Free PP] (mM)	[Free $FeCl_3$] (mM)	$K_I \times 10^{-3}$	$K_{IV} \times 10^{-6}$
5.36	3.41	0.37	42.5	125
6.62	2.15	1.02	30.0	139
7.30	1.34	2.12	26.1	150

On the other hand if more than 10% by volume of methanol is added to the chloroform solution, the PP in Fe(III)–SAPP is completely displaced by methanol molecules, and the sitting-atop complex can no longer exist in solution as shown by the visible spectra.

Experimental

The dimethyl ester of protoporphyrin was prepared by the method of Grinstein,[11] with the exception that recrystallized samples of hemin, supplied by Fisher Scientific Company, recrystallized (97 + %), were used instead of fresh blood as the raw material. The m.p. of the dimethyl ester of protoporphyrin so prepared is 221°. The anhydrous ferric chloride has a m.p. of 282°.

All visible spectra were taken on a Cary Recording Spectrophotometer. The infrared spectra were taken with a Perkin–Elmer Recording Infrared Spectrophotometer with a matched pair of 0.1 mm. sodium chloride cells. Deuterated chloroform, 99% $CDCl_3$, was used as solvent to dissolve the Fe(III)–SAPP for infrared studies. All the measurement were made at room temperatures of 20 to 23°.

The N,N'-bis-(2-aminoethyl) diamide I was prepared by dissolving the dimethyl ester of protoporphyrin in excess of ethylenediamine and heating the mixture at 100° for several hours under nitrogen atmosphere in a sealed tube. The excess ethylenediamine was removed by vacuum evaporation. The purified product I was completely soluble in water.

Acknowledgment.—This work was supported in part by a research grant (USPHS-RG-4483) from the Division of Research Grants, U. S. Public Health Service.

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[CONTRIBUTION FROM THE ELECTRON TUBE DIVISION, RADIO CORPORATION OF AMERICA, LANCASTER, PENNSYLVANIA]

Preparation of the Compound $7MgO \cdot 2SnO_2 \cdot As_2O_5$

BY ARTHUR L. SMITH

RECEIVED DECEMBER 9, 1959

Analysis of a portion of the system $MgO–SnO_2–As_2O_5$ by means of X-ray diffraction discloses the existence of the compound $7MgO \cdot 2SnO_2 \cdot As_2O_5$. The compound may be prepared by heating the respective oxides in requisite proportion at 1200° for 4 hr. The characteristic X-ray diffraction pattern of the compound is given.

Introduction

Compounds containing all three type oxides, MO, MO_2 and M_2O_5, are relatively rare. The present compound was discovered during an investigation to improve the luminescence of the phosphor $6MgO \cdot As_2O_5$:Mn by coactivation with tin(IV) oxide. Anomalies in the luminescence data prompted a study of the ternary system. Because the MgO + SnO_2 and MgO + As_2O_5 edges have been defined through the work of previous investigators, only that portion of the ternary which was necessary to identify the new compound was studied.

The work of Tanaka,[1] Berezhnov,[2] Coffeen[3] and Coughanour, *et al.*,[4] on the magnesium oxide–tin(IV) oxide solid-state reaction may be summarized as follows: Two compounds exist, $2MgO \cdot SnO_2$ and $MgO \cdot SnO_2$. There is complete agreement that the compound $2MgO \cdot SnO_2$ is thermally stable to at least 1550°. Although Coffeen claimed thermal stability of the compound $MgO \cdot SnO_2$ above 1000°, Coughanour, in agreement with Tanaka, found it to be unstable in the region 800–1000°, decomposing to $2MgO \cdot SnO_2$ and SnO_2. The present work, all conducted in this system at 1000° or above, failed to detect the presence of $MgO \cdot SnO_2$. This further confirms the work of Coughanour and Tanaka.

The MgO + As_2O_5 reactions are more complicated than those of MgO+SnO_2 because of the volatility of arsenic pentoxide. Guerin[5] and Travnicek, *et al.*,[6] have noted the tendency of MgO+As_2O_5 compounds to lose As_2O_3 + O_2 during heating. Guerin states that $MgO \cdot As_2O_5$ loses arsenic oxide at 500° to give $2MgO \cdot As_2O_5$, which, in turn, loses arsenic oxide to form $3MgO \cdot As_2O_5$ at 900°. He also considered the orthoarsenate to be unstable but did not realize that its decomposition led to a new and definite compound. Travnicek, *et al.*, found that at temperatures above 1000° the loss of arsenic pentoxide from the orthoarsenate leads to the compound $6MgO \cdot As_2O_5$. This compound can be prepared directly by firing the requisite proportions of the oxides and is stable to at least 1250°. The present investigation supports Travnicek's findings, but the decomposition of the orthoarsenate has been found to be reasonably slow (about 10 to 20% decomposition at 1200° for 4 hr.).

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(5) Henri Guerin, *Compt. rend.*, **204**, 1740 (1937).

(6) M. Travnicek, F. Kroger, The P. J. Botden and P. Zalm, *Physica*, **18**, #1, 33 (1952).

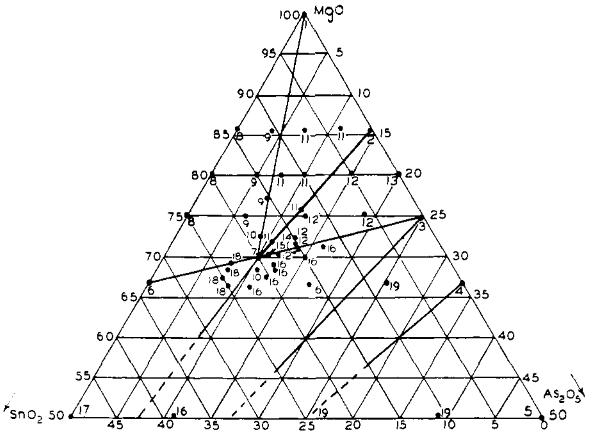

Fig. 1.—Mole compositions fired at 1200°; products obtained: 1, MgO; 2, $6MgO \cdot As_2O_5$; 3, $3MgO \cdot As_2O_5$; 4, $2MgO \cdot As_2O_5$; 5, $2MgO \cdot As_2O_5$ + ?; 6, $2MgO \cdot SnO_2$; 7, $7MgO \cdot 2SnO_2 \cdot As_2O_5$; 8, MgO + $2MgO \cdot SnO_2$; 9, MgO + $2MgO \cdot SnO_2$ + $7MgO \cdot 2SnO_2 \cdot As_2O_5$; 10, $2MgO \cdot SnO_2$ + $7MgO \cdot 2SnO_2 \cdot As_2O_5$; 11, MgO + $6MgO \cdot As_2O_5$ + $7MgO \cdot 2SnO_2 \cdot As_2O_5$; 12, $6MgO \cdot As_2O_5$ + $3MgO \cdot As_2O_5$ + $7MgO \cdot 2SnO_2 \cdot As_2O_5$; 13, $6MgO \cdot As_2O_5$ + $3MgO \cdot As_2O_5$; 14, $3MgO \cdot As_2O_5$ + $7MgO \cdot 2SnO_2 \cdot As_2O_5$; 15, MgO + $7MgO \cdot 2SnO_2 \cdot As_2O_5$; 16, SnO_2 + $3MgO \cdot As_2O_5$ + $7MgO \cdot 2SnO_2 \cdot As_2O_5$; 17, SnO_2 + $2MgO \cdot SnO_2$; 18, $2MgO \cdot SnO_2$ + SnO_2 + $7MgO \cdot 2SnO_2 \cdot As_2O_5$; 19, $3MgO \cdot As_2O_5$ + $2MgO \cdot As_2O_5$ + SnO_2.

No publication could be found concerning any compound formation in the ternary system $MgO-SnO_2-As_2O_5$.

Experimental

Magnesium carbonate (Special Luminescence Grade, Mallinckrodt), arsenic pentoxide (Reagent Grade, Baker and Adamson) and stannic oxide (Reagent Grade, Fisher) were used. The first two compounds received no purification, but the stannic oxide was refluxed repeatedly with fresh hydrochloric acid until the acid showed no tinge of yellow. The stannic oxide then was dried at 110°. Requisite quantities of the three compounds were slurried in water and dried at 160°. Firing was conducted in silica crucibles in air at 1200° for 2 hr. The product of the reaction was then milled in water for 16 hr. in a pebble mill, dried at 160° and refired as before. One series was fired at 1000° to gather information on possible mechanisms of reaction.

X-Ray diffraction analysis was performed by means of a Norelco X-ray diffractometer having a copper target tube with a nickel filter. The diffractometer operated at 40 kv., and 20 ma. Scanning of the 2 θ angle was at a rate of one degree per minute. Each sample was scanned from 70 degrees down to 10 degrees 2 θ.

Results and Discussion

Figure 1 summarizes the sample compositions (in mole %) and the product obtained at the 1200° firing temperature. The analysis of these data produced the phase diagram shown in Fig. 2. Along the edges of any triangle, the only species that coexist at equilibrium are the end members. Within any triangle, the only species that coexist at equilibrium are those presented by the compounds at the apexes. Dotted lines represent probable tie lines. The lower right-hand corner of the diagram is uncertain because of the volatility of arsenic pentoxide.

The new compound $7MgO \cdot 2SnO_2 \cdot As_2O_5$ does not form in 4 hr. at 1000°; only the simple magnesium stannate and various arsenates can be found. Reaction is incomplete in 4 hr. at 1100°, but it is probable that complete reaction would be obtained at greatly lengthened firing periods. At 1200°, reaction is complete and equilibrium is established in 4 hr.

A few runs were made by firing first at 700° for 2 hr., then 2 hr. at 900°, followed by 2 hr. at 1200°. This graduated-temperature technique was used to determine whether the volatility of arsenic pentoxide would affect the reaction, but no over-all change was observed. The arsenates, however, when fired in the above fashion, definitely showed loss of arsenic pentoxide, in agreement with the findings of others.

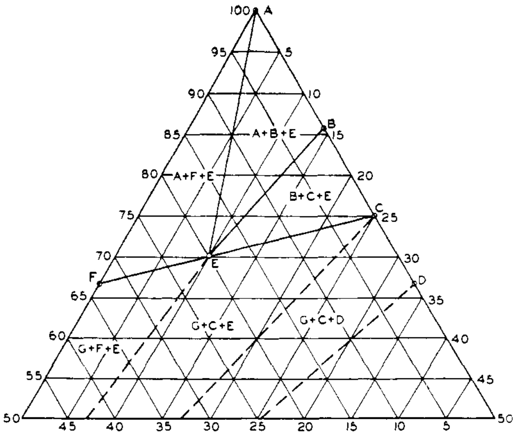

Fig. 2.—Compositional diagram of the system $MgO-SnO_2-As_2O_5$ at 1200°; products obtained: A, MgO; B, $6MgO \cdot As_2O_5$; C, $3MgO \cdot As_2O_5$; D, $2MgO \cdot As_2O_5$; E, $7MgO \cdot 2SnO_2 \cdot As_2O_5$; F, $2MgO \cdot SnO_2$; G, SnO_2.

TABLE I

X-RAY DIFFRACTION PATTERN OF THE COMPOUND $7MgO \cdot 2SnO_2 \cdot As_2O_5$

"d" Value	Intensity	"d" Value	Intensity
4.87	0.75	2.27	0.15
4.20	1.00	2.13	.50
3.98	0.20	2.06	.20
3.42	.70	1.95	.20
3.02	.15	1.91	.10
2.98	.20	1.84	.20
2.90	.50	1.82	.15
2.80	.95	1.74	.10
2.78	.85	1.72	.25
2.74	.60	1.70	.25
2.70	.10	1.64	.10
2.54	.45	1.62	.20
2.45	.10	1.60	.10
2.40	.55	1.59	.15
2.34	.35	1.56	.10
2.32	.25	1.54	.10
2.30	.20	1.51	.30
		1.50	.70

At 1200°, the phase diagram of the system is simple. No complications of extensive solid solution are present; however, there is some loss of arsenic pentoxide on the right side, particularly on the lower right side. Because magnesium arsenates are formed by the solution reaction between magnesium carbonate and arsenic pentoxide, the method of first slurrying and then milling the original 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.

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