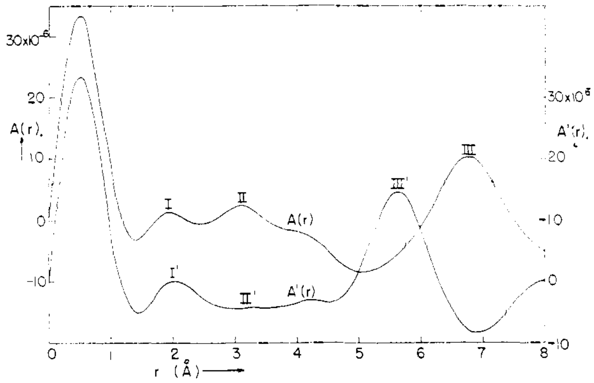

Fig. 3.—Radial distribution function of the Magnus green salt, $A(r)$, and of Magnus pink salt, $A'(r)$.

orbital terms as a configuration interaction involvgni some metal–metal bonding.[19b] The closest distance between Pt atoms in MPS would not be less than 5 Å. as seen from peak III′ in Fig. 3. The remarkable colors of MGS must result from the metal interaction, while MPS, which has no such interaction, does not differ materially in color from finely divided $Pt(NH_3)_4Cl_2$, and its pink color must be due to $Pt(NH_3)_4^{++}$ ions. Experimentally there is little doubt that MGS is the stable form of the Magnus salts, and this may be due to the extra metal interaction. Presumably accidents of nucleation produce the pink salt, but it may well be that packing considerations, by themselves, would favor the pink salt since the type of packing in the green salt is rare. It would also be interesting to learn whether there is an appreciable activation energy for forming the Pt–Pt bond in the green salt.

Acknowledgments.—The authors wish to express their thanks to Messrs. Russell A. Bonham and Peter Vossos for their assistance in some of the numerical computations and to Mr. E. Miller Layton for obtaining the infrared spectra. Dr. Don S. Martin and his students kindly supplied MGS and MPS, and contributed to our interest in this problem.

AMES, IOWA

[CONTRIBUTION NO. 511 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Solubility of the Post-Transition Metals in their Molten Halides[1]

BY JOHN D. CORBETT, SAMUEL VON WINBUSH AND FRANK C. ALBERS

RECEIVED FEBRUARY 20, 1957

The solubilities of the respective metals in molten PbI_2, $SbCl_3$, SbI_3, $ZnCl_2$, ZnI_2, CdI_2 and $GaBr_2$ are reported. An interpretation of the solution of the post-transition representative metals in their molten halides is presented in terms of the formation of slightly stable subhalides. The apparent stabilities of the lower halides increase both with increasing atomic weight of the metal within a group, and with increasing atomic weight of the halide with a given metal, except for cadmium. The halide effect is attributed to a corresponding decrease in the extent to which the higher oxidation state of the metal is stabilized by complex formation with halide. The relative stabilities of the metal-halide complexes observed parallel those reported in aqueous solution for the same ions, including the inversion in order found for cadmium. The formation of gaseous subhalides of antimony, bismuth and gallium is indicated by transport experiments. A direct correspondence is found between those systems in which gaseous subhalides of appreciable stability are formed and those in which metal dissolves in the molten salt to an appreciable extent. Diamagnetic solutes are formed in the zinc, cadmium, gallium, antimony and bismuth systems.

Introduction

The problem presented by the apparent solution of such metals as cadmium,[2] bismuth,[3] cerium,[4] the alkalies,[5,6] and the alkaline earths[7] in their respective molten halides has not received a completely satisfactory explanation. Although the possibility of the formation of colloidal metal or "pyrosoles" in the process has been eliminated, interpretations in terms of energy bands for the metal's electrons,[8] the formation of subhalides,[2,3,9] or a combination of these concepts[5] has been suggested. The phenomenon appears to be limited to the liquid state, in that only an intimate mixture of the original components is obtained on solidification of these solutions.

Although generally small metal solubilities had been found previously in this Laboratory for lead, tin, aluminum, thallium and silver systems,[10] subsequent investigations have revealed larger interactions in other post-transition metal–metal halide melts. In addition, evidence has been obtained supporting the interpretation of these solubilities in terms of the formation of slightly stable lower halides.

Results

The data obtained are given in Table I. The number of significant figures reported is indicative of the reproducibility of the measurement. In the liquid state only the Cd–CdI_2 system is different in color from the pure salt. The resulting solids are quite distinctive, however, for all but the Pb–PbI_2 and Zn–$ZnCl_2$ systems at the lowest temperatures

[1] Presented in part at the 129th meeting of the American Chemical Society, Dallas, Texas, April 12, 1956. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] G. von Hevesy and E. Löwenstein, *Z. anorg. allgem. Chem.*, **187**, 266 (1930).

[3] B. Eggink, *Z. physik. Chem.*, **64**, 449 (1908).

[4] D. Cubicciotti, THIS JOURNAL, **71**, 4119 (1949).

[5] M. A. Bredig, J. W. Johnson and W. T. Smith, *ibid.*, **77**, 307 (1955).

[6] M. A. Bredig, H. R. Bronstein and W. T. Smith, *ibid.*, **77**, 1454 (1955).

[7] D. D. Cubicciotti and C. D. Thurmond, *ibid.*, **71**, 2149 (1949).

[8] D. D. Cubicciotti, *ibid.*, **74**, 1198 (1952).

[9] K. Grjotheim, F. Grönvold and J. Krogh-Moe, *ibid.*, **77**, 5824 (1955).

[10] J. D. Corbett and S. von Winbush, *ibid.*, **77**, 3964 (1955).

reported, and for the Ga–$GaBr_2$ system. These observations will be discussed subsequently.

TABLE I

System	Temp., °C.	Mole % dissolved metal	Method[a]	Color Liquid	Color Solid
Pb–PbI_2	438	0.024	B	Dark red	Yellow
	597	0.15	B	Dark red	Dirty-
	700	0.41	B	Dark red	yellow
Sb–$SbCl_3$	273	0.018	B	Clear	Gray
Sb–SbI_3	201	1.69	C	Black	Black
	300	3.5	C	Black	Black-
	400	5.8	C	Black	metallic
Zn–$ZnCl_2$	498	0.182	B	Clear	Clear
	298	1.64	B	Clear	Black
Zn–ZnI_2	498	0.28	B	Yellow	Black
	617	1.0	B	Yellow	Black
	667	1.65	B	Yellow	Black
Cd–CdI_2	410	0.63	B	Black	Dark-
	600	1.5	B	Black	gray
Ga–$GaBr_2$	170	9.30	B	Clear	Yellow

[a] Methods: B, loss in weight of metal phase; C, weight of dissolved metal.

Literature values are available for only the zinc chloride and the cadmium iodide systems. Von Hevesy and Löwenstein[2] reported that 10^{-4} mole % zinc dissolved in zinc chloride at 500°, as determined by a "titration" of a colored melt. Since no colored melts have been observed in the course of this work, it is uncertain as to what they were measuring. The same authors[2] reported a solubility of 7.8 mole % cadmium in cadmium iodide at 600°, about five times larger than that found here. As described in the Experimental section, values of this magnitude can be obtained readily by method B under non-isothermal conditions where metal may be transported to cooler portions of the salt or the container, for such distributed metal apparently does not readily reaggregate with the bulk phase.

Discussion

Any interpretation of the so-called "solution" of metals in their molten salts should account for a number of facts concerning these interactions. The formation of true solutions has been well substantiated for a large number of systems, where a marked depression of the freezing point of the salt is observed on solution of metal.[2–9] Moreover, these metals apparently are soluble only in salts of the same metal, indicating a specific interaction between the metal and the cation of the salt,[11] and yet only a mixture of the original components is usually obtained on solidification of the melt. In addition, any explanation should give reason to the marked variation in solubility of the various metals in their salts.

It will be seen that the formation of a class of slightly stable subhalides offers a satisfactory interpretation for the behavior of systems involving the post-transition representative metals and their halides. Although this concept has been suggested by previous workers, it has not received a general acceptance. This has been due to both the absence of a substantiated isolation of such a subhalide among the better known examples of this phenomenon, as well as the lack of correlation of either the relative magnitudes of the solubilities among diverse systems or with the occurrence of the same lower halides under other conditions.

For the purposes of qualitative discussion, the known solubilities of the post-transition metals in their molten halides are arranged in a periodic table fashion in Table II. Known "lower" halides are indicated in parentheses. For consistency the data are given at a fixed temperature in each group.[12]

TABLE II

SOLUBILITIES OF POST-TRANSITION METALS IN THEIR MOLTEN HALIDES[a]

II		III		IV		V	
		$AlCl_3$	$\sim 10^{-7}$[d]				
		AlI_3	0.02[e]				
$ZnCl_2$	0.61[b]	$GaCl_2$	2[f]				
		$GaBr_2$	9[b]				
ZnI_2	0.87[b]	GaI_2	40[g]				
$CdCl_2$	15[c]	InX_2	50	$SnCl_2$	0.003[f]	$SbCl_3$	0.02[b]
$CdBr_2$	14[c]	(InX)		$SnBr_2$	.009[h]		
CdI_2	1.5[b]					SbI_3	3.1[b]
HgX_2	50	(TlX)		$PbCl_2$	.006[f]	$BiCl_3$	23[i]
(Hg_2X_2)				PbI_2	.05[b]	$BiBr_3$	40[i]

[a] Data for the four groups in mole per cent. metal at 600, 230, 500 and 270°, respectively (*cf.* footnote 12). [b] This work. [c] Ref. 2. [d] L. M. Foster, A. S. Russell and C. N. Cochran, THIS JOURNAL, **72**, 2580 (1950); L. M. Foster, private communication. [e] Calculated from ref. 10 and ΔH^0 given by F. Irmann, *Helv. Chim. Acta*, **188**, 1449 (1950). [f] Ref. 10. [g] Ref. 13. Similarly small temperature coefficients of solubility have been found in the other gallium systems. [h] Value reported in ref. 10 was in error. [i] Ref. 3.

Two systematic relationships are apparent in this arrangement. First, without exception, an increase in atomic weight of the metal within a group results in an increase in the solubility in a given halide. In the second and third groups this effect culminates in the formation of stable mercury(I) and indium(I) halides. A similar behavior is well known for the relative stabilities of the +2 and +3 states in the fourth and fifth groups. The implications of the trend observed in these two groups for still lower states will be discussed later.

These systems also show a rather marked regularity in the change in solubility of a given metal with variation in halide ion. In the third, fourth and fifth groups the solubility of metal, or the amount of the lower halide formed, increases in the order chloride, bromide, iodide. The trend is particu-

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(11) The more trivial examples of direct reduction of the salt by added foreign metal are, of course, being disregarded. For example, the apparent solution of lead in cadmium chloride, as well as a large number of metals in bismuth trichloride, seemingly involves simple oxidation–reduction reactions. The initial metal addition produces the characteristic color of the metal–metal halide melt of the original salt; ultimately, the separation of a pure or alloyed phase containing the metal of the initial salt occurs.

(12) These temperatures, 600, 230, 500 and 270°, resp., were chosen so as to best fit the temperatures at which solubilities had been determined. For interpolation and extrapolation, plots of log solubility *vs.* $1/T$ were used; these have been found to be linear for all systems with solubilities of less than 2% that have been investigated at three temperatures. This behavior would be expected for equilibria of the type discussed herein. Exactly the same conclusions that follow could be obtained using a fixed temperature interval above the melting points of the salts in each group.

(13) J. D. Corbett and R. K. McMullan, THIS JOURNAL, **77**, 4217 (1955).

larly striking in the gallium systems; metal is precipitated when the metal-saturated chloride melt is solidified, while GaBr[14] and GaI,[13] stable in the solid state, are formed with the heavier halides.[15] Generally speaking, the stabilities of solid subhalides with respect to disproportionation show a corresponding relationship, being greatest with the iodide. At least in the molten state this halide effect can be attributed primarily to the decrease in basicity of the halide ion that accompanies an increase in atomic weight, in turn diminishing the extent to which the more acidic, higher oxidation state is stabilized by complex formation with halide ion. As a result greater reduction by metal, corresponding to greater stability toward disproportionation, is observed with the heavier halides.[16] Although the solubilities in the zinc systems show the same halide relationship, the inversion of the apparent stabilities of the cadmium(I) halides is quite evident (Table II). It is interesting to note that solid mercury(I) chloride, bromide and iodide behave similarly,[9] with standard free energies of disproportionation of 8.0, 6.6 and 2.5 kcal./mole, respectively.[17] Moreover, the reversal in the relative stabilities of the halide complexes of cadmium(II) and mercury(II) that is implied by these results is not without precedent. In aqueous solution the formation constants of the halide complexes of these two ions are in the order $I^- > Br^- > Cl^-$, whereas zinc(II) shows the more common relationship $Cl^- > Br^- > I^-$.[18] The anomalous behavior of cadmium and mercury has been attributed to multiple bond formation with the ligand.[19]

A strong point in favor of the interpretation of these metal–metal halide systems in terms of the formation of lower oxidation states is afforded by observations on the same systems in the gaseous state at comparable temperatures. In the cases under consideration there is a direct correspondence between the systems in which the metal dissolves in its fused halide to a significant extent and those in which gaseous subhalides of appreciable stability are known. As described in the Experimental section, rather definite evidence for a lower halide of antimony, bismuth and gallium has been obtained from observations on the transport of metal by vapors of the normal salt at temperatures where the vapor pressure of the metal alone is negligible. Similar or equivalent results have been reported for zinc, cadmium and bismuth, and for aluminum at higher temperatures.[20] On the other hand, visible transport of metal is not found in the lead and tin systems (Experimental section)[10,17] where the small solubilities are indicative of less stable, lower halides.

In this light the existence of these particular subhalides in the liquid but not the solid state is not unexpected. Although these compounds have insufficient stability to exist as pure solid phases, their presence at elevated temperatures when dissolved at less than unit activity in the parent salt is quite reasonable. Thus a stable solid subhalide can be obtained from such a solution only when reduction by metal produces a liquid that exceeds the composition of the normal halide–lower halide phase eutectic. Again, such a situation is observed in the Ga–$GaBr_2$ and Ga–GaI_2 systems, but not with Ga–$GaCl_2$. It may be that the inability to isolate cadmium(I) as well as possibly alkaline earth(I) and Ce(I?) halides from their respective binary systems, in spite of the rather large solubilities of metal observed,[2,4,7] is a consequence of the hypothetical eutectic being considerably removed in composition from the parent salt. Relatively low melting points for these lower halides might account for this. The possibility of the formation of lower oxidation states in the alkaline earth and cerium systems has been considered by Brewer.[21] However, extension of this concept to the rather unique alkali metal–alkali halide systems[5,6] would be quite speculative, particularly in view of the unusual M_2X product that would be involved.

In most cases it is possible to formulate the lower halides present in the systems under consideration on the basis of chemical knowledge and the observed magnetic properties. The formation of diamagnetic solutes has been specifically established for metal-metal halide melts involving $CdCl_2$,[22] $ZnCl_2$, GaX_2, SbI_3 and $BiCl_3$; the solubilities in the tin and lead halides are too small to allow detection of possible paramagnetic products (see Experimental section). Thus it seems fairly certain that Cd_2^{+2}, analogous to Hg_2^{+2}, occurs in the cadmium systems.[9,16] Similarly, Zn_2^{+2} is the most likely product from the solution of zinc in its halides. The simple monohalides are unquestionably formed in the aluminum and gallium systems.[10,15,16] The much smaller solubilities in the tin and lead systems only indicate a low stability for either the M_2^{+2} or M^+ products. In this connection it should be noted that Karpachev and co-workers[23] have concluded on the basis of e.m.f. measurements that Pb^+, Cd^0 (or Cd_2^{+2}) and Li^0 or Li_2^+ are formed in the respective metal–metal chloride solutions.

Bismuth(I) halides doubtless are formed in the bismuth systems,[16,24] although the observed dia-

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(14) J. D. Corbett and A. Hershaft, unpublished research.

(15) Although the simplest formula has been used for the gallium "dihalides," these compounds have been shown to be Ga(I)[Ga(III)X_4] (R. K. McMullan and J. D. Corbett, to be published; L. A. Woodward, G. Garton and H. L. Roberts, *J. Chem. Soc.*, 3723 (1956)).

(16) A reduction in the amount to which the higher oxidation state is complexed by halide ion and thereby stabilized can also be brought about by the introduction of a stronger Lewis acid. Use of $AlCl_3$ for this purpose has allowed the preparation of stable Cd(I), Bi(I) and Ga(I) tetrachloroaluminates from the respective metal–metal chloride systems (J. D. Corbett and R. K. McMullan, THIS JOURNAL, **78**, 2906 (1956)). The concepts developed in the present paper, together with the elucidation of the nature of $GaCl_2$ (footnote 15), led to these acid-stabilization results.

(17) L. Brewer, *et al.*, "The Chemistry and Metallurgy of Miscellaneous Materials—Thermodynamics," L. L. Quill, Ed., NNES IV-19B, McGraw–Hill Book Co., New York, N. Y., 1950, p. 113.

(18) S. Ahrland, *Acta Chem. Scand.*, **10**, 723 (1956).

(19) I. Leden and J. Chatt, *J. Chem. Soc.*, 2936 (1955).

(20) Summarized in ref. **17**, pp. 121, 241–242, 252.

(21) Ref. **17**, pp. 119, 124.

(22) J. Farquharson and E. Heymann, *Trans. Faraday Soc.*, **31**, 1004 (1935).

(23) S. Karpachev, A. Stromberg and E. Jordan, *Compt. rend. acad. sci. URSS*, **36**, 101 (1942); S. Karpachev and A. Stromberg, *Zhur. Fiz. Khim.*, **13**, 39 (1939); S. Karpachev and F. Jordan, *ibid.*, **14**, 1495 (1940).

(24) There is considerable disagreement in the literature as to the existence of Bi(I) and/or Bi(II) halides in the solid state. No isolation of a given halide has been substantiated (Ref. **17**, p. 251, see also T. Sokolova, *Izvest. Sektora Fiz-Khim Anal., Inst. Obshchei Neorg. Khim.*,

magnetism is rather unexpected. Seemingly, either pairing of the $6p^2$ valence electrons or the formation of metal–metal bonds has occurred. The oxidation state present in the diamagnetic solutions of antimony in its triiodide is not as obvious. By analogy with bismuth a less stable Sb(I) might be expected. However, the +2 oxidation state, as known in P_2I_4 and As_2I_4,[25] cannot be ruled out solely by the magnitude of the solubility. Investigations of the equilibria in the gas phase are expected to allow a distinction to be made.

Experimental

Solubility Determination Methods.—In cases where the metal is liquid at the equilibration temperature, suspension of metal droplets in the salt is usually not observed.[10] In these cases, direct determination of the loss in weight of metal when equilibrated with a known amount of salt (method B) results in a considerable gain in accuracy and ease of measurement over that possible by direct analytical determination. The clear melt in the Sb–$SbCl_3$ system also allowed this method to be used with a solid metal. For the zinc halides, $SbCl_3$ and $GaBr_3$, the weight of salt sublimed *in vacuo* from the broken ampoule onto the weighed metal in the equilibration vessel was obtained by difference, as previously described for the tin systems.[10] The cadmium and lead iodides were weighed in air (see Materials).

The known amounts of salt and metal were equilibrated, except as later noted, in small evacuated tubes in tubular furnaces controlled with Celectray or Brown Proportioning controllers. The temperatures were measured with chromel–alumel couples calibrated by Leeds and Northrup. Equilibration times of 3–16, 1–2, 5–8, 5–10 and 24 hr. for PbI_2, $SbCl_3$, ZnX_2, CdI_2 and $GaBr_2$, resp., were used. The Pyrex or Vycor containers were then quenched with an air blast or cold water; there was no evidence of segregation during this process. The coherent metal button was recovered, washed with water and reweighed. With the $GaBr_2$ system, the metal was frozen prior to opening the tube. Acetone was used to separate the button from adhering salt in order to avoid the additional metal produced when $GaBr_2$ reacts with water. In cases where occlusion of salt within the button was suspected, the metal was remelted under vacuum, alone or with an alkali halide flux.[10] The buttons both before and after use could be so remelted with weight losses of 0.1 to 0.7 mg. No evidence for solution of salt in liquid metal was found in these systems.

With the Cd–CdI_2 system, the application of method B initially gave very erratic values of 2 to 5 mole % metal dissolved at 410°. More constant temperature control, as obtained with a shunted Marshall Tube Furnace and a proportioning controller, resulted in values of 0.8 to 1.5% at 410° and 6 to 10% at 600°. The scattered and, as were later found, high values were probably due to transport of the volatile metal, either directly (b.p. 765°) or as a subhalide, to the cooler upper walls of the container. This difficulty was substantially eliminated by equilibration of the salt and metal in containers in which the free volume was as small as possible. After the salt had been fused, the Vycor apparatus was sealed from the line and the salt quantitatively melted and sublimed down onto the metal in a 13 × 20 mm. bulb, which was then detached. In this fashion a sample was obtained which filled greater than 95% of the container (and only once exceeded that volume), thus reducing the possible temperature gradients within the system to a minimum. The bulbs were also jacketed by a closed tube within the furnace. The average deviations obtained at 410 and 600° were 0.014 and 0.17 mole %, respectively; the values reported are probably, at worst, 10% higher than the true solubilities.

With Sb–SbI_3, since the metal was solid at the temperature used, the saturated samples initially were gravity-filtered *in situ* through a medium or coarse sintered-glass disk sealed in the container. Sublimation of the salt from a weighed portion of the filtrate allowed a direct determination of the weight of metal therein (method C). This sublimation was initiated at 100° and the temperature slowly raised to 250° over a period of 12 hours; under these conditions loss of metal by entrainment or by subhalide formation (see Transport) was not encountered. However, particularly for equilibrations above 300°, erratic values were obtained due to transport of metal *via* a subhalide to other portions of the tube during the initial equilibration. Crystals of metal were often readily visible on the filtrate side of the sintered disk before the sample was inverted for filtration. The following technique was devised to overcome this difficulty: a 12 × 25 mm. tube, with a disk sealed near the middle, was almost completely filled with sublimed SbI_3. Metal had been previously placed on top of the filter, so that saturation of the lower portion of the salt was effected only by diffusion through the disk. In addition, the container was immersed in a molten $NaNO_3$ bath within the furnace. The values at 400° were thus reduced from a range of 3 to 8% to 5.8 ± 0.2% dissolved metal. Microscopic examination of metal remaining after sublimation of the salt showed the presence of only amorphous metal, and no crystals >1 μ in size.

During preliminary studies on this system, the formation of true solutions of metal in salt was established by the observation that metal lowered the vapor pressure of the triiodide. A small tube containing metal in a well in one end and salt in the other was placed in a furnace with a known temperature gradient; temperatures were also checked with couples in glass fingers projecting into salt and metal. It was observed that the salt distilled against a 4° temperature gradient onto the metal at 430°.

As indicated in Table I, the appearance of the quenched salts in most cases was typically that of an intimate mixture of salts and metal. However, with $ZnCl_2$ containing 0.18% metal, the water-quenched solid was a clear glass, quite similar to that obtained on rapid cooling of the pure molten salt. On heating, crystallization of the salt occurred at 120°, while the darkening characteristic of finely divided metal appeared rather sharply at 180°. The colorless glass was completely soluble in anhydrous ether, with the precipitation of metal after about 4 hr. Preliminary attempts to isolate the probable zinc (I) chloride therein were unsuccessful.

Materials.—The determination of solubilities by weight loss of the metal phase required the absence of non-metallic impurities soluble in the salt. For this reason zinc (Bunker Hill Electrolytic, 99.99%) was vacuum-fused and washed with acid to remove the oxide. Cadmium (Fisher Reagent) was repeatedly fused in a helium atmosphere alone, or with $CdCl_2$. Gallium (Aluminum Company of America, 99.9%) was treated with dil. HCl, frozen in small pellets and washed with distilled water. Lead (Fisher, Test Lead) was treated as previously described.[10] Antimony (Fisher Reagent) was used directly. The success of these procedures, as well as the absence of metallic reducing impurities, was shown by the consistency in results obtained on re-use of the same metal sample.

In order to avoid erroneous metal solubilities resulting from reactive impurities in the salts, particularly water and the resulting hydrolysis products, all the salts were prepared and handled by techniques dictated by their sensitivity to moisture, and, except for CdI_2, were vacuum sublimed onto metal just previous to equilibration.

Lead(II) iodide was precipitated from solutions of Reagent grade KI and $Pb(NO_3)_2$, vacuum dried and sublimed. The 20 to 30-g. portions used were weighed in air. For some of the measurements, metal-saturated salt was purified for re-use by heating the salt in a closed tube at 500° with excess I_2, separating the iodine in a side arm at −80° and then vacuum subliming the salt.

Antimony(III) chloride was prepared from the elements, using excess metal, and was vacuum-sublimed at about 100° into small fragile ampoules for storage.

Antimony(III) iodide (Fisher purified) was found to be sufficiently pure to be used directly after one sublimation. Measurements made with salt prepared from the elements gave the same results.

Akad. Nauk. SSSR, **21**, 159 (1952)). ADDED IN PROOF.—The preparation of pure BiCl has been accomplished recently in this Laboratory, J. D. Corbett, unpublished research.

(25) F. Jaeger and H. Doornbosch, *Z. anorg. allgem. Chem.*, **75**, 261 (1912). The phase diagram presented by these authors for the Sb–SbI_3 system certainly seems in error. Although they indicate the formation of a solution of 13 mole % salt in metal at 169°, such a process has not been observed below 400°. They did not investigate the salt-rich phase.

Zinc chloride also was prepared from the elements. Since $ZnCl_2$ cannot be separated from metal by sublimation, the salt was heated extensively with excess chlorine. It was then sublimed at 500°, and melted into fragile containers containing 3 to 5 g. each. The resulting salt evolved no hydrogen when contacted with metal; considerable amounts of this gas, presumably from dissolved water and HCl, were obtained when commercial $ZnCl_2$ was used after one vacuum sublimation.

Zinc iodide was prepared in a V-shaped Vycor tube from metal and excess, vacuum-sublimed iodine, heating the metal to 700° and the iodine to 200°. The product was transferred in air, triply sublimed after removal of the I_2, and similarly stored in 2 to 3-g. batches.

Owing to thermal decomposition, CdI_2 cannot be vacuum sublimed without appreciable contamination of the product with free metal. Hence it was prepared directly from the elements in a sealed tube and the excess I_2 and traces of HI condensed in a side arm at $-190°$ and sealed off. The salt was then sublimed at 450° in the closed tube. For equilibration a 10 to 15-g. sample was weighed in air and then melted *in vacuo* (without decomposition) before the metal was introduced under helium.

For the Ga–$GaBr_2$ system, $GaBr_3$ was prepared from the metal and excess, P_2O_5-dried bromine, sublimed and sealed in ampoules. The $GaBr_2$ was then formed as the initial product during the equilibration with a weighed excess of metal.

Transport Studies.—Observations on the stabilities of gaseous subhalides were carried out in the manner already described for tin and lead.[10] Transport of antimony was obtained when SbI_3 was distilled at $<10^{-2}$ mm. over metal heated as low as 300°. Metal alone would not sublime at this temperature, as expected from a calculated vapor pressure of *ca.* 10^{-10} atm.[26] Similarly, $BiCl_3$ caused transport of Bi, and GaX_2 of Ga at 400°. Studies of this type with lead are, however, limited by the vapor pressure of the metal to temperatures below about 575°.[10] With PbI_2, where the natural color of the solid salt prevents visual detection of metal at less than about 0.1 mole %, transport of lesser amounts either directly or *via* a subhalide does occur below 500°, as detected by direct solubility measurements with salt sublimed from a metal-saturated sample.

Magnetic Susceptibility Observations.—A qualitative Gouy method was used to establish the diamagnetism of metal-containing melts of SbI_3, $ZnCl_2$, GaX_2 and $BiCl_3$. The salts, containing less metal than necessary for saturation at the temperature used, were sealed in small fused silica tubes equipped with evacuated jackets to lessen the rate of cooling. These were lowered from the furnace to between the pole pieces of a magnet with an inhomogeneous field of maximum intensity of about 12000 gauss. A deflection out of the field, indistinguishable from the pure molten salt, was always observed when the magnet was turned on. Experiments with dilute aqueous solutions of paramagnetic salts indicated that the method should be quite capable of detecting paramagnetism in the systems studied if such species had been formed in the expected amounts.

(26) Ref. 17, p. 31.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Praseodymium Oxides. IV. A Study of the Region $PrO_{1.83}$–$PrO_{2.00}$[1]

BY C. L. SIEGLAFF AND L. EYRING

RECEIVED JANUARY 19, 1957

This is a study of the phase relationships of the higher praseodymium oxides. X-Ray powder diagrams of quenched, analyzed samples were taken to determine the phases present. A two-phase system was found for the region $PrO_{1.83}$–$PrO_{2.00}$ at preparation temperatures below 350° and oxygen pressures less than ten atmospheres. Lattice constants are given for the various phases found.

Introduction

Several investigations of the praseodymium oxides beyond Pr_2O_3 have been reported recently.[2–8] The oxide system below Pr_6O_{11} has been extensively studied, but in the region Pr_6O_{11} to PrO_2 there is apparent disagreement as to the phases present. Through the use of X-ray diffraction techniques on samples prepared under equilibrium conditions a study of this region has been carried out.

Experimental Methods

Materials.—The Pr_6O_{11} used in these experiments was obtained from Professor F. H. Spedding, Iowa State College, Ames, Iowa, as 99.9+% pure Pr_6O_{11} with no other rare earth cations present in detectable amounts. The oxygen used in the preparation of quenched samples was commercial tank oxygen.

Apparatus for the Preparation of Quenched Samples.—The constant volume apparatus used in preparing the samples below ten atm. oxygen pressure was similar in principle to the one described previously.[3] Since the measurements were made at relatively high pressures, the system was constructed of metal instead of glass. The reaction vessel was an "Inconel X" cylinder bored and fitted with a flanged platinum liner. The brass valves used in the system were designed to have a very small internal free space and were constructed in a manner such that the volume was reproducible in either the open or closed positions.

The pressure was measured by a Wallace and Tiernan, Model No. FA 145, 0-5080 mm. dial manometer. In order to maintain constant volume conditions the manometer had to be isolated from the sorption system, since the manometer worked on an expanding capsule principle. The isolation of the manometer was accomplished by means of a sensitive, specially designed small volume differential pressure gage operating as a null instrument.

The maximum uncertainty in the composition, as measured by the pressure change, is estimated at 0.4%. Weighing of the samples before and after the oxidation-quenching procedure gave a check of the method since there was no appreciable change in oxygen content when the samples were quenched.

Samples prepared at high temperatures and high oxygen pressures were treated in an "Inconel X" autoclave. The procedure and a similar apparatus have been previously described.[3]

X-Ray diagrams were taken in a 114.6 mm. diameter camera using exposure times of about 12 hours.

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[1] Taken from a thesis by C. L. Sieglaff for the Ph.D. Degree, State University of Iowa, Iowa City, Iowa. Support for this work was given by the Atomic Energy Commission.

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