A Low Temperature Synthesis for Powder-form Intermetallics and Other Compounds

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A novel synthesis for the preparation of intermetallic and other compounds in substantially quantitative yields and conversions has been developed and demonstrated to be generally applicable with the preparation of twenty-eight compounds in several classes. The synthesis is simple and rapid and uses a temperature of 100° and atmospheric pressure. It consists of the reduction of aqueous solutions containing the elements in the stoichiometric ratio called for in the product, by addition to aqueous hydrazine or hypophosphorous acid solutions. Intermetallics, antimonides, arsenides, tellurides, ternaries and non-stoichiometric compounds are prepared. In some cases, two different compounds from the same elements are prepared by varying only the elemental proportions.

I. Introduction

In the course of investigating the phenomenon of reduction of solutions of metallic salts to the free metal, it was decided to see whether reduction of mixed solutions of certain metal ions in the desired stoichiometric ratio would yield intermetallic and other compounds, instead of simple elemental mixtures.

Dumesnil[1] prepared a black crystalline precipitate, which chemical analysis indicated was Hg_3As_2, by shaking and heating a mixture of sodium hypophosphite with the required proportions of As_2O_3 and $HgCl_2$ in dilute HCl. He did not definitely establish that the product was not a mixture. Triche and Cros[2] prepared and identified HgTe similarly, using SO_2 or H_3PO_2 as a reducing agent. Segui-Cros[3] prepared a mixture of PdTe and $PdTe_2$ by co-reduction of mixed solutions of $PdCl_2$ and sodium tellurite using HCl solutions of hydrazine sulfate or SO_2. She postulated that the relative proportions of the two tellurides formed do not vary necessarily in the same way as do the percentages of tellurium and palladium in the starting solutions but that this seems to be influenced by the HCl concentration. Segui-Cros' hypothesis was that H_2Te might be formed

$$3Te + 2H_2O \longrightarrow 2H_2Te + TeO_2$$

Later, Segui-Cros and Triche,[4] in very similar work, suggested that palladium telluride could be formed by the mechanism of direct union of the elements, a conclusion which the present work appears to support and extend to many classes of compounds. In addition, the writer has found that most of his preparations are made in alkaline solutions; that individual compounds rather than mixtures are usually obtained; that some combinations yield two separate compounds from the same elements by changing only the proportions of the elements; and that the reaction is a general one applicable to several classes of compounds.

Keeping in mind those metals whose ions could readily be reduced to the free element in aqueous solutions, Hansen,[5] Pearson[6] and ASTM[7] were consulted to see which element pairs gave compounds

(1) E. Dumesnil, *Compt. rend.*, **152**, 868 (1911).

(2) H. Triche and M. Cros, *ibid.*, **242**, 2567 (1956).

(3) M. Segui-Cros, *Bull. soc. chim. France*, 451 (1960).

(4) M. Segui-Cros and H. Triche, *Compt. rend.*, **251**, 1127 (1960).

(5) M. Hansen, "Constitution of Binary Alloys," McGraw-Hill Book Co., New York, N. Y., 1958.

(6) W. B. Pearson, "A Handbook of Lattice Spacings and Structures of Metals and Alloys," Pergamon Press, New York, N. Y., 1958.

(7) J. V. Smith, "Index to the X-Ray Powder Data File, ASTM," Philadelphia, Penna., 1959.

whose lattice parameters or X-ray patterns were known. These would be used for identification of the prepared samples.

II. Experimental and Results

Apparatus and Procedure.—Separate solutions, A and B, of the starting metals or compounds indicated in Table I were prepared. Unless otherwise stated in the table, solutions A and B were then mixed together, with rinsing, giving a clear, homogeneous solution of the two metal ions in the exact stoichiometric ratio desired. The reducing solution indicated was made up in a covered 1 liter beaker and heated unless otherwise specified in Table I. Just as the boiling temperature was reached, the metals solution was added carefully in a fine stream, with constant stirring. The reduction was usually very vigorous and much gas was evolved. The reduction beaker was covered and the contents boiled 1.5 hr., except where otherwise indicated in Table I, rinsing down occasionally any precipitate which accumulated above the liquid. This was then suction-filtered through a dried, tared, sintered-glass filtering crucible. It was washed thoroughly, rinsed with methanol and air-dried on top of the oven to constant weight.

Materials.—All raw materials were B&A Reagent quality or equivalent.

Where Hg element was used, its HNO_3 solution was heated after solution was complete, to insure oxidation to Hg(II). This would lessen hydrolytic precipitation at the stage where the metals solutions were rinsed together prior to adding to the reducing solution.

In some cases, the component elements could be dissolved together in the same beaker, but usually faster solution was obtained in separate beakers. Thus, Pt and Au require aqua regia as a solvent, whereas Hg is only slowly soluble in aqua regia because of a coating of HgCl on the globule.

Where dilute acids or bases were used, as in 1:4 NH_4OH, the volume of active component is given first and that of H_2O second.

Experiments.—X-Ray powder patterns were obtained using a General Electric XRD-3 Diffractometer, equipped with $CuK\alpha$ radiation filtered through nickel foil (λ = 1.5418 Å.). The instrument settings were: X-ray tube current, 15 mamp.; X-ray tube potential, 50 kV.; defining slit, 1°; Soller slit, wide; detector slit, 0.2°; target-to-beam angle, 4°; scanning rate, 2°/min.; recorder range, 2; time constant, B; and recorder chart speed, 0.4 in./min.

Discussion

It was considered important to add the mixed metals to the reducing agent, rather than in the reverse sequence, to avoid contamination of the desired product with possible insoluble hydrolysis products.

It will be noted that intermetallic formation under these conditions is not necessarily dependent upon use of mercury which, being liquid, can dissolve and form such compounds with many elements. The bismuthides, as well as alpha trigold platinum and tricopper palladium and many others, are as readily prepared as the mercury intermetallics. HgTe also was made and confirmed by XRD using either ammoniacal dextrose or phenyl-

TABLE I

Compound and formula	A and B in solvent	Composition of reducing solution	% Yield and X-ray diffraction analysis
		Intermetallics	
Tetramercury platinum, β Hg$_4$Pt	(A) 2.0061 g. of Hg in 12 ml. of hot 1:1 HNO$_3$ (B) 0.4877 g. of Pt in 10 ml. of 1:1 Aqua Regia	7 g.[a] of N$_2$H$_4$·2HCl 150 ml. of H$_2$O 50 ml. of NH$_4$OH	99.8%. Excellent agreement with ASTM, with one very weak extra line. No free elements were detected. The compound was well-crystallized (>0.1 μ)
Dimercury platinum ξHg$_2$Pt	(A) 1.3374 g. of Hg in 10 10 ml. of hot 1:1 HNO$_3$ (B) 0.6503 g. of Pt in 8 ml. of concd. Aqua Regia	7 g.[a] of N$_2$H$_4$·2HCl 150 ml. of H$_2$O 50 ml. of NH$_4$OH	99.9%. ξ Hg$_2$Pt was the major component, mixed with a minor amount of beta Hg$_4$Pt. The Hg$_2$Pt was in excellent agreement with ASTM. No detectable free elements or other crystalline matter were present
Platinum trigold, α PtAu$_3$	(A) 0.9850 g. of Au in 8 ml. of 1:1 Aqua Regia (B) 0.3252 g. of Pt in 4 ml. of concd. Aqua Regia	10 g.[a] of N$_2$H$_4$·2HCl 150 ml. of H$_2$O 50 ml. of NH$_4$OH	101.2%. Sample was within experimental error for α Au$_3$Pt as reported by Pearson. Free elements were not detected although detection limits could be rather high. Crystallite size ~100 Å.
Copper mercury, CuHg	(A) 0.3977 g. of CuO in 4 ml. of 1:1 HNO$_3$ (B) 1.0831 g. of HgO in 6 ml. of 1:1 HCl	25 ml. of 50% H$_3$PO$_2$ 150 ml. of H$_2$O	95.0%. The product was in excellent agreement w h ASTM for CuHg
Mercury trigold, HgAu$_3$	(A) 0.9850 g. of Au in 10 ml. of 1:1 Aqua Regia (B) 0.3347 g. of Hg in 6 ml. of hot 1:1 HNO$_3$	5 g. of N$_2$H$_4$·2HCl 150 ml. of H$_2$O 50 ml. of NH$_4$OH	99.1%. Excellent agreement with ASTM for Au$_3$Hg. No detectable free elements. Very well crystallized, the crystallite size being >0.1 μ
Palladium mercury, δ PdHg	(A) 1.0831 g. of HgO in 8 ml. of 1:1 HNO$_3$ (B) 0.5320 g. of Pd in 10 ml. of 1:1 Aqua Regia	7 g. of N$_2$H$_4$·2HCl 150 ml. of H$_2$O 50 ml. of NH$_4$OH	100.4%. Excellent agreement with ASTM for δ HgPd. No free elements were detected. The crystallite size is ~100 Å.
Tricopper palladium, Cu$_3$Pd	(A) 0.6354 g. of Cu in 6 ml. of 1:1 HNO$_3$ (B) 0.3547 g. of Pd in 6 ml. of 1:1 Aqua Regia	5 g. of N$_2$H ·2HCl 75 ml. of H$_2$O 35 ml. of NH$_4$OH	98.3%. Agreed with ASTM data for Cu$_3$Pd. No free elements were detected. The crystallite size was in the range of 100 Å.
Silver mercury with 45 atom % Hg, ϵ Ag$_{0.55}$-Hg$_{0.45}$	(A) 1.8688 g. of AgNO$_3$ in 10 ml. of H$_2$O (B) 1.8055 g. of Hg in 10 ml. of hot 1:1 HNO$_3$	5 g. of N$_2$H$_4$·2HCl 150 ml. of H$_2$O 50 ml. of NH$_4$OH	98.3%. Excellent agreement with data for ϵ AgHg (45 atom % Hg) as reported in Hansen. Well crystallized, with no free elements or other crystalline matter detectable
Disilver trimercury (moschellandsbergite) Ag$_2$Hg$_3$	(A) 1.1326 g. of AgNO$_3$ in 10 ml. of H$_2$O (B) 2.0061 g. of Hg in 10 ml. of hot 1:1 HNO$_3$	5 g. of N$_2$H$_4$·2HCl 150 ml. of H$_2$O 50 ml. of NH$_4$OH	97.4%. All lines could be accounted for as reported in Hansen for Ag$_2$Hg$_3$. No free elements were visible, and the sample was well crystallized (>0.1 μ)
		Bismuthides	
Palladium dibismuthide, β PdBi$_2$	(A) 0.5320 g. of Pd in 6 ml. of 1:1 Aqua Regia (B) 2.0900 g. of Bi in 14 ml. of 1:1 Aqua Regia	18 ml.[b] of 50% H$_3$PO$_2$ 100 ml. of H$_2$O	99.3%. β PdBi$_2$ was the only detectable crystalline component
Platinum dibismuthide, PtBi$_2$	(A) 0.6503 g. of Pt in 7 ml. concd. Aqua Regia (B) 1.3934 g. of Bi in 10 ml. of 1:1 HNO$_3$	(I) 18 ml.[c] of 50% H$_3$PO$_2$ 75 ml. of H$_2$O 10 ml. of HCl (II) 5 g. of N$_2$H$_4$·2HCl 75 ml. of H$_2$O 40 ml. of NH$_4$OH	102.2%. PtBi$_2$ was the major component. There was also a small amount of Bi and considerable unidentifiable matter
		Antimonides	
Palladium antimonide, PdSb	(A) 0.5320 g. of Pd in 6 ml. of concd. Aqua Regia (B) 1.6697 g. of KSbOC$_4$-H$_4$O$_6$·$^{1}/_{2}$H$_2$O in 30 ml. of H$_2$O	18 ml.[d] of 50% H$_3$PO$_2$ 100 ml. of H$_2$O	102.5%. Simple triangular lattice, hexagonal system, with c/a = 1.37 as reported for PdSb in Hansen

TABLE I (*Continued*)

Compound and formula	A and B in solvent	Composition of reducing solution	% Yield and X-ray diffraction analysis
Trisilver antimonide (dyscrasite), Ag_3Sb	(A) 5.0967 g. of $AgNO_3$ in 15 ml. of H_2O (B) 3.3394 g. of $KSbOC_4$-$H_4O_6\cdot\frac{1}{2}H_2O$ in 40 ml. of H_2O	30 ml.[d] of 50% H_3PO_2 150 ml. of H_2O	100.0%. The major component was Ag_3Sb. Minor components were Ag and Sb elements
Dicopper antimonide, Cu_2Sb	(A) 1.2708 g. of Cu in 8 ml. of 1:1 HNO_3 (B) 3.3394 g. of $KSbOC_4$-$H_4O_6\cdot\frac{1}{2}H_2O$ in 40 ml. of H_2O	18 ml.[d] of 50% H_3PO_2 100 ml. of H_2O	99.7%. Agreed very well with ASTM data for Cu_2Sb. No other crystalline matter was detected
Gold diantimonide, $AuSb_2$	(A) 0.9850 g. of Au in 10 ml. of 1:1 Aqua Regia (B) 1.2176 g. of Sb in 3 ml. of H_2O + 3 g. of tartaric acid + 3 ml. of HNO_3	18 ml.[d] of 50% H_3PO_2 150 ml. of H_2O	99.8%. Largely $AuSb_2$ with small amounts of free Au and Sb as the only other crystalline components

Arsenides

Compound and formula	A and B in solvent	Composition of reducing solution	% Yield and X-ray diffraction analysis
Tricopper arsenide (domeykite), β Cu_3As	(A) 1.1931 g. of CuO in 12 ml. of 1:1 HCl (B) 0.4946 g. of As_2O_3 in 15 ml. of 1:4 NH_4OH followed by 20 ml. of concd. HCl	(I) 18 ml.[e] of 50% H_3PO_2 50 ml. of H_2O 30 ml. of HCl (II) 10 g. of $N_2H_4\cdot2HCl$ 50 ml. of H_2O 100 ml. of NH_4OH	101.4%. The product was essentially β Cu_3As, with no detectable free elements
Nickel arsenide (niccolite), NiAs	(A) 0.7585 g. of NiO ($\approx$0.5871 g. of Ni) in 5 ml. of 1:1 HCl (B) 0.9891 g. of As_2O_3 in 20 ml. of 1:4 NH_4OH followed by 20 ml. of concd. HCl	(I) 18 ml.[e] of 50% H_3PO_2 50 ml. of H_2O 30 ml. of HCl (II) 15 g. of $N_2H_4\cdot2HCl$ 120 ml. of H_2O 115 ml. of NH_4OH	103.3%. The only detectable crystalline component was NiAs as extremely small crystallites

Tellurides

Compound and formula	A and B in solvent	Composition of reducing solution	% Yield and X-ray diffraction analysis
Platinum ditelluride, $PtTe_2$	(A) 0.9755 g. of Pt in 10 ml. of concd. Aqua Regia (B) 1.2761 g. of Te in 16 ml. of 1:1 Aqua Regia	15 g. of $N_2H_4\cdot2HCl$ 150 ml. of H_2O 50 ml. of NH_4OH	100.1%. $PtTe_2$ was the only detectable crystalline component and gave a very strong pattern
Disilver telluride (hessite), Ag_2Te	(A) 3.3979 g. of $AgNO_3$ in 10 ml. of H_2O, followed by 15 ml. of NH_4OH (B) 1.2761 g. of Te in 16 ml. of 1:1 Aqua Regia followed by 25 ml. of NH_4OH	15 g. of $N_2H_4\cdot2HCl$ 150 ml. of H_2O 50 ml. of NH_4OH	99.5%. The sample gave a strong pattern for Ag_2Te (hessite), with no other detectable crystalline matter
Empressite $\sim Ag_{11}Te_7$	(A) 3.3979 g. of $AgNO_3$ in 10 ml. of H_2O, followed by 15 ml. of NH_4OH (B) 1.6195 g. of Te in 16 ml. of 1:1 Aqua Regia, followed by 35 ml. of NH_4OH	5 g. of $N_2H_4\cdot2HCl$ 100 ml. of H_2O 25 ml. of NH_4OH	99.6%. Empressite, with no visible free elements or Ag_2Te
Mercuric telluride (coloradoite), HgTe	2.0724 g. of Hg in 10 ml. of hot 1:1 HNO_3 followed by 3 ml. of concd. HCl. To this is added 1.3190 g. of Te and 16 ml. of 1:1 Aqua Regia	15 g. of $N_2H_4\cdot2HCl$ 150 ml. of H_2O 50 ml. of NH_4OH	98.8%. Essentially crystalline HgTe. No other crystalline matter was detected. Line broadening indicated very small crystallite size ($\sim$0.1 micron)
Palladium monotelluride, PdTe	(A) 0.5320 g. of Pd in 8 ml. of 1:1 Aqua Regia (B) 0.6381 g. of Te in 8 ml. of 1:1 Aqua Regia	5 g. of $N_2H_4\cdot2HCl$ 100 ml. of H_2O 50 ml. of NH_4OH	100.7%. The sample was largely PdTe. It contained a small amount of $PdTe_2$, but no detectable free elements
Palladium ditelluride, $PdTe_2$	(A) 0.5320 g. of Pd in 8 ml. of 1:1 Aqua Regia (B) 1.2761 g. of Te in 16 ml. of 1:1 Aqua Regia	15 g. of $N_2H_4\cdot2HCl$ 100 ml. of H_2O 50 ml. of NH_4OH	99.8%. The sample had a strong pattern for $PdTe_2$. Four very weak lines could have represented traces of Pd and Te
Bismuth telluride (tellurbismuth), Bi_2Te_3	(A) 1.3933 g. of Bi in 10 ml. of 1:1 HNO_3 (B) 1.2761 g. of Te in 14 ml. of 1:1 Aqua Regia	30 g.[f] of Citric acid 10 g. of $N_2H_4\cdot2HCl$ 125 ml. of H_2O 60 ml. of NH_4OH	100.8%. The only visible crystalline component was Bi_2Te_3. Line broadening indicated crystallite size <0.1 μ

TABLE I (*Continued*)

Compound and formula	A and B in solvent	Composition of reducing solution	% Yield and X-ray diffraction analysis
Lead telluride (altaite), PbTe	(A) 1.0361 g. of Pb in 12 ml. of 1:4 HNO₃ (B) 0.6381 g. of Te in 14 ml. of 1:1 Aqua Regia	2 g.^{g} of tartaric acid 25 ml. of N₂H₄·H₂O 5 ml. of H₂O 15 ml. of NH₄OH	102.8%. The sample was in excellent agreement with ASTM for PbTe. It displayed a strong pattern, with no detectable free elements. The crystallite size was <0.1 μ

Ternaries

Trisilver gold ditelluride (petzite), Ag₃AuTe₂	(A) 1.6988 g. of AgNO₃ in 10 ml. of H₂O (B) 0.6567 g. of Au in 8 ml. of 1:1 Aqua Regia (C) 0.8507 g. of Te in 10 ml. of 1:1 Aqua Regia	10 g. of N₂H₄·2HCl 50 ml. of H₂O 30 ml. of NH₄OH ^{h}	100.0%. The sample was largely petzite, with minor amounts of sylvanite and traces of Ag, Au and Ag₂Te
Silver gold tetratelluride (sylvanite), AgAuTe₄	(A) 0.4247 g. of AgNO₃ in 5 ml. of H₂O (B) 0.4925 g. of Au in 6 ml. of 1:1 Aqua Regia (C) 1.2761 g. of Te in 16 ml. of 1:1 Aqua Regia	As for petzite, above,	100.0%. The sample was a mixture of sylvanite and Te, with minor amounts of petzite

Non-stoichiometric compounds

Copper telluride, Cu₂₋ₓTe where x ∼0.6 (rickardite)	(A) 1.1136 g. of CuO in 10 ml. of 1:1 HNO₃ (B) 1.2761 g. of Te in 16 ml. of 1:1 Aqua Regia	15 g. of N₂H₄·2HCl 150 ml. of H₂O 50 ml. of NH₄OH	99.1%. The major^f component was Cu₂₋ₓTe, where x ∼0.6. A minor amount of free Te was present

^{a} NH₃ from the reducing solution caused a ppt. to form in the metal solutions as they were added; this was ignored, and the ppt. rinsed in at the last, with policing. ^{b} The Bi and Pd solutions were not mixed before addition. The Bi solution was added, first to the reducing solution at room temperature, using a little of this mixture to rinse out the Bi beaker, following with H₂O rinses. Then the Pd solution was added quickly, with rinsing, and the whole heated to boiling and boiled 1.5 hr. ^{c} The Pt solution was rinsed into the Bi solution and the mixture of these added to boiling reducing solution I. After digesting at boiling for 2 minutes, reducing solution II was added carefully. ^{d} The metal and Sb solutions were not mixed before addition. The Sb solution was added first to the reducing solution which was at room temperature, then the metal solution was quickly added. This was only then heated to boiling (homogeneous precipitation) and boiled 1.5 hr. ^{e} In the case of the Cu₃As, the Cu and As₂O₃ solutions were mixed and added to boiling reducing solution I in a 1 liter beaker. Upon returning to the boiling point, this was boiled for 1 further minute before beginning the cautious addition of reducing solution II. Reaction was very vigorous because of the high acidity of one solution and high NH₄OH content of the other. In the case of the NiAs, the nickel solution was added to reducing solution I at room temperature, then the As solution was added. This was heated to boiling and boiled for 1 minute before adding reducing solution II, as above. ^{f} The Bi and Te solutions were mixed, without using rinse water, by pouring back and forth. Some of the hot liquor was used as a rinse for these beakers, followed by H₂O. ^{g} The Pb and Te solutions were not mixed prior to addition. The Pb solution was added first to the reducing solution at room temperature, followed by rinsing, then addition of the Te solution. Note that hydrazine hydrate was used with PbTe, rather than the dihydrochloride. ^{h} Holding the Au solution in abeyance, 30 ml. of NH₄OH was added to the Te solution, then the Ag solution was added. Just as the reducing solution reached boiling, the Au solution was added to the Te-Ag mixture, and this added to the reducing solution as a well-stirred light brown slurry. The metals beaker was rinsed with hot liquor first, then H₂O. ^{i} Holding the Au solution in abeyance, 30 ml. of NH₄OH was added to the Te solution, then the Ag solution was added. Just as the reducing solution reached boiling, the Au solution was added to the Te-Ag mixture, and this added to the reducing solution as a well-stirred light brown slurry. The metals beaker was rinsed with hot liquor first, then H₂O. ^{j} Other Cu:Te ratios were also tried in attempts to make other copper tellurides. These always gave only rickardite, above, along with free Cu or Te.

hydrazine as reducing agent, and HgAu₃ using acidified ammonium sulfite.

There is a wide divergence in the chemistry of the elements involved, as well as in the reducing agents and conditions used. Twelve elements in seven groups from opposite sides and the middle of the Periodic Chart react variously in hot or cold, strongly basic and strongly acidic media with several very different reducing agents, to produce twenty-eight compounds in a stoichiometry predictable by weighing and using the same general method.

It is statistically improbable that this could occur predictably under such a diversity of conditions unless the simplest common conditions for compound formation existed for all the preparations. It would seem that this condition would be that the compounds are formed by the mechanism of direct union of the elements themselves, while intimately mixed in a very finely divided and active state. It is considered remarkable for this to occur in quantitative yields and conversions for so many types of compounds at temperatures of 100° and atmospheric pressure.