Crystal growth, structure and phase studies on gold halides
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Summary

Only very corrosive substances attack gold, the most noble metal. In this study the reactivity and the phase diagrams of gold with the halogens chlorine, bromine and iodine have been investigated. Owing to the noble behaviour of gold, its halides are sensitive to heat; on heating they decompose into the elements. In closed systems the halogen pressures increase to values larger than one atmosphere at rather low temperatures (about 250°C).

The stability of the compounds as a function of temperature and halogen pressure is very important for choosing the proper conditions for preparation and crystal growth of gold halides. It was possible to prepare large crystals of AuCl at the high-temperature side of a temperature gradient of 250° - 280°C (chlorine pressure of one atm) or 304° - 327°C (chlorine pressure of about 2 atm); the transport occurs via AuCl\(_6\)(g).

I-AuBr and P-AuBr have been grown at relatively low bromine pressures (about 1 atm and less). Only for I-AuBr a promoter, aluminium, was used; in this case the compound AuAlBr\(_6\)(g) probably is responsible for the chemical vapour transport. The crystals of I-AuBr grow at the high-temperature side of a gradient of 185° - 210°C (bromine pressure of about 1 atm). Crystals of P-AuBr were grown without the use of a promoter at about 120°C.

The crystal structures of AuCl, I-AuBr and P-AuBr have been determined and compared with that of AuI. I-AuBr is isostructural with AuCl: space group \(I4_1/amd\), \(Z=8\) and \(a=6.940\ \text{Å}, c=9.252\ \text{Å}\) for I-AuBr; \(a=6.734\ \text{Å}, c=8.674\ \text{Å}\) for AuCl. P-AuBr is isostructural with AuI: space group \(P4_2/ncm\), \(Z=4\) and \(a=4.396\ \text{Å}, c=12.146\ \text{Å}\) for P-AuBr, compared with \(a=4.359\ \text{Å}, c=13.711\ \text{Å}\) for AuI.

The structures consist of zig-zag chains, in which the gold atoms are linearly coordinated by the halogen atoms. The angle \(\text{Au-X-Au}\) changes from 92°, to 92.3°, to 77.1° and to 72.6° in the sequence AuCl, I-AuBr, P-AuBr and AuI. In the same sequence the Au-Au distances in the chain change from 3.37 Å, to 3.47 Å, to 3.04 Å and to 3.08 Å. The packing of the zig-zag chains is different in the two structures. The bromine (iodine) and gold atoms in P-AuBr (AuI) form square planar nets for the bromine and gold layers perpendicular to the c-axis. The Au-Au distances inside the chains are equal to the shortest distances of gold atoms of two mutually parallel chains. The sequence of layers of Au and Br in P-AuBr is Au/Br/Br/Au/Br/Br/Au. Therefore P-AuBr and AuI can also be considered as layered compounds.

It has been found that only AuBr has structural transitions. Four modifications exist; the sequence of their stabilities was studied by differential thermal analysis, differential scanning calorimetry and X-ray analysis.
The most noble diagrams of the noble gases have been determined. Its halides form the most stable, increase to temperature.

Bromine (g) has been found as a promoter, which facilitates transport. The bromine pressure at the high temperature is 280°C.

Promoter at P-AuBr have been 3.47 Å, and a=6.940 Å, respectively. P-AuBr is stable up to about 80°C, I-AuBr is stable between 80°C and 197°C, I-AuBr between 197°C and 298°C and bcc-AuBr (body-centered cubic) between 298°C and 330°C. Above 330°C a liquid phase exists. The heats of transition of P-AuBr → I-AuBr and I-AuBr → bcc-AuBr amount to 360 ± 40 and 915 ± 70 cal/mole, respectively. The heat of transition bcc-AuBr → liquid is of the same order as that of I-AuBr → bcc-AuBr. For bcc-AuBr (a=4.880 Å, Z=2) a disordered structure is proposed, in which gold is statistically distributed over the positions 8(c) of space group Im3m. α-AuBr, probably has a structure related to that of I-AuBr.

In the gold-chlorine system three solid state compounds exist: Au2Cl6, Au4Cl8 and AuCl. Phase studies show that on heating Au4Cl8(s) probably disproportionates at 111°C into Au2Cl6(s) and AuCl(s). At 260°C and a chlorine pressure of 1.4 atm a eutectic is found at composition AuCl2. Au2Cl6 melts at 304°C; AuCl(s) decomposes peritectically at 342°C and a chlorine pressure of about 3 atm into Au(s) and a liquid with composition AuCl1.45. The heat of fusion of Au2Cl6 amounts to 29 ± 5 kcal/mole.

In the gold-bromine system the existence of Au2Br6 and AuBr has been established; moreover, two fcc phases (face-centered cubic) of unknown composition were found. A eutectic was observed at 262°C and a composition between AuBr and AuBr. Au2Br6 melts at 292°C; the heat of fusion is about 20 kcal/mole.

In the gold-iodine system AuI and two fcc phases with compositions between AuI and Au exist. AuI decomposes at 203°C peritectically into a fcc phase and an iodine melt in which a small amount of AuI is dissolved. The other fcc phase is formed at about 114°C under exclusion of light.

Finally, the phase diagram of the pseudo-binary system AgI-AuI has been determined. A new compound AgAuI2 was found, with two structural transitions at 55°C and 127°C. The high-temperature form, α-AgAuI2, has a bcc-structure (a=5.091 Å, Z=1) in which both silver and gold are disordered, but in different sites; this phase forms a broad range of solid solutions. A eutectic is present at 86°C and composition Ag0.30Au0.70; above this temperature the solid solution with a disordered structure is formed.