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The Chemistry and Free Energy of Formation of Silver Nitride

Silver nitride, Ag_3N , an extremely sensitive explosive compound, forms from ammoniacal solutions of silver oxide. This is a potential hazard to laboratory workers using Tollens reagent and silvering solutions. An excess of aqueous ammonia, 4 to 1 mol, is required to dissolve Ag_2O to form the ammine complex. Upon loss of ammonia by evaporation, solutions of the ammine complex produce black solids consisting of Ag_3N , Ag_2O , or mixtures. If the solution is relatively concentrated, the solids will contain much Ag_3N . If the solution contains less than about 5% ammonia, the solids will be predominately Ag_2O and nonexplosive. Aging of Ag_2O solids in an amount of strong ammonia too small for complete solution causes conversion to Ag_3N . On the basis of the chemical behavior we estimated that standard free energy of formation of Ag_3N to be $314.4 \pm 2.5 \text{ kJ mol}^{-1}$.

For more than 200 years, it has been known that the addition of aqueous ammonia to silver oxide can produce explosive solids formerly termed "fulminating silver" (Gmelin, 1971; Mellor, 1922). This explosive behavior is due to formation of silver nitride, Ag_3N . Ammoniacal solutions of silver salts can produce the same explosive dark solids if a strong fixed base, such as sodium hydroxide, is added to the solution (L.A.C., 1827; Raschig, 1886). However, this potential hazard has not prevented the general use of silvering solutions, Tollen's reagent, and other ammoniacal silver solutions, and, despite the usual cautionary statements, there have been many unexpected detonations in ammoniacal silver solutions which have

accumulated dark colored solids.

Earlier papers (MacWilliams and Hazard, 1977; Shanley et al., 1968) have reported the results of our studies of silver nitride formation. This report discusses the results of further studies and provides guidance for avoiding hazard. Other explosive silver species such as silver fulminate, $\text{Ag}(\text{ONC})$, and silver azide, AgN_3 , (Gmelin, 1971; Mellor, 1922; Luchs, 1966) do not form from ammoniacal preparations.

Our study provides the information required to define the phase relationships in Figure 1. Various chemical species can be postulated in this system, including silver ammine ions, $\text{Ag}(\text{NH}_3)^+$ and $\text{Ag}(\text{NH}_3)_2^+$; and hydroxyl ion,

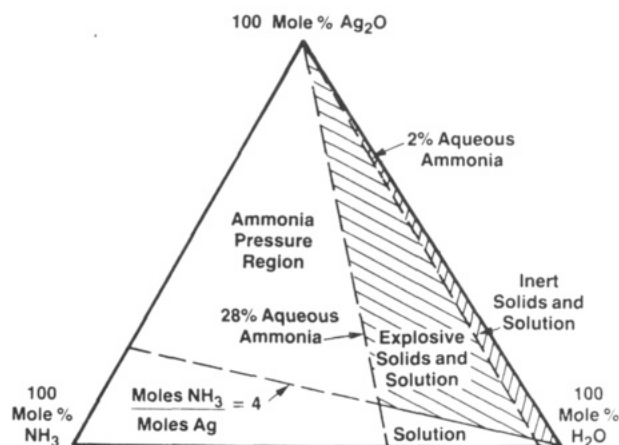


Figure 1. Phase relationships in the system Ag_2O - NH_3 - H_2O .

OH^- ; as well as silver amide, AgNH_2 ; imide, Ag_2NH ; and nitride, Ag_3N . All these species are derived formally from silver oxide, ammonia, and water. Most experimental and practical work with silver ammine ion has involved aqueous solutions under ordinary conditions. This limits experiments in aqueous ammonia to 28 wt % NH_3 content or less. In Figure 1, we designate the region of higher concentrations as the "ammonia pressure region". We have made no studies in this region. We have confirmed that all compositions of aqueous ammonia and pure silver oxide containing at least 4 mol of ammonia/(mol of silver) form homogeneous solutions (Olmer, 1924a; Whitney and Melcher, 1903). (Note, commercial silver oxide contains enough silver metal to leave a very small, ammonia-insoluble residue.) This observation is in accord with the common observation that an excess of ammonia (about 2-fold in excess of the amount in the silver diammine complex) is required to bring silver oxide into solution. These homogeneous solutions are not subject to explosive or other violent reaction. Conversion to explosive solids is associated with insufficient ammonia for complete solution; the hazard is most acute in the case of a deficiency of strong ammonia solution.

All compositions containing less than about 4 mol of ammonia/(mol of silver) will contain a solid phase. Depending on the conditions, this solid may be inert silver oxide or a mixture containing silver nitride. We have found that solid silver oxide in contact with aqueous ammonia stronger than about 2.5 wt % NH_3 converts spontaneously to the nitride. At room temperature, 20 °C, conversion is extensive or complete in a few minutes with 28% ammonia but may take a day or more using 2.5% ammonia. Conversion is accelerated at 40 °C and very greatly retarded at 5 °C. In our work, explosive solids have not been observed even after prolonged exposure of silver oxide to ammonia weaker than about 2.5%. Olmer (1924b), when studying the extremely slow nonexplosive decomposition of sealed solutions of ammoniacal silver oxide which were not allowed to evaporate, reported that deposition of silver and release of nitrogen did not occur at concentrations of ammonia below 3.0% at temperatures around 15 °C.

When we allowed clear solutions of silver oxide in ammonia to lose ammonia, for example, by exposure in open containers, dark-colored solids appeared, usually in the region of the air-solution interface. A crust begins to form as soon as the mole ratio of ammonia to silver falls below 4, at which point the formation of silver oxide would be expected. If ammonia depletion is rapid, as with spilled solutions, the dark precipitate which appears is inert silver oxide. Crusts forming at the solution-air interface in open

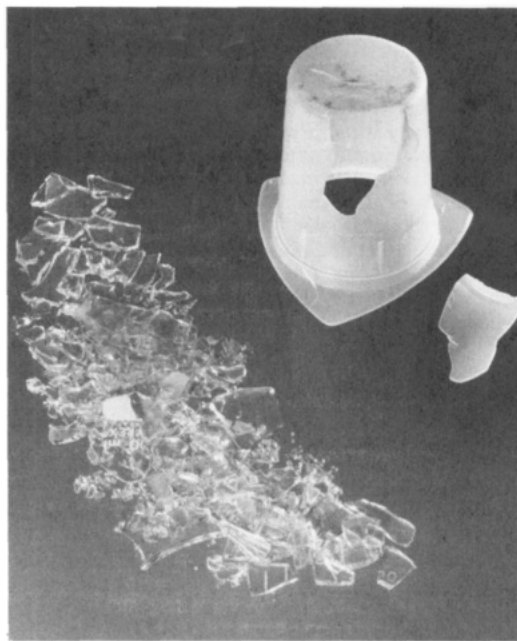


Figure 2. Damage to each of two 100-mL beakers, glass and polypropylene, resulting from spontaneous detonation of 0.5 g of Ag_2O in an atmosphere of ammonia.

vessels may also be predominately silver oxide at first. We find that such crusts and precipitates become explosive in contact with aqueous ammonia stronger than 2.5%, as in the case with silver oxide added to a deficiency of ammonia solution.

Silver oxide exposed to the vapor over strong ammonia converts to explosive silver nitride. For example, silver oxide in the vapor space over 28% aqueous ammonia in a closed container usually explodes within 24 h without overt external intervention, indicating rapid and extensive conversion to Ag_3N . See Figure 2. We observed that silver oxide does not react with dry gaseous ammonia, confirmed that a stream of moist air containing ammonia attacks a silver mirror (Carey-Lea, 1892), and ascertained that a stream of moist nitrogen containing ammonia does not.

Silver nitride forms from solution at concentrations of Ag^+ , H^+ , and NH_4^+ that do not permit easy determination by electrometric measurement; therefore, examination of precipitates by X-ray diffraction was our principal analytical procedure and provided all the analytical information we were able to obtain concerning the solid products formed in this study (Juzza and Hahn, 1940). Most freshly prepared inert solids exhibited only the lines of silver oxide. Some nonexplosive solids and all explosive solids exhibited the lines of both silver oxide and silver nitride. Many of the samples which proved to be explosive did not survive the minimum handling required to move them, container and all, to the X-ray stage. Some mixtures only cracked when disturbed. Two or three slightly disruptive explosions sometimes might be elicited by repeated mechanical disturbance of the same sample. More vigorously explosive samples propagated throughout their mass leaving no visible residue. Even among supersensitive materials, silver nitride is a striking example of a compound "teetering on the edge of existence". Under the circumstances, we did not succeed in developing data on the proportion of silver nitride required for explosive behavior in these mixtures.

The thermochemistry of the silver-ammonia system is fully documented in standard handbook data, except for silver amide, imide, and nitride. We have found no thermochemical data on the hypothetical amide and imide.

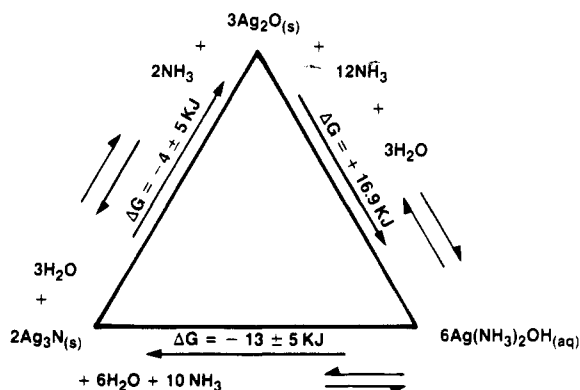


Figure 3. Thermochemical relationships in the system Ag_2O - NH_3 - H_2O .

Earlier work (Juzza and Hahn, 1940; Hahn and Gilbert, 1949) provides values for the standard heat of formation of silver nitride, +199 kJ mol and +255 kJ, respectively. Anderson and Parlee (1970) offer a value of +230 kJ mol for the standard free energy of formation of the nitride, but this value is based only on analogy with other nitrides and depends upon a long extrapolation. Our study provides no basis for estimating the heat of formation of silver nitride. We make a new estimate of the standard free energy of formation of silver nitride on the basis of chemical behavior. Our value of $+314.4 \pm 2.5 \text{ kJ mol}^{-1}$ was calculated as described below.

Figure 3 depicts free energy relationships among silver oxide, silver nitride, and silver ammine hydroxide. Thermochemical data are from NBS Technical Note 270-4 (Wagman et al. 1969), except for the free energy of formation of Ag_3N . This value was estimated from the following expression:



From eq 1, an expression for the desired free energy term can be written:

$$\begin{aligned} G_f(\text{Ag}_3\text{N(s)}) &= \frac{3}{2}G_f(\text{Ag}_2\text{O(s)}) + G_f(\text{NH}_3(\text{aq})) - \\ &\quad \frac{3}{2}G_f(\text{H}_2\text{O(l)}) - \frac{1}{2}G_r \\ &= -312.4 - \frac{1}{2}G_r \text{ kJ mol}^{-1} \end{aligned} \quad (2)$$

where G_f = free energy of formation and G_r = free energy of reaction.

We have found that silver oxide and nitride are interconvertible by manipulation of the ammonia concentration. The relationship is then of an equilibrium nature with a small free energy change. Accordingly, the term for free energy of reaction in eq 2 will contribute little to the free energy of formation.

G_r can be estimated from the observed effects of manipulating the ammonia concentration. We have observed that silver oxide readily converts to the nitride in 1.52 M ammonia solution, as judged by explosibility. No such conversion is observed in 0.76 M ammonia. Although explicit observation of the reverse transition is difficult, we note that silver nitride is desensitized, presumably by conversion to the oxide, in very dilute ammonia.

Using 1.52 M as a near minimum concentration for nitride formation, we relate G_r , the free energy of reaction, to the equilibrium constant for reaction 1.

$$G_r = -RT \ln K \quad (3)$$

$$K = 1/[\text{NH}_3]^2 \quad (4)$$

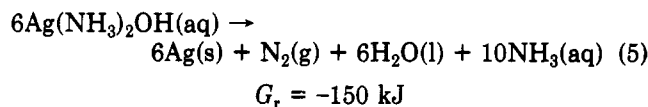
Our X-ray diffraction data indicate that silver oxide becomes explosive when a fraction is converted to silver

nitride. We make the assumption that the required fraction lies between the limits of 10 and 90%. At least limits, G_r in eq 2 assumes values of +1.6 and -9.5 kJ mol⁻¹, respectively. We have adopted the value of $-4 \pm 5 \text{ kJ mol}^{-1}$ as the best available estimate for the free energy of reaction 1. The free energy of formation of silver nitride can now be estimated as $+314.4 \pm 2.5 \text{ kJ mol}^{-1}$.

The Anderson and Parlee estimate of +230 kJ mol⁻¹ is much too low to account for the observed chemical behavior. For example, it indicates that silver oxide would be converted to the nitride in 10^{-13} M ammonia.

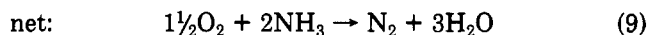
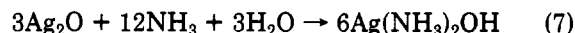
The data in Figure 3 show that formation of either silver oxide or silver nitride from silver ammine hydroxide is about equally favorable from the energetic point of view. Nevertheless, silver oxide is the first product formed upon loss of ammonia from silver ammine solutions. As noted, conversion to nitride soon follows unless the ammonia concentration is below about 1.5 M.

Silver ammine solutions are neither thermochemically nor kinetically stable in storage, even when protected against ammonia loss. Slow evolution of gas and deposition of solids occur in a sealed system. Olmer (1924a,b) demonstrated that the solid is silver metal and the gas is nitrogen. The overall reaction can be written as follows:



Although the decomposition is highly spontaneous, it cannot attain a high rate because of the large thermal sink provided by the water content of the solution. Decomposition tends to cease almost entirely after a major fraction of the dissolved silver has been deposited. From the thermochemistry it is clear that there can be no truly stable intermediate stage in this decomposition, but Olmer's data strongly suggest some metastable intermediate species with a remarkably low decomposition rate. As indicated in Figure 3, silver nitride is extremely unstable with respect to its elements, as is evidenced by its explosive behavior.

We show in the summation below, the complete silver, ammonia, oxygen reaction sequence as silver-catalyzed oxidation of ammonia with accumulation of metastable intermediate products.



Registry No. Ag_3N , 20737-02-4; Ag_2O , 20667-12-3; NH_3 , 7664-41-7.

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ADDITIONS AND CORRECTIONS

Group-Contribution Flory Equation of State for Vapor-Liquid Equilibria in Mixtures with Polymers
 [Volume 29, Number 5, Page 875]. Fei Chen, Aage Fredenslund,* and Peter Rasmussen

Page 878. There is a misprint in (28) and the next two lines below it. They should read

$$\ln \gamma_i^{\text{att}} = \frac{1}{2} z q_i \left\{ \frac{1}{RT} [\epsilon_{ii}(\bar{v}) - \epsilon_{ii}(\bar{v}_i)] + 1 - \ln \sum_j \theta_j \times \right. \\ \left. \exp[-(\Delta \epsilon_{ij} - T \Delta S_{ij}^{\text{hb}})/RT] - \right. \\ \left. \left[\frac{\sum_j \theta_j \exp(-\Delta \epsilon_{ij} - T \Delta S_{ij}^{\text{hb}})/RT}{\sum_k \theta_k \exp(-\Delta \epsilon_{kj} - T \Delta S_{kj}^{\text{hb}})/RT} \right] \right\} \quad (28)$$

where φ_i is a segment volume fraction and θ_i is a surface area fraction:

$$\varphi_i = \frac{x_i V_i^*}{\sum_j x_j V_j^*} \quad \theta_i = \frac{x_i q_i}{\sum_j x_j q_j}$$