# Thermodynamics of gold-sulphide clusters in ore vapors: exploring phase diagrams of $Au_mS_nH_x$ nanoclusters using atomistic simulations

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We have studied the thermodynamic stability of gold clusters ranging from $Au_3$ to $Au_{17}$ and their sulfur/hydrogen-containing forms at high temperatures using particle swarm, density functional theory (DFT) and MP2 atomistic simulations. The focus of this work is to construct reliable phase diagrams of $Au_mS_nH_x$ nanoclusters, in order to predict their size, composition, shape and distribution in volcanic and hydrothermal ore vapors. We will initially focus on the $Au_3S_nH_x$ and $Au_{17}S_nH_x$ systems, the phase relationships in $Au_3S_nH_x$ and $Au_{17}S_nH_x$ and examine how temperature and partial pressures of $H_2$, $H_2S$, and $S_n$ influence the stability of $Au_mS_nH_x$. The figure below shows the phase diagram obtained for $Au_3$ at 298 K under a broad range of partial pressures of $H_2$ and sulfur gas, together with $H_2S$ isobars at $10^{-5}$, $10^{-2}$ and 10 atm. As seen, in the region of low $pH_2$ and $pS_2$ pure $Au_3$ remains stable, however, when the pressure of $H_2$ and $S_2$ increases, adsorption of $H_2$ and $S_2$ onto $Au_3$ edges takes place, producing $Au_3H_6$, $Au_3S_6$ and $Au_3S_4H_2$ clusters. MP2 calculations have also been undertaken to obtain *p*-T phase diagrams of $Au_3S_n$ and $Au_3S_nH_x$, and these show that $Au_3$ and $Au_3S$ exist only in low $pS_2$ vapor and at high temperatures (>800 K), whereas S-rich phases $Au_3S_2$ and $Au_3S_4$ become more stable at T≈450-700 K and $pS_2$≈$10^{-7}$-$10^{-2}$ atm. This approach has been applied to larger gold clusters, in particular, we have examined interactions between $H_2$, $H_2S$ and $S_n$ species at edge, corner and face sites of $Au_{17}$, and will present phase diagrams for the $Au_{17}S_nH_x$ system at *p*-T conditions characteristic of volcanic gases.