

On the Mechanisms of Formation of M^0 -nanoparticles via the Reduction of M^nL_m Complexes

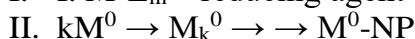
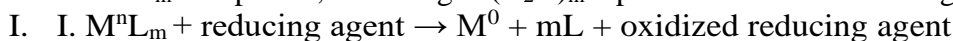
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It is commonly suggested that the mechanism of formation of M^0 -nanoparticles, M^0 -NPs, via the reduction of M^nL_m complexes, including $M(H_2O)_m^{n+}$ proceeds via the following scheme:



However, the redox potentials of most reducing agents used do not enable the reduction of M^nL_m to M^0_{atoms} . This is due to the following: The redox potential of the couple $M(H_2O)_m^{n+}/M^0_{(s)}$ can be calculated from the following equation:

$$E^0(M(H_2O)_m^{n+}/M^0_{(s)}) = (\Delta G^0_{\text{evaporation}} + \Delta G^0_{\text{ionization}} + \Delta G^0_{\text{hydration/solvation}})/nF$$

Clearly if one wants to calculate the redox potential of an atom no evaporation is involved and therefore $\Delta G^0_{\text{evaporation}}$ is not contributing. Therefore, the redox potentials of atoms are:

$$E^0(M(H_2O)_m^{n+}/M^0_{(\text{atom})}) = E^0(M(H_2O)_m^{n+}/M^0_{(s)}) - (\Delta G^0_{\text{evaporation}}/nF)$$

As a result most $E^0(M(H_2O)_m^{n+}/M^0_{(\text{atom})})$ are very negative and the mechanism of formation of M^0 -NPs does not involve the formation of M^0_{atoms} .

The mechanisms of formation of Ag^0 -NPs via the reduction of $Ag(H_2O)_2^+$ by H_2 and by BH_4^- will be discussed in detail.