Catalytic Silver Reduction in Sulphide Containing Silver Chloride Melts

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In silver chloride melts, containing small mole fractions of silver sulphide ($\sim 10^{-2} - 10^{-3}$), silver ion reduction takes place when solid silver is present. The rate of reaction is constant with time and proportional to the area of the metal. In the temperature range $780\ \mathrm{K} < T < 890$ an apparent energy of activation of $1.3 \cdot 10^2\ \mathrm{kJ\ mol^{-1}}$ is obtained.

Introduction

In a number of papers [1, 2, 3] we reported on the solubility of silver in its molted halides as well as on the properties of the solution. Recently we found that the thermodynamic functions of solvation strongly depend on the presence of small fractions of divalent cations. This investigation is still in progress and will be reported later. In the present note we will report on an unexpected reaction which occurs when Ag_2S is used as a dopant.

Experimental

In each run, about 30 g of silver chloride were melted in fused quartz vessels, using an electric furnace. The temperature was measured with a Ni/NiCr thermocouple which, protected by a quartz tubing, was directly inserted into the melt. In order to oxidize any photolytically formed silver, a stream of chlorine was bubbled through the melt for at least 1 h. Finally a constant stream of argon replaced the chlorine and effected permanent stirring of the melt.

In order to obtain desired fractions of sulphide, weighed portions of Ag_2S p.a. from Merck, Darmstadt, were added to the melt. In most of the experiments, the initial mole fraction of silver sulphide was $x_{Ag_2S} = 5.0 \cdot 10^{-3}$. Silver sheets (99.99%) were washed with diluted aqueous solutions of potassium cyanide, rinsed with distilled water, dried and carefully weighed. Then they were dropped into the melt. Here they stayed for times between 20 and 24 hours. Finally the melt was removed, the metal sheets washed with diluted aqueous ammonia, rinsed with distilled water and, after drying, weighed again.

Results

Unexpectedly, during all experiments, the mass of silver increased. Figure 1 shows that at a given temperature the mass increases linearly with time. In Fig. 2 we plotted the increase in mass after 24 h

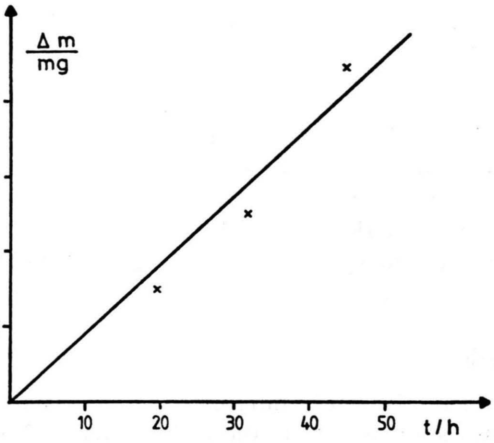

Fig. 1. Mass increase Δm in silver vs. time. $T = 830\ \mathrm{K}$, $x_{Ag_2S} = 5 \cdot 10^{-3}$, $A_{Ag} \cong 1.5\ \mathrm{cm^2}$.

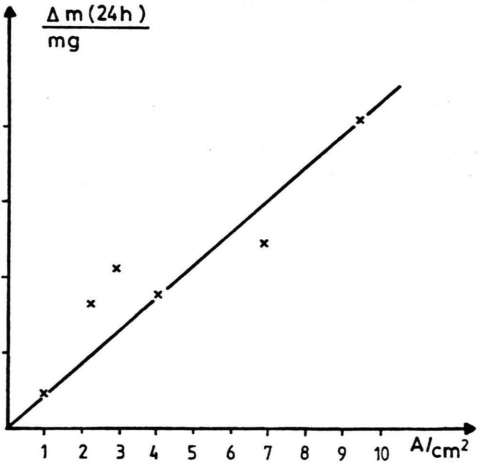

Fig. 2. Mass increase Δm in silver at 24 h vs. area A of silver sheet. $T = 818\ \mathrm{K}$, $x_{Ag_2S} = 5 \cdot 10^{-3}$.

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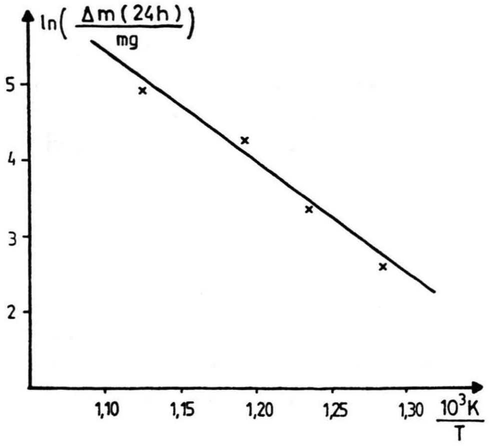

Fig. 3. Logarithm of mass increase Δm in silver at 24 h vs. reciprocal temperature. $x_{\mathrm{Ag_2S}} = 1 \cdot 10^{-2}$.

as a function of the metal surface, exposed to the melt. Finally, in Fig. 3, the mass increase per 24 h is plotted logarithmically vs. the reciprocal temperature. These experiments were done with an initial mole fraction $x_{\mathrm{Ag_2S}} = 1.0 \cdot 10^{-2}$ and lead to an apparent energy of activation of about $1.3 \cdot 10^2$ kJ/mol.

Discussion

All the results can be interpreted by the assumption that silver ions from the melt are reduced by sulphur ions. In the absence of metallic silver, a stable liquid phase is formed from silver chloride and silver sulphide. Apparently a catalyst is needed to allow a redox reaction to proceed. From the photographic development, silver is known to be an excellent catalyst for silver ion reduction. We, therefore, conclude that the mass increase of our silver sheets is due to a heterogeneously catalyzed silver ion reduction by sulphur ions. Figure 2 shows that the rate of reaction is proportional to the metal surface. As can be seen from Fig. 1 it follows a zero order kinetics. A tentative reaction equation could be

$$2\,\mathrm{Ag^+} + 2\,\mathrm{S^{--}} \rightarrow 2\,\mathrm{Ag} + \mathrm{S_2^{--}}.$$

If this stoichiometry is correct, the consumption of the $\mathrm{S^{--}}$ initially present would be between 10% and 80% in our experiments. The observed zero kinetics then would lead to the conclusion that a surface reaction is rate determining. The decrease in silver ion concentration would be smaller if higher polymer anions would be formed according to

$$(2n-2)\,\mathrm{Ag^+} + n\,\mathrm{S^{--}} \rightarrow (2n-2)\,\mathrm{Ag} + \mathrm{S_n^{--}}.$$

Sulphide ions with $n > 2$ are nonlinear species and should have IR-active vibration modes. To check this we quenched a small portion of the reaction mixture rapidly between rotating copper cylinders down to room temperature. No IR signals could be detected with the thin sheets obtained by this procedure.

Acknowledgements

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