# Electrochemical reduction of silver thiosulphate complexes
# Part I: Thermodynamic aspects of solution composition

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Deposition of silver from electrolyte solutions is of major importance in the industrial applications of photographic development and electroplating. Prior to the kinetic study of the reduction of silver thiosulphate complexes, the concentrations, activities and activity coefficients of all components formed in $AgNO_3-Na_2S_2O_3-NaNO_3$ solutions are calculated, starting from the measurement of the equilibrium potential. In view of the high ionic strength of the solutions (greater than $0.1 \, mol \, kg^{-1}$), the ion interaction model is applied for the estimation of the activity coefficients, inevitably imposing the use of an iterative calculation routine. The activity coefficients are shown to comply with known thermodynamic laws, supporting the appropriateness of the model, together with the approximations.

## List of symbols

| | |
|---|---|
| $a$ | activity (M) |
| $c$ | concentration (M) |
| $d$ | density ($kg \, dm^{-3}$) |
| $h$ | hydration number |
| $m$ | molality ($mol \, kg^{-1}$) |
| $x$ | molfraction |
| $y$ | activity coefficient (molarity scale) |
| $z$ | charge of an ion |
| $E_0$ | equilibrium potential vs NHE (V) |
| $I$ | ionic strength (M or $mol \, kg^{-1}$) |
| $M$ | molecular weight ($kg \, dm^{-3}$) |
| $T$ | temperature (K) |

*Greek symbols*

| | |
|---|---|
| $\beta$ | stability constant |
| $\gamma$ | activity coefficient (molality scale) |
| $\nu$ | stoichiometric coefficient |
| $\phi$ | osmotic coefficient |

*Indices*

| | |
|---|---|
| f | free (uncomplexed) |
| s | solvent |
| t | total |
| − (or a) | anion |
| + (or c) | cation |
| ± | mean quantity |

## 1. Introduction

In photography thiosulphate is used as complexing agent for silver [1, 2]. Little is known, however, about the kinetics of the reduction of silver thiosulphate complexes, which is the basic reaction in image formation. Furthermore, the use of thiosulphate as a complexing agent is not restricted to photographic application. In silver plating poisonous cyanic silver salt solutions are usually used [3] but in view of increasing environmental considerations cyanide-free baths for silver plating have now to be developed.

In both applications, silver concentrations of the order of $10^{-1}$ M are (preferably) used. The kinetics of the reduction of silver thiosulphate complexes will be determined in solutions in the practical concentration range. Besides silver, they contain a high amount of thiosulphate as complexing agent. This results in solutions with high ionic strength where the difference between the concentration and the activity of the species cannot be ignored. Therefore, prior to a kinetic study, the concentrations, activities and activity coefficients (hereinafter called the concentration parameters) of all present components are determined.

## 2. Theory

### 2.1. *Working equations for the calculation of the concentration parameters*

In $AgNO_3-Na_2S_2O_3-NaNO_3$ solutions complexes are formed between $S_2O_3^{2-}$ ions and $Ag^+$ ions on one hand and $Na^+$ ions on the other [4-6].

For thiosulphate activities in the range $5 \times 10^{-4}-2$ M the composition of the solution is described by Equations 1-14 [4], using the following notation:

L for the complexing agent $S_2O_3^{2-}$
$AgL_x$ for the complexes $Ag(S_2O_3)_x^{(2x-1)-}$, $x = 2, 3$
NaL for the complex $NaS_2O_3^-$

$$(c_{Ag^+})_t = c_{AgL_2} + c_{AgL_3} \tag{1}$$

$$(c_L)_t = (c_L)_f + c_{NaL} + 2c_{AgL_2} + 3c_{AgL_3} \tag{2}$$

$$(c_{Na^+})_t = (c_{Na^+})_f + c_{NaL} \tag{3}$$

$$a_{AgL_2} = \beta_{12}(a_{Ag^+})_f(a_L)_f^2 \tag{4}$$

$$a_{AgL_3} = \beta_{13}(a_{Ag^+})_f(a_L)_f^3 \tag{5}$$

$$a_{NaL} = \beta(a_{Na^+})_f(a_L)_f \tag{6}$$

$$(a_L)_f = (y_L)_f(c_L)_f \tag{7}$$

$$(a_{Na^+})_f = (y_{Na^+})_f(c_{Na^+})_f \tag{8}$$

$$a_{AgL_2} = y_{AgL_2}c_{AgL_2} \tag{9}$$

$$a_{AgL_3} = y_{AgL_3}c_{AgL_3} \tag{10}$$

$$a_{NaL} = y_{NaL}c_{NaL} \tag{11}$$

$$\log\beta_{12} = 13.47 \quad [5] \tag{12}$$

$$\log\beta_{13} = 13.77 \quad [5] \tag{13}$$

$$\log\beta = 0.59 \quad [6] \tag{14}$$

Equations 1–3 are the mass balances respectively for silver, thiosulphate and sodium, expressed in terms of concentrations. In the silver mass balance the concentration of uncomplexed silver ions $(c_{Ag^+})_f$ is neglected, which assumes that a large excess of $S_2O_3^{2-}$ ions is present. Owing to the stability constant of $Ag(S_2O_3)^-$, $\log\beta_{11} = 8.82$ at 293 K [5], its contribution is negligible in Equations 1 and 2 in the selected concentration range of $S_2O_3^{2-}$. Equations 4–6 describe the equilibrium between the complexes and the corresponding free ions, relating their activities. Equations 7–11 give the relationship between concentration and activity of the components, introducing the activity coefficient. Activities and activity coefficients of individual ionic species are set equal to the mean activities and activity coefficients of the electrolytes to which they belong.

For thiosulphate activities between $5 \times 10^{-4}$ and $5 \times 10^{-2}$ M, the amount of $Ag(S_2O_3)_3^{5-}$ in the solution is negligible [4]. In Equations 1 and 2 the last term is omitted, and Equations 9 and 10 are not relevant. To know the composition of the solution for a given total silver, thiosulphate and sodium concentration 13 parameters remain to be determined. With a set of nine equations, four must be measured or calculated independently. $(a_{Ag^+})_f$ is deduced from the measurement of the equilibrium potential of the solution against a silver electrode [7]:

$$E_{0_{Ag/Ag^+}}(\text{vs NHE}) = 0.799 + 0.059\log(a_{Ag^+})_f \tag{15}$$

$(y_{S_2O_3^{2-}})_f$, $(y_{Na^+})_f$ and $y_{NaS_2O_3^-}$ are calculated using the ion interaction model, using tabulated values of specific parameters [8] (see below). The ion interaction model is chosen because of the high ionic strength of the solutions $(I > 0.1 \text{ mol kg}^{-1})$.

The calculation of the remaining parameters is straightforward.

At higher thiosulphate activities, both $Ag(S_2O_3)_2^{3-}$ and $Ag(S_2O_3)_3^{5-}$ are present [4], and the complete set of 11 equations and 16 unknowns must be considered. Since the activity coefficients of the complexes cannot be calculated with the ion interaction model, an additional equation relating them to one another is required for the determination of the remaining parameters.

## 2.2. Working equations for the calculation of the activity coefficients based on the ion interaction model

The ion interaction model is based on statistical mechanics and yields thermodynamic functions from the knowledge of the interionic potential of mean force. The basic equation in this approach is the osmotic equation:

$$\phi - 1 = -\frac{1}{6ckT}\sum_i\sum_j c_ic_j \int_c^\infty \left(\frac{\partial u_{ij}}{\partial r}\right)g_{ij}4\pi r^3 \, dr \tag{16}$$

where $\phi$ is the osmotic coefficient, $u_{ij}$ the potential of mean force, $g_{ij}$ the radial distribution function, $c_{ij}$ the concentration of the $i$th solute species and $c$ the total concentration of all solute species. Given the osmotic coefficient, the activity coefficient may be derived by thermodynamic methods. The derivation of the equations is found in [8].

In a mixture of electrolytes the mean activity coefficient $\gamma_\pm$ of electrolyte $M_{\nu_+}X_{\nu_-}$, relative to the molality scale of concentrations, complies with Equation 17 [8, 9]:

$$\ln\gamma_\pm = |z_+z_-|A + \frac{2\nu_+}{\nu}\sum_a m_a\left[B_{Ma} + \left(\sum mz\right)C_{Ma}\right]$$

$$+ \frac{2\nu_-}{\nu}\sum_c m_c\left[B_{cX} + \left(\sum mz\right)C_{cX}\right]$$

$$+ \sum_c\sum_a m_cm_a\left(|z_+z_-|B'_{ca} + \frac{2\nu_+\nu_-}{\nu}C_{ca}\right) \tag{17}$$

with

$$A = -A'\left[\frac{I^{1/2}}{1+1.2I^{1/2}} + \frac{2}{1.2}\ln(1+1.2I^{1/2})\right] \tag{18}$$

for $A' = 0.391$ at $T = 298$ K [8]; and

$$B_{ca} = 2\beta_{ca}^0 + \frac{\beta_{ca}^1}{2I}[1 - (1+2I^{1/2} - 2I)\exp(-2I^{1/2})] \tag{19}$$

for $\beta_{ca}^0$ and $\beta_{ca}^1$ = specific parameters, tabulated in [8]; $C_{ca}$ = specific parameter, independent of $I$,

tabulated in [8]; and

$$B'_{ca} = \frac{dB_{ca}}{dI} = \frac{\beta^1_{ca}}{2I^2}[-1 + (1 + 2I^{1/2} + 2I)$$

$$\times \exp(-2I^{1/2})] \tag{20}$$

$$\sum mz = \sum_c m_c z_c = \sum_a m_a |z_a| \tag{21}$$

$$I = \frac{1}{2}\sum_i z_i^2 m_i \tag{22}$$

The terms describing the interactions between ions of the same sign are not taken into account, since they are expected to be very small [8].

Equation 17 allows calculation of the activity coefficients on condition of known composition of the solution, which makes the use of an iterative calculation routine necessary.

### 2.3. Calculation routine

For the calculations, the solution is considered as a mixture of three electrolytes:

(i) $NaNO_3$ with concentration $= (c_{NO_3^-})_t = (c_{Ag^+})_t + c_{NaNO_3}$,

(ii) $Na_2S_2O_3$ with concentration $= (c_{S_2O_3^{2-}})_f$,

(iii) $Na(NaS_2O_3)$ with concentration to be calculated iteratively.

This means that for the calculation of the activity coefficients of components other than silver components, the interactions with the latter are omitted.

Concentrations and activity coefficients are converted from the molarity to the molality scale and

vice versa with Equations 23-25 [8]:

$$c_i = \frac{m_i d}{1 + \sum_i m_i M_i} \tag{23}$$

$$y_i = \frac{m_i d_0}{c_i}\gamma_i \tag{24}$$

$$d = \frac{\sum_i Q_i m_i d_i}{\sum_i Q_i m_i} \tag{25}$$

with $d =$ density of the mixture; $d_0 =$ density of the pure solvent, i.e. water, and equal to $0.997 \, kg \, l^{-1}$ at 298 K; $d_i =$ density of a pure solution of electrolyte $i$ at equal total ionic strength $I$ (molality scale!) as the mixture (values in [4]); $Q_i = 1$ for 1,1 electrolytes; $Q_i = 3$ for 2,1 electrolytes; and $Q_i = 4$ for 2,2 electrolytes.

#### 2.3.1. Calculation routine for low thiosulphate activities. In the case of $(a_{S_2O_3^{2-}})_f$ between $5 \times 10^{-4}$ and $5 \times 10^{-2}$ M all silver is present as $Ag(S_2O_3)_2^{3-}$ [4] and its concentration is equal to the total silver concentration.

The iterative calculation routine is represented in Fig. 1. The input parameters are double boxed. Initially, the $NaS_2O_3^-$ molality is set to zero. Together with the activity coefficients, the concentrations of $(S_2O_3^{2-})_f$, $(Na^+)_f$, $(Na^+)_f$ and $NaS_2O_3^-$ are calculated. Iteration is continued up to constant ionic strength. With the value of $(a_{Ag^+})_f$ from the measurement of the equilibrium potential, the calculation
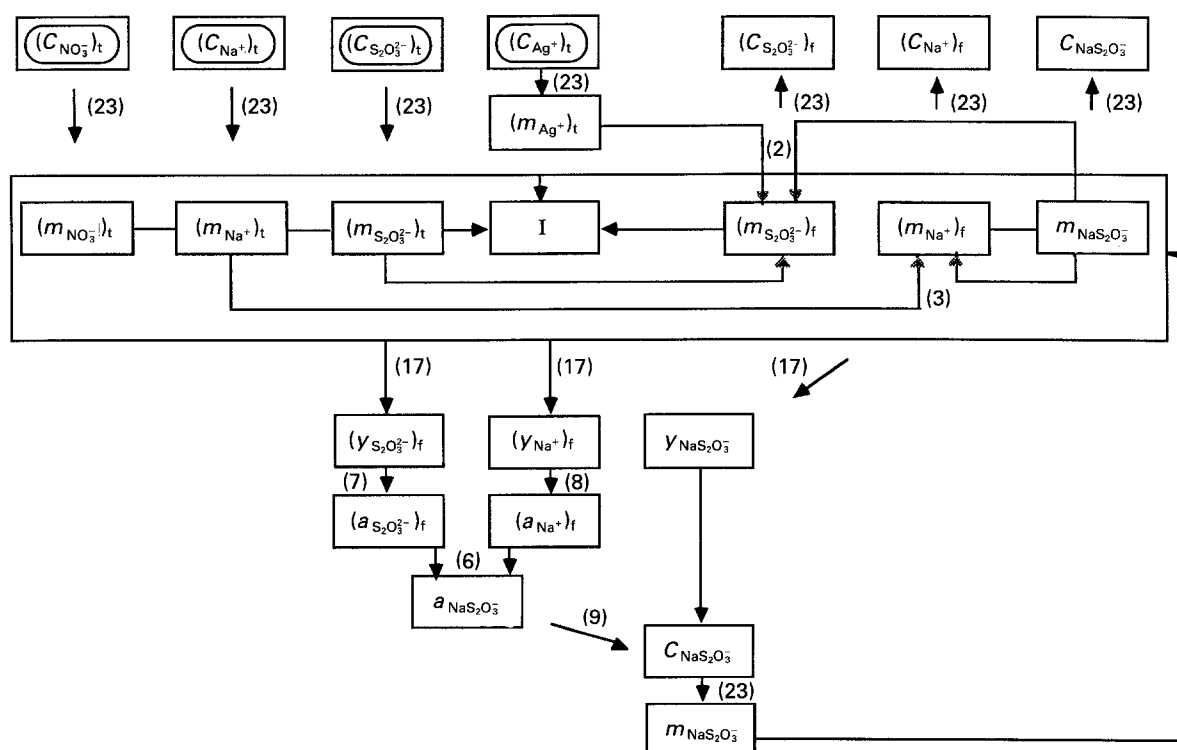


Fig. 1. Calculation routine for the concentration parameters of solutions with low thiosulphate activities. (The parenthetical numbers refer to the equations used for calculation).

of the activity, and the activity coefficient of $Ag(S_2O_3)_2^{3-}$ is straightforward.

### 2.3.2. Calculation routine for high thiosulphate activities.

Both $Ag(S_2O_3)_2^{3-}$ and $Ag(S_2O_3)_3^{5-}$ are present [4], and their concentrations are unknown. As a first approximation, the concentration of $Ag(S_2O_3)_3^{5-}$ is set to zero. The same calculation scheme as for the solutions with low thiosulphate content is applied for the activity and activity coefficient of $(S_2O_3^{2-})_f$, $(Na^+)_f$ and $NaS_2O_3^-$. With the input of the value of $(a_{Ag^+})_f$ from the equilibrium potential, the activities of the complexes follow from Equations 4 and 5.

It is assumed that the activity coefficients are mainly determined by the electrostatic interactions between the complex ions and their counter ions. All terms but the first are neglected in Equation 17. $A(I)$ being the same function of the ionic strength for both complexes, as shown by Equation 18, it is found that the activity coefficients are related by Equation 26:

$$y_{Ag(S_2O_3)_3^{5-}} = [y_{Ag(S_2O_3)_2^{3-}}]^{5/3} \qquad (26)$$

The conversion factors from the molality to the molarity scale are ignored. With this additional equation, the activity coefficients and concentrations of the complexes and the other remaining parameters are sorted from the set of equations. Iteration is continued up to constant ionic strength.

## 3. Experimental details

The solutions were prepared with twice demineralized water and the following chemicals: $AgNO_3$ (p.a. Agfa Gevaert), $Na_2S_2O_3$ and $NaNO_3$ (p.a. Merck). They were deaerated by nitrogen bubbling.

Measurement of the equilibrium potential was performed with a millivoltmeter (Minisis 6000, Tacussel, accuracy $\pm 0.1$ mV) on a silver electrode (99.99% purity, Johnson and Matthey) against a calomel reference electrode with saturated KCl solution (Tacussel), under thermostatic conditions $(25.0 \pm 0.1^\circ$ C). The liquid junction potential is neglected because the cell under investigation contains an excess of inert electrolyte of nearly uniform concentration and reactant species in much smaller concentrations. In this case, the cell potential is given by the Nernst equation (15) [10].

## 4. Results and discussion

The equilibrium potentials were measured in various $AgNO_3-Na_2S_2O_3-NaNO_3$ solutions as a function of the total silver, total thiosulphate and sodium nitrate concentration and the results are listed in Table 1. The concentration parameters were calculated according to the routines explained in Section 2, and listed in Table 1.

Adding $NaNO_3$ to the solution has a double effect: (a) it acts as a supporting electrolyte making the activity coefficient of the complex independent of its concentration: compare in Table 1 series 1.0 to 4.0; 1.1 to 4.1; 1.2 to 4.2 and 1.3 to 4.3 with series 1 to 4; and (b) it has an important side effect on the complex formation between $Ag^+$ and $S_2O_3^{2-}$ through the formation of $NaS_2O_3^-$.

For solution series 1 to 4 a linear increase in the logarithm of the activity coefficient of $NaS_2O_3^-$ with the $NaNO_3$ molality is found, illustrated in Fig. 2 for solution series 1. The linear dependence indicates that the variation is predominantly due to hydration effects [11, 12]. Furthermore, from the slope of the straight line, the hydration number of $NaS_2O_3^-$ can be calculated [11, 12]:

$$h_{Na(NaS_2O_3)} = [\text{slope}/0.018] - h_{NaNO_3} + 2 \qquad (29)$$

with $h_{NaNO_3} = 1$ [4, 8, 11]. The value of the slope is 0.1 for the four series of solutions, resulting in a hydration number of 6.5 for $Na(NaS_2O_3)$, which is in good agreement with the value of 7 for the hydration number of $Na_2S_2O_3$ [4, 8, 11].

The osmotic equation being the basis of the ion interaction model, it is not surprising that a relationship between the activity coefficient and the hydration number is found. Indeed, for an aqueous solution of an electrolyte with stoichiometric coefficient $\nu$, the osmotic coefficient is related to the water activity $a_s$ by Equation 30 [8]:

$$\ln a_s = -\frac{\nu m\phi}{55.51} \qquad (30)$$

and $a_s$ in its turn is, by the molfraction $x_s$, related to the hydration number:

$$x_s = \frac{1 - 0.018}{1 + 0.018m(\nu - h)} \qquad (31)$$

The variation of the activity coefficients of the complexes as a function of the total thiosulphate
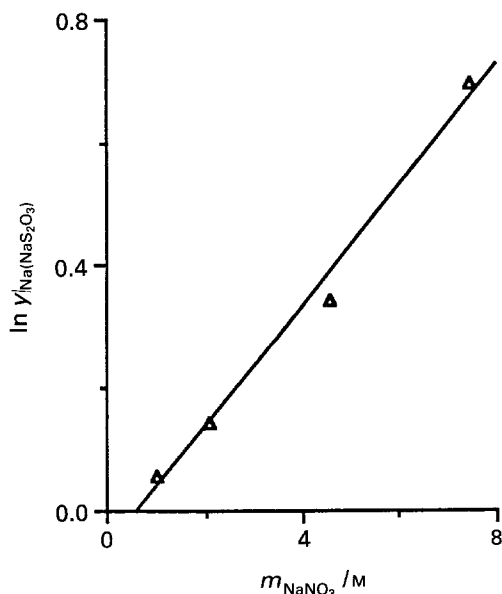


Fig. 2. Variation of the activity coefficient $y$ of $NaS_2O_3^-$ as a function of the molality of $NaNO_3$. Composition of the solution: $(c_{Ag^+})_t = 1.2 \times 10^{-3}$ M and $(c_{S_2O_3^{2-}})_t = 2.7 \times 10^{-2}$ M.

*Table 1. Concentration parameters at $T = 298$ K for silver thiosulphate solutions with (a) low and (b) high thiosulphate concentrations. $L^{2-} = S_2O_3^{2-}$*

(a) Concentration parameters at $T = 298$ K for silver thiosulphate solutions with low thiosulphate concentrations. $L^{2-} = S_2O_3^{2-}$

| No. | $(c_{Ag^+})_t$ /M | $(c_{L^{2-}})_t$ /M | $(c_{NaNO_3})_t$ /M | $(E_0)_{Ag/Ag^+}$ /V vs NHE | $(a_{Ag^+})_f$ /M | $(c_{L^{2-}})_f$ /M | $(y_{L^{2-}})_f$ | $(a_{L^{2-}})_f$ /M | $c_{NaL^-}$ /M | $y_{NaL^-}$ | $c_{AgL_2^{3-}}$ /M | $y_{AgL_2^{2-}}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $1.2 \times 10^{-3}$ | $2.7 \times 10^{-2}$ | — | 0.031 | $1.0 \times 10^{-13}$ | $2.3 \times 10^{-2}$ | 0.65 | $1.5 \times 10^{-2}$ | $1.6 \times 10^{-3}$ | 0.87 | $1.2 \times 10^{-3}$ | 0.51 |
| 2 | $4.9 \times 10^{-3}$ | $6.0 \times 10^{-2}$ | — | 0.032 | $1.0 \times 10^{-13}$ | $4.3 \times 10^{-2}$ | 0.58 | $2.5 \times 10^{-2}$ | $7.2 \times 10^{-3}$ | 0.85 | $4.9 \times 10^{-3}$ | 0.39 |
| 3 | $1.1 \times 10^{-2}$ | $9.7 \times 10^{-2}$ | — | 0.037 | $1.2 \times 10^{-13}$ | $6.2 \times 10^{-2}$ | 0.53 | $3.3 \times 10^{-2}$ | $1.3 \times 10^{-2}$ | 0.85 | $1.1 \times 10^{-2}$ | 0.35 |
| 4 | $2.0 \times 10^{-2}$ | 0.14 | — | 0.039 | $1.3 \times 10^{-13}$ | $8.2 \times 10^{-2}$ | 0.49 | $4.0 \times 10^{-2}$ | $1.9 \times 10^{-2}$ | 0.91 | $2.0 \times 10^{-2}$ | 0.31 |
| 1.0 | $1.2 \times 10^{-3}$ | $2.7 \times 10^{-2}$ | 0.92 | 0.051 | $2.1 \times 10^{-13}$ | $1.3 \times 10^{-2}$ | 0.43 | $5.6 \times 10^{-3}$ | $1.2 \times 10^{-2}$ | 1.14 | $1.2 \times 10^{-3}$ | 0.17 |
| 1.1 | $1.2 \times 10^{-3}$ | $2.7 \times 10^{-2}$ | 1.92 | 0.058 | $2.8 \times 10^{-13}$ | $1.1 \times 10^{-2}$ | 0.37 | $4.1 \times 10^{-3}$ | $1.4 \times 10^{-2}$ | 1.30 | $1.2 \times 10^{-3}$ | 0.12 |
| 1.2 | $1.2 \times 10^{-3}$ | $2.7 \times 10^{-2}$ | 3.92 | 0.067 | $3.9 \times 10^{-13}$ | $1.0 \times 10^{-2}$ | 0.35 | $3.5 \times 10^{-3}$ | $1.5 \times 10^{-2}$ | 1.64 | $1.2 \times 10^{-3}$ | 0.11 |
| 1.3 | $1.2 \times 10^{-3}$ | $2.7 \times 10^{-2}$ | 5.92 | 0.064 | $3.5 \times 10^{-13}$ | $0.9 \times 10^{-2}$ | 0.39 | $3.5 \times 10^{-3}$ | $1.6 \times 10^{-2}$ | 2.53 | $1.2 \times 10^{-3}$ | 0.11 |
| 2.0 | $4.9 \times 10^{-3}$ | $6.0 \times 10^{-2}$ | 0.82 | 0.049 | $1.9 \times 10^{-13}$ | $2.7 \times 10^{-2}$ | 0.44 | $1.2 \times 10^{-2}$ | $2.3 \times 10^{-2}$ | 1.07 | $4.9 \times 10^{-3}$ | 0.16 |
| 2.1 | $4.9 \times 10^{-3}$ | $6.0 \times 10^{-2}$ | 1.82 | 0.057 | $2.7 \times 10^{-13}$ | $2.3 \times 10^{-2}$ | 0.38 | $8.7 \times 10^{-3}$ | $2.7 \times 10^{-2}$ | 1.24 | $4.9 \times 10^{-3}$ | 0.12 |
| 2.2 | $4.9 \times 10^{-3}$ | $6.0 \times 10^{-2}$ | 3.82 | 0.062 | $3.2 \times 10^{-13}$ | $2.0 \times 10^{-2}$ | 0.35 | $7.0 \times 10^{-3}$ | $3.0 \times 10^{-2}$ | 1.64 | $4.9 \times 10^{-3}$ | 0.10 |
| 2.3 | $4.9 \times 10^{-3}$ | $6.0 \times 10^{-2}$ | 5.82 | 0.064 | $3.5 \times 10^{-13}$ | $1.9 \times 10^{-2}$ | 0.39 | $7.4 \times 10^{-3}$ | $3.1 \times 10^{-2}$ | 2.48 | $4.9 \times 10^{-3}$ | 0.11 |
| 3.0 | $1.1 \times 10^{-2}$ | $9.7 \times 10^{-2}$ | 0.70 | 0.049 | $1.9 \times 10^{-13}$ | $4.2 \times 10^{-2}$ | 0.43 | $1.8 \times 10^{-2}$ | $3.3 \times 10^{-2}$ | 1.07 | $1.1 \times 10^{-2}$ | 0.17 |
| 3.1 | $1.1 \times 10^{-2}$ | $9.7 \times 10^{-2}$ | 1.70 | 0.056 | $2.6 \times 10^{-13}$ | $3.4 \times 10^{-2}$ | 0.37 | $1.3 \times 10^{-2}$ | $4.1 \times 10^{-2}$ | 1.20 | $1.1 \times 10^{-2}$ | 0.11 |
| 3.2 | $1.1 \times 10^{-2}$ | $9.7 \times 10^{-2}$ | 3.70 | 0.066 | $3.8 \times 10^{-13}$ | $2.9 \times 10^{-2}$ | 0.35 | $1.0 \times 10^{-2}$ | $4.6 \times 10^{-2}$ | 1.59 | $1.1 \times 10^{-2}$ | 0.10 |
| 3.3 | $1.1 \times 10^{-2}$ | $9.7 \times 10^{-2}$ | 5.70 | 0.064 | $3.5 \times 10^{-13}$ | $2.8 \times 10^{-2}$ | 0.39 | $1.1 \times 10^{-2}$ | $4.7 \times 10^{-2}$ | 2.45 | $1.1 \times 10^{-2}$ | 0.11 |
| 4.0 | $2.0 \times 10^{-2}$ | 0.14 | 0.56 | 0.047 | $1.8 \times 10^{-13}$ | $5.8 \times 10^{-2}$ | 0.43 | $2.5 \times 10^{-2}$ | $4.2 \times 10^{-2}$ | 1.00 | $2.0 \times 10^{-2}$ | 0.16 |
| 4.1 | $2.0 \times 10^{-2}$ | 0.14 | 1.56 | 0.059 | $2.9 \times 10^{-13}$ | $4.6 \times 10^{-2}$ | 0.37 | $1.7 \times 10^{-2}$ | $5.4 \times 10^{-2}$ | 1.16 | $2.0 \times 10^{-2}$ | 0.12 |
| 4.2 | $2.0 \times 10^{-2}$ | 0.14 | 3.56 | 0.065 | $3.6 \times 10^{-13}$ | $3.9 \times 10^{-2}$ | 0.35 | $1.4 \times 10^{-2}$ | $6.1 \times 10^{-2}$ | 1.57 | $2.0 \times 10^{-2}$ | 0.10 |
| 4.3 | $2.0 \times 10^{-2}$ | 0.14 | 5.56 | 0.062 | $3.2 \times 10^{-13}$ | $3.7 \times 10^{-2}$ | 0.39 | $1.4 \times 10^{-2}$ | $6.3 \times 10^{-3}$ | 2.36 | $2.0 \times 10^{-2}$ | 0.10 |

(b) Concentration parameters at $T = 298$ K for silver thiosulphate solutions with high thiosulphate concentration. $L^{2-} = S_2O_3^{2-}$

| No. | $(c_{Ag^+})_t$ /M | $(c_{L^{2-}})_t$ /M | $(E_0)_{Ag/Ag^+}$ /V vs NHE | $(a_{Ag^+})_f$ /M | $(c_{L^{2-}})_f$ /M | $y_{L^{2-}}$ | $(a_{L^{2-}})_f$ /M | $c_{NaL^-}$ /M | $y_{NaL^-}$ | $c_{AgL_2^{3-}}$ /M | $y_{AgL_2^{3-}}$ | $c_{AgL_3^{5-}}$ /M | $y_{AgL_3^{5-}}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 5 | 0.04 | 0.58 | -0.015 | $1.6 \times 10^{-14}$ | 0.29 | 0.39 | 0.11 | 0.20 | 0.98 | 0.024 | 0.24 | 0.014 | 0.09 |
| 6 | 0.10 | 0.72 | 0.010 | $4.2 \times 10^{-14}$ | 0.30 | 0.32 | 0.09 | 0.18 | 0.89 | 0.063 | 0.18 | 0.038 | 0.06 |
| 7 | 0.07 | 0.92 | -0.026 | $1.0 \times 10^{-14}$ | 0.40 | 0.35 | 0.14 | 0.37 | 1.04 | 0.034 | 0.18 | 0.030 | 0.06 |
| 8 | 0.11 | 1.02 | -0.022 | $1.2 \times 10^{-14}$ | 0.41 | 0.31 | 0.13 | 0.34 | 0.96 | 0.052 | 0.11 | 0.057 | 0.03 |
| 9 | 0.14 | 1.08 | -0.008 | $2.1 \times 10^{-14}$ | 0.42 | 0.30 | 0.12 | 0.33 | 0.95 | 0.073 | 0.13 | 0.070 | 0.03 |
| 10 | 0.11 | 1.25 | -0.031 | $0.9 \times 10^{-14}$ | 0.46 | 0.32 | 0.14 | 0.51 | 1.04 | 0.048 | 0.11 | 0.061 | 0.03 |
| 11 | 0.20 | 1.43 | -0.016 | $1.5 \times 10^{-14}$ | 0.46 | 0.27 | 0.13 | 0.47 | 0.97 | 0.090 | 0.08 | 0.123 | 0.01 |
| 12 | $1.3 \times 10^{-3}$ | 0.25 | -0.072 | $1.7 \times 10^{-15}$ | 0.17 | 0.50 | 0.08 | 0.08 | 0.98 | $9.9 \times 10^{-4}$ | 0.36 | $3.3 \times 10^{-4}$ | 0.18 |
| 13 | $5.5 \times 10^{-3}$ | 0.51 | -0.069 | $1.9 \times 10^{-15}$ | 0.28 | 0.46 | 0.13 | 0.22 | 1.08 | $3.4 \times 10^{-3}$ | 0.27 | $2.0 \times 10^{-3}$ | 0.11 |
| 14 | $1.3 \times 10^{-2}$ | 0.78 | -0.069 | $1.9 \times 10^{-15}$ | 0.36 | 0.43 | 0.15 | 0.38 | 1.15 | $6.8 \times 10^{-3}$ | 0.20 | $6.1 \times 10^{-3}$ | 0.07 |
| 15 | $2.5 \times 10^{-2}$ | 1.06 | -0.076 | $1.5 \times 10^{-15}$ | 0.41 | 0.41 | 0.17 | 0.59 | 1.21 | $1.1 \times 10^{-2}$ | 0.12 | $1.5 \times 10^{-2}$ | 0.03 |

concentration is very complex, due to the fact that $S_2O_3^{2-}$ acts, not only as complexing agent, but also as supporting electrolyte.

## 5. Conclusion

An iterative calculation routine has been set up for the determination of the concentration parameters of $AgNO_3-Na_2S_2O_3-NaNO_3$ solutions. Introducing a number of simplifications, activity coefficients have been determined and found to comply with known thermodynamic laws.

In a subsequent paper, these data will be applied for the determination of the mechanism and the kinetic parameters of the reduction of silver thiosulphate complexes.

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