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Mercurimetric Titration of Chloride in Presence of Sodium Nitroprusside as Indicator

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INTRODUCTION

A titration procedure aims to determine the concentration of a solute in a solution tested, in presence of an indicator used for registration of the end point (e) of the titration. For example, Cl\textsuperscript{-} ions are determined in Mohr's method by titration with AgNO\textsubscript{3} standard solution, in presence of K\textsubscript{2}CrO\textsubscript{4} in the titrand \cite{1-3}; the end point is indicated here by the Ag\textsubscript{2}CrO\textsubscript{4} precipitate. In the Liebig method of cyanide determination, KCN solution is titrated with AgNO\textsubscript{3} solution; the end point is indicated here by AgCN precipitate \cite{4,5}, as auto-indicating species. In the Denigès' modification of the Liebig titration, the solution of KCN + KI + NH\textsubscript{3} is titrated with AgNO\textsubscript{3} solution; the end point is indicated here by AgI precipitate \cite{4,6}.

The present paper gives an evaluation of systematic error in mercurimetric titration of chloride in presence of sodium nitroprusside Na\textsubscript{2}Fe(CN)\textsubscript{5}NO\textcdot2H\textsubscript{2}O as indicator \cite{7-10}. The nitroprusside ions, Fe(CN)\textsubscript{5}NO\textsuperscript{-}2, form a white precipitate of HgFe(CN)\textsubscript{5}NO \cite{11,12}. The titration is performed at pH = 1.5 – 2 \cite{13}.

Here and in further parts of this paper, the charges \(z\) of the corresponding species \(X^z\) \((i=1,2,...)\) are omitted, when written in terms of molar concentrations, i.e., the notation \([X]\) is applied here, for simplicity.

Some preliminary remarks

The system considered is an example of electrolytic non-redox system. The electrolytic non-redox (and redox too) systems can be considered according to GATES principles \cite{14}, if all

(i) qualitative (specification of components forming a system, and species in the system thus formed),
(ii) qualitative (concentration of components), and
(iii) physicochemical (thermodynamic equilibrium constants) is available. Any non-redox system is formulated with use of charge and concentration balances, and complete set of expressions for equilibrium constants. Charge balance involves charged species of a system.

The set of concentration balances involves relations between concentrations of components and species, formulated – separately – for particular elements or cores \(\neq H, O\). For a redox system, the set of elemental balances is completed by Generalized Electron Balance (GEB), formulated on the basis of the \(2f(0) - f(H)\) balance \cite{15}, within GATES/GEB. Some examples of redox systems were presented also in this Journal \cite{16}.
Static and dynamic electrolytic systems are distinguished. A dynamic system is realized in titration, where V mL of titrant T is added into V₀ mL of titrand D, and V₀+V mL of D+T mixture is obtained at defined point of the titration [17]. Concentrations of solutes (a) in D are denoted by C₀ (for analyte), C₁, C₂, C₃, etc., and (b) in T by C (for reagent), C₁, C₂, etc. In the reference system considered here, Hg(NO₃)₂ (C) is the reagent, NaCl (C₀) is the analyte, Na₄Fe(CN)₆NO⋅2H₂O (Cᵥ) is the indicator. Moreover, HNO₃ (C₁) is the component in T that prevents precipitation of HgO when Hg(NO₃)₂, solution is prepared as T.

Within GATES there are considered, among others, the systems in which a solid phase is formed. Examples of this kind are provided e.g. in [6]. There may also be a change in the solid phase composition, see e.g. [18].

The results of calculations preformed according to GATES principles with use of iterative computer programs [14], can be presented graphically on the related 2D diagrams, where the fraction titrated

\[ \phi = \frac{C V}{C₀ V₀} \]  

is marked on the abscissa, as an independent variable, where C and C₀ are expressed in mol/L, V and V₀ in mL. This is the simple way to normalize the respective graphs, i.e., the independence of their shape from the V₀ value.

The ϕ plays also the key role in formulation of Generalized Equivalence Mass (GEM) concept [19], compatible with GATES principles. Within GEM formulation, the end (e) and equivalence (eq) points are related to the titration curve. At the end point, the visual titration is terminated, when indicated by a desired/ pre-assumed color change of the D+T mixture, or by the first appearance of a solid phase, e.g. AgI in the Liebig-Denigès method [6], or HgFe(CN)₆NO in the titration considered here. Turbidity in D+T provides the appropriate indicator (indicating component), e.g. KI in the Liebig-Denigès method, or Na₄Fe(CN)₆NO⋅2H₂O (Cᵥ) in the system considered here we have ϕₑ=1/2. The difference ϕₑ - ϕₐ, when compared with the uncertainty of ϕ value, is acceptable from the one-drop error viewpoint when |ϕₑ - ϕₐ| < 0.003 [19].

**Calculation procedure**

The calculation specified below differs significantly from the one usually practiced in GATES, where a complete set of independent balances and equilibrium constants is applied. In particular, the GATES procedure can be applied to the model D+T system with NaCl (C₀) + Na₄Fe(CN)₆NO⋅2H₂O (Cᵥ) as titrand D (V₀), and Hg(NO₃)₂ (C₁) + HNO₃ (C₂) as titrant T (V). However, the mercurimetric titration is applied also for the chloride samples from more complex media, where composition of a sample matrix is undefined [20]. Some kinds of the samples were also tested in clinical laboratories, e.g. [21]. Other indicators were also applied for this purpose, see [22].

In the simplified calculation procedure, charge balance and other concentration balances (except for Cl and Hg, and nitroprusside) are omitted. The concentration balances are confined to monophase system, including the end (e) point, i.e. the first point of the titration, where the solubility product \( K_{sp} = [\text{Hg}][\text{Fe(CN)}]_{6} \), pKₐsp = 8.6) of HgFe(CN)₆NO is valid.
From concentration balances for Cl and Hg:

$$[Cl] + \sum_{i=1}^{4}[HgCl_i] = \frac{CV}{V_e + F}$$

(9)

$$[Hg] + \sum_{i=1}^{3}[Hg(OH)_i] + \sum_{i=1}^{3}[HgCl_i] = \frac{CV}{V_e + F}$$

(10)

we have, by turns,

$$F = \frac{\sum_{i=1}^{3}[HgCl_i]}{[Hg] + \sum_{i=1}^{3}[Hg(OH)_i] + \sum_{i=1}^{3}[HgCl_i]} = \frac{CV}{V_e + F}$$

(11)

i.e., the fraction titrated (Eq. 1) has the form

$$\phi = \frac{CV}{C_i V_e} - \frac{C_{Cl}}{C} + \frac{[Cl]}{[Cl]}$$

(12)

where

$$F = \frac{\sum_{i=1}^{4}K_{Cl}^i[Cl]}{1 + \sum_{i=1}^{4}K_{Cl}^i[Cl]}$$

(13)

and

$$[Hg(OH)_i] = K_{Cl}^i[Hg][OH]_i = i=1,2, \log K_{Cl}^i = 8.3, 13.2, 14.0, 15.0$$

$$[HgCl] = K_{Cl}^i[Hg][Cl] = i=1,2, \log K_{Cl}^i = 9.3, 14.0, 14.7, 15.0$$

A detailed discussion on the balances (9), (10) leads to conclusion that at the vicinity of the end (e) point, 

$$pCl \approx 4.7, [Hg(OH)_2] \ll [HgOH] \ll [Hg] \ll [HgCl] < [HgCl_2] \gg [HgCl_3] \gg [HgCl_4]$$

and then

$$CV_e = \frac{K_{Cl}^i}{C_i V_e} (V_e + V_e)^2 \cdot \left[K_{Cl}^i + K_{Cl}^{i+} [Cl] [Cl]ight]$$

(15)

If $[Cl] \ll C_i F$, at $V = V_e$ from Equations (12) and (14) we have

$$CV_e = V_e (C_i - [Cl]) \cdot K_{Cl}^i + 2K_{Cl}^{i+} [Cl]$$

(16)

From Equations (15) and (16) we have the equation

$$2A [Cl]^2 + B [Cl] - C_i V_e = 0$$

where

$$A = K_{Cl}^i \frac{K_{Cl}^i}{C_i V_e} (V_e + V_e)^2, B = K_{Cl}^i \frac{K_{Cl}^i}{C_i V_e} (V_e + V_e)^2 + V_e$$

Then we have

$$[Cl] = \frac{\sqrt{\Delta + B} - B}{4A}$$

(17)

where

$$\Delta = B^2 + 8A C_i V_e$$

Setting (17) into (15) gives the equation

$$\frac{2K_{Cl}^i}{C_i C} \left(V_e + V_e\right)^2 \cdot \left(K_{Cl}^i + 2K_{Cl}^{i+} \left(V_e + V_e\right)^2 + \left(V_e + V_e\right)^2\right) - \frac{\sqrt{\Delta + B}}{4A}$$

The $V_e$ value can be found from Equation (18) according to ze-roing procedure, realized with use of a computer program for particular $V_e, C, C_i, K_{Cl}^i, K_{Cl}^{i+}, K_{Cl}^{i+}$, and $K_{Cl}^{i+}$ values, considered as parameters of this equation. Then the relative systematic error involved with mass of chloride determination will be calculated in accordance with the principles of Generalized Equivalence Mass (GEM) formulation [19,24], and illustrated in Figure 2.
Final Comments

The paper provides an example of application of physicochemical (thermodynamic) knowledge involved with gaining the information involved with expected systematic error of analyses made at different concentrations of NaCl (\(C_0\)), \(\text{Na}_2\text{Fe(CN)}_5\text{NO} \cdot 2\text{H}_2\text{O}\) (\(C_{oi}\)) and \(\text{Hg(NO}_3\)\)) (C). Generally, at given C value, the error of chloride analysis grows with a decrease of \(C_0\) and \(C_{oi}\) values, as indicated in Figure 2.

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