Redox titration challenge

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We would like to invite you to participate in the Analytical Challenge, a series of puzzles to entertain and challenge our readers. This special feature of "Analytical and Bioanalytical Chemistry" has established itself as a truly unique quiz series, with a new scientific puzzle published every three months. Readers can access the complete collection of published problems with their solutions on the ABC homepage at http://www.springer.com/abc. *Test your knowledge and tease your wits in diverse areas of analytical and bioanalytical chemistry by viewing this collection.*

In the present challenge, redox titration is the topic. And please note that there is a prize to be won (a Springer book of your choice up to a value of €100). Please read on…

Meet the challenge

Oxidation-reduction (redox) reactions are, by their nature, based on the transfer of electrons between electron-active element(s) in component(s) forming the system, and the species in the static or dynamic system thus formed. For modeling purposes, we assume a closed system separated from its environment by diathermal walls with processes occurring therein in *quasistatic* manner under isothermal

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conditions. The simplest redox systems are evaluated under static conditions where the focus is on closed systems that are in an equilibrium state. Aqueous bromine solution is an example of such a system [1]. Dynamic redox systems are represented by redox titrations, where titrant (T) is gradually added to the titrand (D) and the D + T mixture with the related species, is thus obtained. Titration of NaIO solution (with volume V_0 and concentration C_0) with HCl (with concentration C and the added volume V) is an example of such a procedure [2]. The list of 21 chemical reactions that could presumably take place during this titration, including redox, acid-base, precipitation, and complexation reactions, is given in Table 1 [2]. The titration can be illustrated graphically, with use of the fraction titrated

$$\Phi = \frac{C \cdot V}{C_0 \cdot V_0} \qquad (1)$$

which is taken as an independent variable.

The equilibrium constant (K_{ej}) of the j-th redox reaction ($j = 1, \ldots, 14$) in Table 1, obtained on the basis of mass action law, is related to the standard reduction potentials, E_{0j}, as follows:

$$\log K_{ej} = z_j \cdot A \cdot E_{0j} \qquad (2)$$

where z_j is the number of electrons participating in this reaction and $1/A = (RT/F)\ln 10 = 0.0592$ V, i.e., $A = 16.90$ V^{-1} at 25 °C. The reduction potential (E) of the system is related to the concentration of 'free' electrons [3] as follows:

$$[e^-] = 10^{-A \cdot E} \qquad (3)$$

Additional physicochemical data is the solubility of solid iodine, I_2(s), in water, equal $1.33 \cdot 10^{-3}$ mol/L (at 25 °C) [2]. Based on this information, one of our tasks is to construct the titration curve for the HCl → NaIO system.

Table 1 Physicochemical data related to NaIO titration with HCl

No.	Reaction	Equilibrium equation	Equilibrium data
1	$I_2 + 2e^- = 2I^-$ (for dissolved I_2)	$[I^-]^2 = K_{e1} \cdot [I_2][e^-]^2$	$E_{01} = 0.621$ V
2	$I_3^- + 2e^- = 3I^-$	$[I^-]^3 = K_{e2} \cdot [I_3^-][e^-]^2$	$E_{02} = 0.545$ V
3	$IO^- + H_2O + 2e^- = I^- + 2OH^-$	$[I^-][OH^-]^2 = K_{e3} \cdot [IO^-][e^-]^2$	$E_{03} = 0.49$ V
4	$IO_3^- + 6H^+ + 6e^- = I^- + 3H_2O$	$[I^-] = K_{e4} \cdot [IO_3^-][H^+]^6[e^-]^6$	$E_{04} = 1.08$ V
5	$H_5IO_6 + 7H^+ + 8e^- = I^- + 6H_2O$	$[I^-] = K_{e5} \cdot [H_5IO_6][H^+]^7[e^-]^8$	$E_{05} = 1.24$ V
6	$H_3IO_6^{2-} + 3H_2O + 8e^- = I^- + 9OH^-$	$[I^-][OH^-]^9 = K_{e6} \cdot [H_3IO_6^{2-}][e^-]^8$	$E_{06} = 0.37$ V
7	$HIO = H^+ + IO^-$	$[H^+][IO^-] = K_{I1} \cdot [HIO]$	$pK_{I1} = 10.6$
8	$HIO_3 = H^+ + IO_3^-$	$[H^+][IO_3^-] = K_{I2} \cdot [HIO_3]$	$pK_{I2} = 0.79$
9	$H_4IO_6^- = H^+ + H_3IO_6^{2-}$	$[H^+][H_3IO_6^{2-}] = K_{I3} \cdot [H_4IO_6^-]$	$pK_{I3} = 3.3$
10	$Cl_2 + 2e^- = 2Cl^-$	$[Cl^-]^2 = K_{e7} \cdot [Cl_2][e^-]^2$	$E_{07} = 1.359$ V
11	$ClO^- + H_2O + 2e^- = Cl^- + 2OH^-$	$[Cl^-][OH^-]^2 = K_{e8} \cdot [ClO^-][e^-]^2$	$E_{08} = 0.88$ V
12	$ClO_2^- + 2H_2O + 4e^- = Cl^- + 4OH^-$	$[Cl^-][OH^-]^4 = K_{e9} \cdot [ClO_2^-][e^-]^4$	$E_{09} = 0.77$ V
13	$HClO = H^+ + ClO^-$	$[H^+][ClO^-] = K_{Cl1} \cdot [HClO]$	$pK_{Cl1} = 7.3$
14	$HClO_2 + 3H^+ + 4e^- = Cl^- + 2H_2O$	$[Cl^-] = K_{e10} \cdot [HClO_2][H^+]^3[e^-]^4$	$E_{010} = 1.56$ V
15	$ClO_2 + 4H^+ + 5e^- = Cl^- + 4H_2O$	$[Cl^-] = K_{e11} \cdot [ClO_2][H^+]^4[e^-]^5$	$E_{011} = 1.50$ V
16	$ClO_3^- + 6H^+ + 6e^- = Cl^- + 3H_2O$	$[Cl^-] = K_{e12} \cdot [ClO_3^-][H^+]^6[e^-]^6$	$E_{012} = 1.45$ V
17	$ClO_4^- + 8H^+ + 8e^- = Cl^- + 4H_2O$	$[Cl^-] = K_{e13} \cdot [ClO_4^-][H^+]^8[e^-]^8$	$E_{013} = 1.38$ V
18	$2ICl + 2e^- = I_2 + 2Cl^-$	$[I_2][Cl^-]^2 = K_{e14} \cdot [ICl]^2[e^-]^2$	$E_{014} = 1.105$ V
19	$I_2 + Cl^- = I_2Cl^-$	$[I_2Cl^-] = K_1 \cdot [I_2][Cl^-]$	$\log K_1 = 0.2$
20	$ICl + Cl^- = ICl_2^-$	$[ICl_2^-] = K_2 \cdot [ICl][Cl^-]$	$\log K_2 = 2.2$
21	$H_2O = H^+ + OH^-$	$[H^+][OH^-] = K_w$	$pK_w = 14.0$

Clearly, solving this dynamic system will provide much more than just the titration curve. In fact, it will provide the concentrations of each species at any given point during the titration. Solving this problem is not trivial from the mathematical point of view, and here we offer step-by-step guidance based on the generalized approach to electrolytic systems (GATES) [3, 4]. The information about the reactions that occur in the system cannot be obtained by simple inspection of the data in Table 1. Rather, this assessment can be done only by solving the interrelated elemental and charge balances, which are represented by equilibrium equations in Table 1. For modeling of HCl → NaIO system, we offer step-by-step guidance based on the generalized approach to electrolytic systems (GATES). GATES includes the generalized electron balance (GEB) concept, which is independent from the charge and concentration balances and completes, within GATES/GEB, the set of equations necessary for thermodynamic resolution of redox systems of any degree of complexity, assuming the use of all relevant, physicochemical knowledge available in literature. The GEB, as it is formulated here, relates the electrons introduced by components with electron-active elements (iodine in NaIO and chlorine in HCl) with the electrons of these elements involved in the related iodine and chlorine species that are formed during the titration process. For example, each IO_3^- ion contains $Z_I - 5$ iodine electrons, each molecule of ICl contains Z_I iodine electrons and

Z_{Cl} chlorine electrons and so on, where $Z_I = 53$ and $Z_{Cl} = 17$.

The challenge

Consider a $V_0 = 10$ mL sample of NaIO solution ($C_0 = 0.01$ mol/L), which is titrated with a HCl solution ($C = 0.10$ mol/L). On the basis of qualitative and quantitative information specified in Table 1, construct the titration curves: $E = E(\Phi)$, pH = pH(Φ), and speciation curves $\log[X_i^{z_i}] = f_i(\Phi)$ for the various iodine and chlorine species, $X_i^{z_i}$, in this system. To solve this Challenge, the readers are advised to accomplish the sequence of the following activities:

1. Complete the equation for charge balance

$$(+1) \cdot [H^+] + (-1) \cdot [OH^-] + (+1) \cdot [Na^+] + \ldots = 0 \quad \text{(F1)}$$

2. Complete the equation for concentration balance of all iodine species

$$1 \cdot [I^-] + 3 \cdot [I_3^-] + 1 \cdot [IO_3^-] + \ldots = C_0 V_0 / (V_0 + V) \quad \text{(F2)}$$

3. Complete the equation for concentration balance equation of all chlorine species

$$1 \cdot [Cl^-] + 2 \cdot [Cl_2] + 1 \cdot [HClO] + \ldots = CV/(V_0 + V) \qquad (F3)$$

4. Complete the generalized electron balance equation involving all iodine and chlorine species

$$(Z_I - 5) \cdot ([HIO_3] + [IO_3^-]) + \ldots + 2 \cdot Z_I \cdot [I_2] + \ldots$$
$$+ (Z_I + Z_{Cl}) \cdot [ICl] + \ldots =$$
$$= (Z_I - 1) \cdot C_0 \cdot V_0/(V_0 + V) + \ldots \qquad (F4)$$

5. Complete the equality for concentration balance of sodium:

$$1 \cdot [Na^+] = \ldots \qquad (F5)$$

6. Establish four independent (unknown) variables: pH, E, pI, and pCl, where pI = $-\log[I^-]$, and pCl = $-\log[Cl^-]$.

7. For all chemical reactions 1–21 in Table 1, write down the dependent variables from the corresponding equilibrium equations in terms of the four independent variables: pH, E, pI, and pCl. As an example,

for reaction 1 : $[I^-]^2 = K_{e1} \cdot [I_2][e^-]^2 \longrightarrow$

$10^{-2pI} = 10^{2AE_{01}} \cdot [I_2] \cdot 10^{-2AE} \longrightarrow [I_2] = 10^{2A(E-E_{01})-2pI}$

for reaction 2 : $[I^-]^3 = K_{e2} \cdot [I_3^-][e^-]^2 \longrightarrow$

$10^{-3pI} = 10^{2AE_{01}} \cdot [I_2] \cdot 10^{-2AE} \longrightarrow [I_3^-] = 10^{2A(E-E_{02})-3pI}$

and so on.

8. Owing to the limited solubility of iodine, establish the following equations for $[I_2]$ and $[I_2(s)]$:

if $[I_2]_{total} < 1.33 \cdot 10^{-3}$, then $[I_2]_{total} = [I_2]$ and $[I_2(s)] = 0$
if $[I_2]_{total} > 1.33 \cdot 10^{-3}$, then $[I_2] = 1.33 \cdot 10^{-3}$ and

$[I_2(s)] = [I_2]_{total} - 1.33 \cdot 10^{-3}$,
where $[I_2]_{total} = [I_2] + [I_2(s)]$.

9. Substitute Eq. F5 in F1 and solve the set of equations F1–F4 for various values of V. For this purpose, applying F1 = P1, rewrite Eqs. F1, F2, F3, and F4 into the form of equations: P1 = 0, P2 = 0, P3 = 0, and P4 = 0. Formulate the

sum of squares $SS = P1^2 + P2^2 + P3^2 + P4^2$, which can be minimized with the use of an iterative computer program as a function of the four independent variables. This can be achieved either using a commercial mathematical software such as *Matlab*, *Mathematica*, or *MathCad*, or open-source software such as *R*, to name a few.

On the basis of the results of calculations and figures thus obtained:

1. *Indicate the Φ region where iodine is the equilibrium solid phase;*
2. *Establish the equivalence point of the titration corresponding to the inflection point of the titration curve $E = E(\Phi)$ and pH = pH(Φ);*
3. *Formulate the predominant reactions occurring at different stages of the titration, and compare them with yields of accompanying reactions;*
4. *Attach the Excel file with results and graphs for $E = E(\Phi)$, pH = pH(Φ), and speciation curves $\log[X_i^{z_i}] = f_i(\Phi)$ for the various iodine and chlorine species obtained from the calculations.*

References

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