Disproportionation Reactions of HIO and NaIO in Static and Dynamic Systems

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Abstract

The paper refers to disproportionation of HIO and NaIO in aqueous media, in static and dynamic systems. The results of calculations, realized according to GATES/GEB principles, with use of an iterative computer program, are presented graphically. An example of the computer program with all physicochemical knowledge involved in the related algorithm is attached herewith.

Keywords

Disproportionation, Generalized Approach to Electrolytic Systems, Generalized Electron Balance, HIO, NaIO

1. Introduction

Quantitative description of electrolytic redox systems is performed by means of electron, charge and concentration balances, and a complete (not contradictory) set of relations for equilibrium constants, related to the system in question. The electron balance, termed as the Generalized Electron Balance (GEB) obtained according to Approach II to GEB, stems from linear combination 2∙f(H)-f(O) of the elemental balances: f(H) for H, and f(O) for O [1]-[11]. This property was extended on non-aqueous and mixed-solvent media [1] [12] [13], with amphiprotic co-solvents involved. The Approach II is equivalent to the Approach I to GEB, based on the “common pool” of electron-active elements in a system considered. The Approach I, considered as a “short” version of GEB, is applicable in the cases where oxidation numbers for all elements in the redox system are known beforehand [14]-[23]. In the Approach II to GEB, the electron-active and electron-non-active elements are not distinguished, as done in the Approach I. In both Approaches, the roles of oxidants and reductants are not ascribed to particular species \( X^{iz} \), considered as hydrates \( X^{iz} \cdot nW \) in aqueous (\( W = H_2O \)) media. The GEB is the immanent part of

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Some elements form compounds and species at three or more oxidation degrees. In particular, iodine forms the species on six oxidation degrees \((-1, -1/3, 0, 1, 5, 7)\) of this element. There are possible transitions between different species, associated with change of the oxidation state of the element; the relationship between concentrations of these species is determined by means of the corresponding standard potential value. The relations of another kind are expressed, inter alia, by the dissociation constants, ionic product of water, stability constants of complexes, solubility products, and other equilibrium constants. The possibility of these transitions is determined by the kinetics of the relevant reactions [3]; these transitions are defined as the paths of the appropriate chemical reactions [7]. The occurrence of the relevant reaction is possible after crossing the corresponding energy barriers (involved with activation energy), which are associated with the delivery of a sufficient energy to the system, to allow the transition in this system. At shortage of this energy, the system is in a metastable state [6]. When applying the thermodynamic approach, we do not consider the time needed for these reactions to proceed; in this case, the quasi-static course of the process is assumed.

From the preliminary, laconic information [24]-[26] one can state that HIO rapidly decomposes by disproportionation: 
\[
5\text{HIO} = \text{HIO}_3 + 2\text{I}_2 + 2\text{H}_2\text{O}
\]
(in the original notation applied there) and its salts rapidly disproportionate to form iodides and iodates. This information will be verified on the basis of the results of calculations, presented graphically on the corresponding speciation diagrams.

Information about kinetics of HIO disproportionation was presented in [27]-[30].

In the present paper, we refer to disproportionation of hypoiiodous acid, HIO, and its salt NaIO; oxidation degree \(+1 \in (-1, 1)\). The calculations are made according to iterative computer program, with the algorithm prepared according to GATES/GEB principles and presented in Appendix. The algorithm contains all the equilibrium constants taken from [31] and referring to forms of iodine and chlorine, used in the calculations related to system, where NaIO is titrated with HCl; in this system, iodine and chlorine are considered as “players” (when perceived from the viewpoint of the Approach I to GEB).

2. Disproportionation in Static Systems

The static systems with C solutions of (1) HIO and (2) NaIO are shown graphically in Figures 1(a)-(c) and Figures 2(a)-(c) with the values \(pC = -\log C\) on the abscissa. The static system indicate pH, E and \(\log \left[ X^\pm \right] \) values related to different concentrations C of the corresponding solutes. The relevant graphs can also be applied to the solutions obtained by gradual dilution of 0.1 mol/L (1) HIO, (2) NaIO and (3) equimolar solution of HIO + NaIO with use of pure water.

2.1. C mol/L HIO

As results from speciation diagram in Figure 1(a), in more concentrated HIO solutions, i.e., at lower pC values, the predominating reactions are as follows:

\[
5\text{HIO} = 2\text{I}_2 + \text{IO}_3^- + 2\text{H}_2\text{O} + \text{H}^+
\]

\[
5\text{HIO} = 2\text{I}_2 + 2\text{IO}_3^- + 2\text{H}_2\text{O} + \text{H}^+
\]

\[
5\text{HIO} = 2\left(\text{I}_2, \text{I}_2 \right) + \text{HIO}_3 + 2\text{H}_2\text{O}
\]

with further dilution of HIO solution, reaction (2b) is accompanied, in an increasing degree, by the reaction

\[
3\text{HIO} = 2\text{I}^- + \text{IO}_3^- + 3\text{H}^+
\]

The change in disproportionation scheme, more significant at pC 4 - 5, resulted in a change of the shapes of the plots: \(E = E(pC)\) (Figure 1(b)) and \(pH = pH(pC)\) (Figure 1(c)).

2.2. C mol/L NaIO

For different pC values, the disproportionation in C mol/L NaIO proceeds there mainly according to the scheme (see Figure 2(a))
Figure 1. The plots of (a) speciation curves for indicated iodine species $X_i^{n_i}$ and (b) E vs. pC, (c) pH vs. pC relationships in C mol/L HIO.

$$\text{HIO} = \text{IO}_3^- + 2\text{I}^- + 3\text{H}^+$$

where $[\text{I}^-]/[\text{IO}_3^-] \cong 2$. The plots: E = E(pC) and pH = pH(pC) are presented in Figure 2(b) and Figure 2(c), respectively.

2.3. Mixture HIO (C mol/L) + NaIO (C mol/L)

During the dilution of equimolar mixture of HIO (C = 0.1 mol/L) + NaIO (C = 0.1 mol/L) with water, in the range of higher C (i.e., lower pC) values we have the disproportionation reactions:

$$5\text{HIO} + \text{OH}^- = \text{IO}_5^- + 2(\text{I}_{2(s)}, \text{I}_2) + 3\text{H}_2\text{O}$$

$$3\text{HIO} = \text{IO}_3^- + 2\text{I}^- + 3\text{H}^+$$

$$4\text{HIO} + 2\text{OH}^- = \text{IO}_3^- + \text{I}_3^- + 3\text{H}_2\text{O}$$

occurring there predominantly, in a comparable degree. Reactions involving $\text{IO}^-$ occur in a much lesser extent. At pC > 2.40, $\text{I}_{2(s)}$ does not exist as an equilibrium solid phase. In very diluted solutions, primarily the reaction (6) takes place.

The curve E = E(pC) passes through a maximum (Figure 3(b)), while the curve pH = pH(pC) passes through
Figure 2. The speciation curves (a) for indicated iodine species $X_i^*$ and (b) $E$ vs. $pC$, (c) $pH$ vs. $pC$ relationships in C mol/L NaIO.

a minimum (Figure 3(c)). This is due to the fact that $dE/dpC < 0$, $dpH/dpC > 0$ for C mol/L HIO (Figure 1(b), Figure 1(c)), while $dE/dpC > 0$, $dpH/dpC < 0$ for C mol/L NaIO (Figure 2(b), Figure 2(c)).

3. Disproportionation in Dynamic Systems

In dynamic systems, the related curves will be plotted on graphs with the fraction titrated

$$\Phi = \frac{C \cdot V}{C_0 \cdot V_0} \quad (8)$$

related to addition of V mL of titrant T (C mol/L B) into V₀ mL of titrand D (C₀ mol/L A); A, B—reagents.

3.1. Titration of HIO ($C_0$, $V_0$) with NaOH ($C$, $V$)

The curves plotted at $V_0 = 10$ mL, $C_0 = 0.01$ mol/L and $C = 0.1$ mol/L, are presented in Figures 4(a)-(c).

At the initial part of the titration we have the reactions:

$$5\text{HIO} + \text{OH}^- = 2\left(\text{I}_2, \text{I}_3\right) + \text{IO}_3^- + 3\text{H}_2\text{O} \quad (9)$$

In the following, at $\Phi$ ca. 0.20 - 0.22, a pronounced increase in $[\Gamma]$ occurs, as a result of reaction

$$3\text{HIO} + 3\text{OH}^- = \text{IO}_3^- + 2\Gamma^- + 3\text{H}_2\text{O} \quad (10)$$
The increase in [I\textsuperscript{−}] is accompanied by an increase in

\[ \left[ I_{2(s)} \right] \rightarrow \left[ I_{3} \right] + \Gamma = I_{5} \]  

This leads to the gradual disappearance of \( I_{2(s)} \) (which is ultimately ended at \( \Phi = 0.5347 \)) and lowering of \( I_{2} \) and \( I_{5} \); all they are disproportionated

\[ 3\left( I_{2(s)}, I_{2}, I_{5} \right) + 6OH^- = IO_5^- + \left( 5,5,8 \right) \Gamma + 3H_2O \]  

At \( \left[ I_{2(s)} \right] > 0 \), we have \( [I_2] = s = \text{const}; s = 1.33 \times 10^{-3} \text{ mol/L is the solubility of } I_{2(s)} \text{ in water, at } 20^\circ \text{C (see Appendix).} \) Finally, the disproportionation of HIO affected by NaOH can be expressed by the equation

\[ 3\text{HIO} + 3OH^- = IO_5^- + 2I^- + 3H_2O \]  

Note that the stoichiometry of the reaction (13) is \( 3:3 = 1:1 \), which corresponds to the jump on the curves (4b) and (4c), occurring at \( \Phi = 1 \). For \( \Phi > 1 \), we have \( [I^-] / [IO_3^-] = 2 \), i.e., the stoichiometry of the products of reaction (13) equals to 1:2. The jumps on the curves \( E = E(\Phi) \) and \( \text{pH} = \text{pH}(\Phi) \) (Figure 4(a), Figure 4(b)) occur at \( \Phi \text{ ca. } 0.2 \) (which corresponds to the stoichiometry 1:5 of the reaction (9)) and at \( \Phi \text{ ca. } 1 \) (which corresponds to the stoichiometry 3:3 = 1:1 of the reaction (13)); the maxima on the corresponding, derivative curves in Figure 5(a), Figure 5(b) fit exactly the stoichiometric ratios.
Figure 4. The speciation curves (a) for indicated iodine species $X^i$ and (b) $E$ vs. $pC$, (c) $pH$ vs. $pC$ relationships in for $V_0 = 10$ mL of $C_0 = 0.01$ mol/L HIO titrated with $C = 0.1$ mol/L NaOH.

Figure 5. The (a) $\Delta pH/\Delta \Phi = (pH_{j+1} - pH_j)/(\Phi_{j+1} - \Phi_j)$, (b) $\Delta E/\Delta \Phi = (E_{j+1} - E_j)/(\Phi_{j+1} - \Phi_j)$ vs. $\Phi = (\Phi_j + \Phi_{j+1})/2$ relationships for the system HIO + NaOH.
3.2. Titration of NaIO (C₀, V₀) with HCl (C, V)

The curves plotted at V₀ = 10 mL, C₀ = 0.01 mol/L NaIO and C = 0.1 mol/L HCl are presented in Figures 6(a)-(d). Initially, the reaction

\[ 3\text{IO}^- = \text{IO}_3^- + 2\text{I}^- \]  

(14)

and then the reaction

\[ 5\text{IO}^- + 4\text{H}^+ = 2\text{I}_2 + \text{IO}_3^- + 2\text{H}_2\text{O} \]  

(15)

occur. Then I\(^-\) from (14) and I\(_2\) from (15) form \(\text{I}_3^-\) in the reaction \(\text{I}_2 + \text{I}^- = \text{I}_3^-\) and \([\text{I}_3^-]\) increases. At \(\Phi = 0.4654\), \(\text{I}_2(s)\) appears as the solid phase

\[ 5\text{IO}^- + 4\text{H}^+ = 2\text{I}_2(s) + \text{IO}_3^- + 2\text{H}_2\text{O} \]  

(16)

At \([\text{I}_2(s)] > 0\), we have \([\text{I}_2] = \text{const.}\) as well. The increase in \([\text{Cl}^-]\), resulted from addition of HCl, causes an increase in \([\text{I}_2\text{Cl}^-]\), and—to a lesser extent—the increases in \([\text{ICl}_2^-]\) and \([\text{ICl}]\). The addition of HCl lowers pH of the solution, and then \([\text{HIO}]\) becomes larger than \([\text{IO}^-]\); \([\text{HIO}_3]\) also increases. In effect, the summary concentration \([\text{HIO}] + [\text{IO}^-]\) after addition of an excess of HCl is higher than in the starting NaIO solution.

In the algorithm (see Appendix), we have allowed the participation of Cl\(^-\) ions from HCl solution in the redox reaction. However, the concentration of Cl\(_2\) and HClO as the main products of Cl\(^-\) oxidation (Figure 6(b)) is

![Figure 6](image-url)

**Figure 6.** The speciation curves for indicated (a) iodine and (b) chlorine species \(X_i^+\) and (c) E vs. \(\Phi\), (d) pH vs. \(\Phi\) relationships in for V₀ = 10 mL of C₀ = 0.01 mol/L NaIO titrated with C = 0.1 mol/L HCl.
quite negligible. This way, one can state that the Cl$^-$ ions practically do not participate the redox reaction as a reducing agent. From linear combination of reactions: (14) and

$$5I^- + IO_3^- + 6H^+ = 3I_2(s) + 3H_2O \quad (17)$$

(multiplication by 5 and 2 resp., cancellations and division by 3, we get the reaction

$$5IO^- + 4H^+ = IO_3^- + 2I_2(s) + 2H_2O \quad (18)$$

with stoichiometry 4:5 = 0.8, which corresponds to $\Phi = 4/5 = 0.8$, where the inflection point on the curves in Figure 6(c) and Figure 6(d) are observed. The $I^-$ and $IO_3^-$ ions are consumed in reactions: (17) and

$$5I^- + IO_3^- + 6H^+ = 8I_2(s) + 3H_2O \quad (19)$$

see Figure 6(a).

4. Final Remarks

The disproportionation reactions in the static and dynamic systems with (a) HIO, (b) NaIO, (c) HIO + NaIO were considered. The static systems were equivalent, in principle, with dynamic systems where the related titrand was diluted with pure water. In the dynamic system where NaIO solution was titrated with HCl, chlorine (Cl) was considered as a second “player”, i.e., possibility of oxidation of Cl$^-$-ions was admitted/pre-assumed. However, as stated on the basis of results of calculations, the concentrations of Cl$_2$ and HClO as the main products of Cl oxidation are extremely low. On this basis, it can be considered that the IO$_3^-$ introduced into the system as NaIO, undergoes disproportionation (not a reduction) reaction. All these calculations were made under assumption that the relevant reactions take place in quasi-static manner, under isothermal conditions. The reactions proceeding in the respective systems were formulated under assumption that all equilibrium constants found in the relevant tables (see Appendix) and then used in the calculations are correct.

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Appendix

function F = System_Na10HCl(x):
%Na10<--HCl
% Titration of V0 mL of Na10 (CO) with V mL HCl (C).

global V Vmin Vstep Vmax V0 C0 f f OH pH E Kw pKw A aa
global I1 I2 I2s HI0 I10 H5I03 H3I03 H3I076 H4I706 H3I706 Na
global logI1 logI2 logI2s logHI0 logHI03 logHI053 logHI053 logHI706
global logH4I706 logH3I706 logNa
global CI CI2 Cl0 Cl0 Cl0 Cl0 Cl0 Cl0 Cl0 Cl0 Cl0 Cl0 Cl0 Cl0 Cl0 Cl0 Cl0 Cl0 Cl0 Cl0
global logCl logCl logCl logCl logCl logCl logCl logCl logCl logCl logCl logCl logCl logCl logCl logCl logCl logCl logCl

E=x(1);
pH=x(2);
p1=x(3);
pCl=x(4);

H=10.^-pH;
pKw=14;
Kw=10.^-14;
OH=Kw./H;
I=10.^-pI;
Cl=10.^-pCl;
A=16.92;
ZCl=17;
ZI=53;

I2=I.^2.*10.^((2.*A.*(E-0.621)))
I3=I.^3.*10.^((2.*A.*(E-0.545)))
I0=I.^1.*10.^((2.*A.*(E-0.49)+2.*pH-2.*pKw))
HIO=10.^10.^((10.6-pH))
I503=I.*10.^((6.*A.*(E-1.08)+6.*pH))
H5I03=I503.*10.^((0.79-pH))
H3I706=I.*10.^((8.*A.*(E-1.24)+7.*pH))
H4I706=H3I706.*10.^(-3.3+pH)
H3I706=I.*10.^((8.*A.*(E-0.37)+9.*pH-9.*pKw));

Cl2=Cl.*2.*10.^((2.*A.*(E-1.359)))
Cl3=Cl.*1.*10.^((2.*A.*(E-0.88)+2.*pH-2.*pKw))
HC1O=ClO.*1.*10.^((7.3-pH))
Cl302=Cl.*1.*10.^((4.*A.*(E-0.77)+4.*pH-4.*pKw))
HC302=ClO.*1.*10.^((4.*A.*(E-1.56)+3.*pH))
Cl4O2=Cl.*1.*10.^((5.*A.*(E-1.5)+4.*pH))
Cl503=Cl.*1.*10.^((6.*A.*(E-1.45)+6.*pH))
C704=Cl.*1.*10.^((8.*A.*(E-1.38)+8.*pH));

I2CI=I2.*1.*10.^((0.2-pCl))
I2Cl=I2.*1.*10.^((A.*(E-1.105)-pCl))
I2CI2=I2.*1.*10.^((2.2-pCl))
Na=Cl0.*V0./(V0+V);

if I2>1.33e-3
  I2s=I2-1.33e-3;
  I2=1.33e-3;
  aA=1;
else
  aA=0;
end;

% Charge balance
F=[(HI+Na-I-I1+I3-I0-I503-H4I706-2*H3I706-CI-Cl0-Cl302-Cl503-Cl704-...-
   2*I2Cl-I2Cl2-C0-V0)/(V0+V)];
% Concentration balance for Cl
(C1+2.*Cl2+HClO+ClO+HCl302+Cl302+Cl402+Cl503+Cl704+12Cl+1ClL...
+2.*KCl2-C*V.)/(V0+V));

% Electron balance
((ZI+1)-1+(3.*ZI+1).*I3+2.*ZI.*(I2+aa.*I2s)+(ZI-1).*H(I0+I0)...
+(ZI-5).*H503+I503)+(ZI-7).*H51706+H41706+H31706)+(ZI+1).*Cl+...
2.*ZCl+Cl2+(ZCl-1).*HClO+ClO+(ZCl-3).*HCl302+Cl302)...
+(ZCl-4).*Cl402+(ZCl-5).*Cl503+(ZCl-7).*Cl704+(2.*ZI+ZCl+1).*I2Cl+...
(ZI-ZCl).*ClI+(ZI-2.*ZCl+1).*Cl2...
-(ZI-1).*C0.*V0+(ZCl+1).*C*V.)/(V0+V));

logl=log10(I);
log3=log10(I3);
log2z=log10(I2z);
log2s=log10(I2s);
logH0=log10(H0);
log0=log10(0);
logH503=log10(H503);
log503=log10(503);
logH51706=log10(H51706);
logH41706=log10(H41706);
logH31706=log10(H31706);
logCl=log10(Cl);
logCl2=log10(Cl2);
logHClO=log10(HClO);
logClO=log10(ClO);
logHCl302=log10(HCl302);
logCl302=log10(Cl302);
logCl402=log10(Cl402);
logCl503=log10(Cl503);
logCl704=log10(Cl704);
logCl2I=log10(Cl2I);
logClI=log10(ClI);
logClz=log10(Cl2);
logNa=log10(Na);

% The end of program
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