Dynamic Buffer Capacities in Redox Systems

Anna Maria Michałowska-Kaczmarczyk1, Aneta Spórna-Kucab2, Tadeusz Michałowski3*

Abstract
The buffer capacity concept is extended on dynamic redox systems, realized according to titrimetric mode, where changes in pH and E are accompanied by changes in potential V values; it is the basic novelty of this paper. Two examples of monotonic course of the related curves of potential E vs. V and pH vs. V relationships were considered. The systems were modeled according to GATES/GEB principles.

Keywords
Thermodynamics of electrolytic redox systems; Buffer capacity; GATES/GEB

Introduction
The buffer capacity concept is usually referred to as a measure of resistance of a solution (D) on pH change, affected by an acid or base, added as a titrant T, i.e., according to titrimetric mode; in this case, D is termed as titrand.

The titration is a dynamic procedure, where V mL of titrant T, containing a reagent B (C mol/L), is added into V_0 mL of titrand D, containing a substance A (C_0 mol/L). The advance of a titration B(C,V) ⇒ A(C_0,V_0) is denoted for brevity as B ⇒ A, is characterized by the fraction titrated [1-4]

\[ \Phi = \frac{C \cdot V}{C_0 \cdot V_0} \]

that introduces a kind of normalization (independence on V_0 value) for titration curves, expressed by \( \Phi = \text{pH} / \text{E} \) (equation 1) for potential E [V] expressed in SHE scale. The redox systems with one, two or more electron-active elements are modeled according to principles of Generalized Approach to Electrolytic Systems with Generalized Electron Balance involved (GATES/GEB), described in details in [5-16], and in references to other authors’ papers cited therein. According to earlier conviction expressed by Gran [17], all titration curves: \( \text{pH} = \text{pH}(\Phi) \) and E = E(\( \Phi \)) for potential E [V] expressed in SHE scale.

**Examples of titration curves**

In this paper, we refer to the disproportionating systems: (S1) NaOH ⇒ HIO and (S2) HCl ⇒ NaIO, characterized by monotonic changes of pH and E values during the related titrations (i.e., the case 1°). In both instances, the values: \( V_0 = 100 \), C_0 = 0.01, and C_0 = 0.1 were assumed. The set of equilibrium data [18-20] applied in calculations, presented in Table 1, is completed by the solubility of solid iodine, \( \text{I}_2 \text{so} \), in water, equal 1.33·10^-3 mol/L. The related algorithms, prepared in MATLAB for S1 (NaOH ⇒ HIO) S2 (HCl ⇒ NaIO) system according to the GATES/GEB principles, are presented in Appendices 1 and 2.

**Dynamic acid-base buffer capacities**

Dynamic buffer capacity was referred previously only to acid-base equilibria in non-redox systems [3,21-23]. However, the dynamic (\( \beta_V \)) and windowed (\( B_V \)) buffer capacities can also be related to acid-base equilibria in redox systems. The \( \beta \) is formulated as follows [3,21]

\[ \beta_V = \frac{dc}{d\text{pH}} \]

where

\[ c = \frac{CV}{V_0 + V} = \text{the current concentration of B in D+T mixture, at any point of the titration. In the simplest case, D is a solution of one substance A (C_0 mol/L), and then equation 3 can be rewritten as follows}

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\[ \beta_V = \frac{dc}{d\Phi} \]

where

\[ \eta = \frac{d\text{pH}}{d\Phi} \]

is the sharpness index on the titration curve. For comparative purposes, the absolute values, \( |\beta_V| \) and \( |\eta| \), for \( \beta_V \) (equations 1,5) and \( \eta \) (equation 6) are considered. At \( C_0/C < 1 \) and small \( \Phi \) value, from equation 3 we get

\[ \beta_V = \Phi \cdot C_0 \cdot \eta \]

The \( \beta_V \) value is the point-estimation and then cannot be used in the case of finite changes (\( \Delta \text{pH} \)) corresponding to an addition of a finite volume of titrant (\( \Phi \), a non-linear function of pH). For this purpose, the ‘windowed’ buffer capacity, \( B_V \), defined by the formula [3,21]
 involves with infinitesimal and finite changes of vs. E for the vs. pH, and vs. pH are plotted in Figures 3, 4.

Table 1: Physicochemical data related to the systems S1 and S2

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Equilibrium equation</th>
<th>Equilibrium data</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>I²⁺ + 2e⁻ = 2I⁻ (for dissolved I₂)</td>
<td>[I²⁺] = K₁[I⁻][e⁻]²</td>
<td>E°₁ = 0.621 V</td>
</tr>
<tr>
<td>2</td>
<td>I⁻ + 2e⁻ = 3I⁻</td>
<td>[I⁻] = K₂[I⁻][e⁻]²</td>
<td>E°₂ = 0.545 V</td>
</tr>
<tr>
<td>3</td>
<td>O²⁻ + H₂O + 2e⁻ = I⁻ + 2OH⁻</td>
<td>[O²⁻][H₂O][e⁻]²</td>
<td>E°₃ = 0.49 V</td>
</tr>
<tr>
<td>4</td>
<td>O²⁻ + 6H⁺ + 6e⁻ = I⁻ + 3H₂O</td>
<td>[O²⁻][H⁺][e⁻]²</td>
<td>E°₄ = 1.08 V</td>
</tr>
<tr>
<td>5</td>
<td>HO₂⁻ + 8e⁻ = I⁻ + 6H₂O</td>
<td>[HO₂⁻][e⁻]²</td>
<td>E°₅ = 1.24 V</td>
</tr>
<tr>
<td>6</td>
<td>HO₂⁻ + 3H₂O + 8e⁻ = I⁻ + 9OH⁻</td>
<td>[HO₂⁻][H₂O][e⁻]²</td>
<td>E°₆ = 0.37 V</td>
</tr>
<tr>
<td>7</td>
<td>HO⁻ + H⁺ = I⁻</td>
<td>[HO⁻][H⁺]</td>
<td>pK₁ = 10.6</td>
</tr>
<tr>
<td>8</td>
<td>HO₂⁻ + H⁺ = I⁻</td>
<td>[HO₂⁻][H⁺]</td>
<td>pK₂ = 0.79</td>
</tr>
<tr>
<td>9</td>
<td>HO₂⁻ = H⁺ + I⁻</td>
<td>[HO₂⁻]</td>
<td>pK₃ = 3.3</td>
</tr>
<tr>
<td>10</td>
<td>Cl⁻ + 2e⁻ = 2Cl⁻</td>
<td>[Cl⁻][e⁻]²</td>
<td>E°₁₀ = 1.359 V</td>
</tr>
<tr>
<td>11</td>
<td>ClO⁻ + H₂O + 2e⁻ = Cl⁻ + 2OH⁻</td>
<td>[ClO⁻][H₂O][e⁻]²</td>
<td>E°₁₁ = 0.88 V</td>
</tr>
<tr>
<td>12</td>
<td>ClO⁻ + 2H₂O + 4e⁻ = Cl⁻ + 4OH⁻</td>
<td>[ClO⁻][H₂O][e⁻]²</td>
<td>E°₁₂ = 0.77 V</td>
</tr>
<tr>
<td>13</td>
<td>HOClO + H⁺ = Cl⁻</td>
<td>[HOClO][H⁺]</td>
<td>pK₅ = 7.3</td>
</tr>
<tr>
<td>14</td>
<td>HOClO + 3H⁺ + 4e⁻ = Cl⁻ + 2H₂O</td>
<td>[HOClO][H⁺][e⁻]²</td>
<td>E°₁₄ = 1.56 V</td>
</tr>
<tr>
<td>15</td>
<td>ClO⁻ + 4H⁺ + 5e⁻ = Cl⁻ + 4H₂O</td>
<td>[ClO⁻][H⁺][e⁻]²</td>
<td>E°₁₅ = 1.50 V</td>
</tr>
<tr>
<td>16</td>
<td>ClO⁻ + 6H⁺ + 6e⁻ = Cl⁻ + 3H₂O</td>
<td>[ClO⁻][H⁺][e⁻]²</td>
<td>E°₁₆ = 1.45 V</td>
</tr>
<tr>
<td>17</td>
<td>ClO⁻ + 8H⁺ + 8e⁻ = Cl⁻ + 4H₂O</td>
<td>[ClO⁻][H⁺][e⁻]²</td>
<td>E°₁₇ = 1.38 V</td>
</tr>
<tr>
<td>18</td>
<td>2ICl + 2e⁻ = I₂ + 2Cl⁻</td>
<td>[ICl][e⁻]²</td>
<td>E°₁₈ = 1.105 V</td>
</tr>
<tr>
<td>19</td>
<td>Cl⁻ + I⁻ = ICl</td>
<td>[ICl][e⁻]²</td>
<td>logK₁ = 0.2</td>
</tr>
<tr>
<td>20</td>
<td>ICO⁻ + Cl⁻ = ICl⁻</td>
<td>[ICl⁻][e⁻]²</td>
<td>logK₂ = 2.2</td>
</tr>
<tr>
<td>21</td>
<td>H₂O + H⁺ = H₂O</td>
<td>[H₂O][H⁺]</td>
<td>pK₃ = 14.0</td>
</tr>
</tbody>
</table>

| Bc | \[\frac{\Delta c}{\Delta \phi H}\] |
| Bv | \[\frac{\Delta c}{\Delta E}\] |

where \(\Delta c\) is defined by equation 2, and then we have

\[
\frac{\Delta c}{\Delta E} = \frac{1}{\Delta E} \int E \beta_v \cdot dE = \frac{c(E + \Delta E) - c(E)}{\Delta E}
\]

**Dynamic buffer capacities \(\beta_v^E\) and \(\beta_v^E\)**

In similar manner, one can formulate dynamic buffer capacities \(\beta_v^E\) and \(\beta_v^E\), involved with infinitesimal and finite changes of potential E values:

\[
\beta_v^E = \frac{dc}{dE} \tag{11}
\]

\[
\beta_v^E = \frac{\Delta c}{\Delta E} \tag{12}
\]

where \(c\) is defined by equation 2, and then we have

\[
\frac{\Delta c}{\Delta E} = \frac{1}{\Delta E} \int E \beta_v \cdot dE = \frac{c(E + \Delta E) - c(E)}{\Delta E}
\]

**Discussion**

Disproportionation of the solutes considered (HIO or NaIO) in D occurs directly after introducing them into pure water. The disproportionation is intensified, by greater pH changes, after addition of the respective titrants: NaOH (in S1) or HCl (in S2), and the monotonic changes of E = E(Φ) and pH = pH(Φ) occur in all instances.

All attainable equilibrium data related to these systems are included in the algorithms implemented in the MATLAB computer program (Appendices 1 and 2). In all instances, the system of equations was composed of: generalized electron balance (GEB), charge balance (ChB) and concentration balances for particular elements ≠ H, O.

In the system S1, the precipitate of solid iodine, \(I_2\), is formed (Figure 5). In the relatively simple redox system S2, we have all four basic kinds of reactions; except redox and acid-base reactions, the solid iodine (\(I_2\)) is precipitated and soluble complexes: I⁻Cl⁻, ICl and ICl⁻ are formed (Figure 6A). Note that \(I_2 + I^- = I_3^-\) is also the complexation reaction.
In the system $S_2$, all oxidized forms of $\text{Cl}^{-}$ were involved, i.e. the oxidation of $\text{Cl}^{-}$ ions was thus pre-assumed. This way, full “democracy” was assumed, with no simplifications [18-20]. However, from the calculations we see that HCl acts primarily as a disproportionating, and not as reducing agent. The oxidation of $\text{Cl}^{-}$ occurred here only in an insignificant degree (Figure 6B); the main product of the oxidation was $\text{Cl}_2$, whose concentration was on the level of $10^{-16} - 10^{-17}$ mol/L.

**Final comments**

The redox buffer capacity concepts: $\beta_V$ and $\beta_E^V$ can be principally related to monotonic functions. This concept looks awkwardly for non-monotonic functions $\text{pH} = \text{pH}(\Phi)$ and/or $E = E(\Phi)$ specified above ($2^o - 4^o$) and exemplified in Figures 7,8,9. For comparison, in isohydric (acid-base) systems, the buffer capacity strives for infinity. In particular, it occurs in the titration $\text{HB} (C,V) \rightarrow \text{HL} (C_0,V_0)$, where $\text{HB}$ is a strong monoprotic acid $\text{HB}$ and $\text{HL}$ is a weak monoprotic acid characterized by the dissociation constant $K_1 = [\text{H}^+][\text{L}^-]/[\text{HL}]$; at $4K_1/C^2 \ll 1$, the isohydricity condition is expressed here by the Michalowski formula $C_0 = C + C^2 \cdot 10^{\Delta\text{pK}_2}$ [24-26].

The formula for the buffer capacity, suggested in [27] after [28], is not correct. Moreover, it involves formal potential value, perceived as a kind of conditional equilibrium constant idea, put in (apparent) analogy with the simplest static acid-base buffer capacity, see criticizing remarks in [29]; it is not adaptable for real redox systems.

Buffered solutions are commonly applied in different procedures involved with classical (titrimetric, gravimetric) and instrumental analyses [30-33]. There are in close relevance to isohydric solutions.
Figure 3: The relations: (A) $\beta_V$ vs. $\Phi$, (B) $\beta_V$ vs. pH, (C) $\beta_V$ vs. E and (D) $\beta^i_V$ vs. $\Phi$, (E) $\beta^i_V$ vs. pH, (F) $\beta^i_V$ vs. E for (S1) NaOH $\Rightarrow$ HIO.

Figure 4: The relations: (A) $\beta_V$ vs. $\Phi$, (B) $\beta_V$ vs. pH, (C) $\beta_V$ vs. E and (D) $\beta^i_V$ vs. $\Phi$, (E) $\beta^i_V$ vs. pH, (F) $\beta^i_V$ vs. E for (S2) HCl $\Rightarrow$ NaIO.
Figure 5: Speciation diagram for the system (S1) NaOH ⇌ HIO.

Figure 6: Speciation diagram for the system (S2) HCl ⇌ NaIO: (A) for iodine species; (B) for oxidized forms of chlorine species.

Figure 7: Case (2²): (A) monotonic pH = pH(V) and (B) non-monotonic E = E(V) plots on the step 3 of the process presented in [6].

[24-26] and pH-static titration [4,34], and titration in binary-solvent systems [12,35]. Buffering property is usually referred to an action of an external agent (mainly: strong acid, HB, or strong base, MOH) inducing pH change, ∆pH, of the solution. Redox buffer capacity is also involved with the problem of interfacing in CE-MS analysis, and bubbles formation in reaction 2H₂O = O₂(g) + 4H⁺ + 4e⁻ at the outlet electrode in CE [36-39].

In Baicu et al. [40], a nice proposal of “slyke”, as the name for (acid-base, pH) buffer capacity unit, has been raised.
Figure 8: Case (3): (A) non-monotonic pH = pH(\Phi) and (B) monotonic E = E(\Phi) functions for the system KBrO₃ \rightarrow NaBr presented in [5].

Figure 9: Case (4): the (A) non-monotonic pH = pH(\Phi) and (B) non-monotonic E = E(\Phi) functions for the system HI \rightarrow KIO₃ presented in [7].

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