Dynamic Buffer Capacities in Redox Systems

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Abstract
The buffer capacity concept is extended on dynamic redox systems, realized according to titrimetric mode, where changes in pH are accompanied by changes in potential E values; it is the basic novelty of this paper. Two examples of monotonic course of the related curves of potential E vs. and pH vs. Φ 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 V0 mL of titrand D, containing a substance A (C0 mol/L). The advance of a titration B(C,V) ⇒ A(C0,V0), 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 V0 value) for titration curves, expressed by pH=pH(Φ), and E=E(Φ) 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: pH=pH(Φ) and E=E(Φ) 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.

Examples of Titration Curves pH=pH(Φ) and E=E(Φ) in redox systems

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 1o). In both instances, the values: V0=100, C0=0.01, and C=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, I2(s), 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.

The titration curves: pH=pH(Φ) and E=E(Φ) presented in Figures 1 and 2 are the basis to formulation of dynamic buffer capacities in the systems S1 and S2.

Dynamic acid-base buffer capacities \( B_V \) and \( B_V' \)

Dynamic buffer capacity was referred previously only to acid-
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Table 1 Physicochemical data related to the systems S1 and S2.

| No. | Reaction | Equilibrium equation | Equilibrium data |
|-----|----------|----------------------|------------------|
| 1   | I₂ + 2e⁻ = 2I⁻ (for dissolved I₂) | [I⁻]² = K_{sw} [I] [e⁻]² | \( E_{\text{em}} = 0.621 \text{ V} \) |
| 2   | I⁻ + 2e⁻ = 3I⁻ | [I⁻]² = K_{sw} [I] [e⁻]² | \( E_{\text{em}} = 0.545 \text{ V} \) |
| 3   | IO⁻ + H₂O + 2e⁻ = I⁻ + 2OH⁻ | [IO⁻] [OH⁻] = K_{sw} [I] [e⁻]² | \( E_{\text{em}} = 0.49 \text{ V} \) |
| 4   | IO⁻ + 6H⁺ + 6e⁻ = I⁻ + 3H₂O | [I⁻] = K_{sw} [IO⁻] [H⁺]² [e⁻]⁶ | \( E_{\text{em}} = 1.08 \text{ V} \) |
| 5   | H₂IO₄⁻ + 7H⁺ + 8e⁻ = I⁻ + 6H₂O | [I⁻] = K_{sw} [H₂IO₄⁻] [H⁺]⁷ [e⁻]⁸ | \( E_{\text{em}} = 1.24 \text{ V} \) |
| 6   | HJ₀₂⁻ + 3H₂O + 8e⁻ = I⁻ + 9OH⁻ | [I⁻] = K_{sw} [HJ₀₂⁻] [e⁻]⁹ | \( E_{\text{em}} = 0.37 \text{ V} \) |
| 7   | HI₀ = H⁺ + IO⁻ | [H⁺] [IO⁻] = K_{sw} [HI₀] | \( pK_{sw} = 10.6 \) |
| 8   | HIO = H⁺ + IO⁻ | [H⁺] [IO⁻] = K_{sw} [HIO] | \( pK_{sw} = 0.79 \) |
| 9   | HJ₀₂⁻ = H⁺ + HJ₀₂⁻² | [H⁺] [HJ₀₂⁻] = K_{sw} [HJ₀₂⁻]² | \( pK_{sw} = 3.3 \) |
| 10  | Cl⁻ + 2e⁻ = 2Cl⁻ | [Cl⁻]² = K_{sw} [Cl⁻] [e⁻]² | \( E_{\text{em}} = 1.359 \text{ V} \) |
| 11  | ClO⁻ + H₂O + 2e⁻ = Cl⁻ + 2OH⁻ | [ClO⁻] [OH⁻] = K_{sw} [Cl⁻] [e⁻]² | \( E_{\text{em}} = 0.88 \text{ V} \) |
| 12  | ClO⁻ + 2H⁺ + 4e⁻ = Cl⁻ + 4OH⁻ | [ClO⁻] [OH⁻] = K_{sw} [Cl⁻] [e⁻]⁴ | \( E_{\text{em}} = 0.77 \text{ V} \) |
| 13  | HClO + H⁺ + CIO⁻ | [H⁺][CIO⁻] = K_{sw} [HClO] | \( pK_{sw} = 7.3 \) |
| 14  | HClO₂ + 3H⁺ + 4e⁻ = Cl⁻ + 2H₂O | [Cl⁻] = K_{sw} [HClO₂][H⁺]³ [e⁻]⁴ | \( E_{\text{em}} = 1.56 \text{ V} \) |
| 15  | ClO₂⁻ + 4H⁺ + 5e⁻ = Cl⁻ + 4H₂O | [ClO₂⁻] = K_{sw} [Cl⁻] [H⁺]⁴ [e⁻]⁶ | \( E_{\text{em}} = 1.50 \text{ V} \) |
| 16  | ClO⁻ + 6H⁺ + 6e⁻ = Cl⁻ + 3H₂O | [Cl⁻] = K_{sw} [ClO⁻] [H⁺]⁵ [e⁻]⁶ | \( E_{\text{em}} = 1.45 \text{ V} \) |
| 17  | ClO⁻ + 8H⁺ + 8e⁻ = Cl⁻ + 4H₂O | [Cl⁻] = K_{sw} [ClO⁻] [H⁺]⁶ [e⁻]⁸ | \( E_{\text{em}} = 1.38 \text{ V} \) |
| 18  | 2ICl + 2e⁻ = I⁻ + 2Cl⁻ | [I⁻][Cl⁻] = K_{sw} [ICl] [e⁻]² | \( E_{\text{em}} = 1.105 \text{ V} \) |
| 19  | ICl = I⁻ + Cl⁻ | [I⁻][Cl⁻] = K_{sw} [ICl] | \( \log K = 0.2 \) |
| 20  | IC₅ = Cl⁻ + Cl⁻ | [IC₅][Cl⁻] = K_{sw} [IC₅] | \( \log K = 2.2 \) |
| 21  | H₂O + H⁺ + OH⁻ | [H⁺][OH⁻] = K_{sw} | \( pK_{sw} = 14.0 \) |

Figure 1 (A) \( \text{pH} = \text{pH}(\Phi) \) and (B) \( \Phi = \Phi(\text{pH}) \) relationships plotted for the system NaOH \( \Rightarrow \) HIO.

Base equilibria in non-redox systems [3,21-23]. However, the dynamic \( \beta_j \) and windowed \( \beta_j \) buffer capacities can be also related to acid-base equilibria in redox systems. The \( \beta_j \) is formulated as follows [3,21).

\[
\beta_j = \frac{\text{dc}}{\text{dpH}} \quad \text{(2)}
\]

where

\[
c = \frac{CV}{V_0 - V} \quad \text{(3)}
\]

It is 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 \( A \) (C₀ mol/L), and then Equation 3 can be rewritten as follows

\[
c = \Phi - \frac{C_0}{C + \Phi \cdot C_0} \quad \text{(4)}
\]
where $\Phi$ is the fraction titrated (Equation 1). Then we get

$$\beta = \frac{dc}{d\Phi} \left| \frac{C}{C+\Phi} - \frac{C}{C} \right|$$

where

$$\eta = \frac{dpH}{d\Phi}$$

is the sharpness index on the titration curve. For comparative purposes, the absolute values, $|\beta|$ and $|\eta|$, for $\beta$ (Equations 1 and 5) and $\eta$ (Equation 6) are considered. At $C_0/C << 1$ and small $\Phi$ value, from Equation 3 we get $a_\Phi = \hat{O}$.

The $\beta$ value is the point–assessment and then cannot be used in the case of finite pH–changes ($\Delta pH$) corresponding to an addition of a finite volume of titrant ($\beta$ is a non–linear function of pH). For this purpose, the 'windowed' buffer capacity, $\beta_v$, defined by the formula [3,21].

$$\beta_v = \frac{\Delta c}{\Delta pH}$$

has been suggested. From extension in Taylor series we have

$$\frac{\Delta c}{\Delta pH} = \beta_v + \frac{\Delta^2 c}{\Delta pH^2} \Delta pH + \frac{\Delta^3 c}{\Delta pH^3} (\Delta pH)^3 + \ldots + \beta_v + \sum_{k=1}^{\infty} \left( \frac{\Delta^k c}{\Delta pH^k} \right)_{\mu}$$

where

$$\left( \frac{d^k c}{d\Phi^k} \right)_{\mu} = \left( \frac{d^{k-1} \beta_v}{d\Phi^{k-1}} \right)_{\mu}$$

From Equations 7 and 9 we see that $\beta V$ is the first approxima-
tion of $BV$. One should take here into account that finite changes ($\Delta pH$) in pH, e.g. $\Delta pH=1$, are involved with addition of a finite volume of a reagent endowed with acid–base properties, here: base NaOH, of a finite concentration, C.

**Dynamic redox buffer capacities $\beta_v^E$ and $\beta_v^E$**

In similar manner, one can formulate dynamic buffer capacities $B_v^E$ and $B_v^E$, involved with infinitesimal and finite changes of potential $E$ values:

$$\beta_v^E = \frac{dc}{dE}$$

$$\beta_v^E = \frac{dc}{dE}$$

Where $c$ is defined by Equation 2, and then we have

$$\frac{\Delta c}{\Delta E} = \beta_v + \sum_{k=1}^{\infty} \left( \frac{d^k \beta_v}{dE^k} \right)_{\mu}$$

where

$$\frac{d^k c}{dE^k} = \left( \frac{d^{k-1} \beta_v}{dE^{k-1}} \right)_{\mu}$$

**Graphical presentation of dynamic buffer capacities in redox systems**

Referring to dynamic redox systems represented by titration curves presented in Figures 1 and 2, we plot the relationships: $\beta_v$ vs. $\Phi$, $\beta_v$ vs. pH, $\beta_v$ vs. E, and $\beta_v^E$ vs. $\Phi$, $\beta_v^E$ vs. pH, $\beta_v^E$ vs. E for the systems: (S1) NaOH $\Rightarrow$ HIO; (S2) HCl $\Rightarrow$ NaIO. The relations: (A) $\beta_v$ vs. $\Phi$, (B) $\beta_v$ vs. pH, (C) $\beta_v$ vs. E and (D) $\beta_v^E$ vs. $\Phi$, (E) $\beta_v^E$ vs. pH, (F) $\beta_v^E$ vs. E are plotted in Figures 3 and 4.
Figure 3 The relations: (A) $\beta_v$ vs. $\Phi$, (B) $\beta_v$ vs. $pH$, (C) $\beta_v$ vs. $E$ and (D) $\beta_v^c$ vs. $\Phi$, (E) $\beta_v^c$ vs. $pH$, (F) $\beta_v^c$ 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) $\beta_v^c$ vs. $\Phi$, (E) $\beta_v^c$ vs. $pH$, (F) $\beta_v^c$ vs. $E$ for (S2) HCl $\Rightarrow$ NaIO.
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 \( E=E(\Phi) \) and \( \text{pH}=\text{pH}(\Phi) \) occur in all instances.

All attainable equilibrium data related to these systems are included in the algorithms implemented in the MATLAB computer program (see 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, \( I_2(s) \), is formed, see 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 \( (I_2(s)) \) is precipitated and soluble complexes: \( I_2Cl^{-1}, ICl \) and \( ICl_2^{-1} \) are formed, see Figure 6A. Note that \( I_2(s) + I^- = I_3^{-1} \) is also the complexation reaction.

In the system S2, all oxidized forms of \( Cl^- \) were involved, i.e. the oxidation of \( Cl^- \) 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 \( Cl^- \) occurred here only in an insignificant degree (Figure 6B); the main product of the oxidation was \( Cl_2 \), whose concentration was on the level ca. \( 10^{-16}-10^{-17} \text{ mol/L} \).

Conclusion

The redox buffer capacity concepts: \( \hat{A}_V \) and \( \hat{E}_V \) 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 \( (2^{\circ}-4^{\circ}) \) and exemplified in Figures 7-9 presented in Appendix 3. For comparison, in isohydric (acid-base) systems, the buffer capacity strives for infinity. In particular, it occurs in the titration HB (C,V) ⇒ HL (C₀,V₀), where HB is a strong monoprotic acid HB and HL is a weak monoprotic acid characterized by the dissociation constant \( K_1=[H^+][L^{-1}]/[HL] \); at \( 4K_1/C^<<1 \), the isohydric condition is expressed here by the Michałowski formula \( C_0 = C + C^1 \cdot 0^{-1} \) [24-26].

The formula for the buffer capacity, suggested by Bard et al. [27] after Levie [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 the study by Michałowska-Kaczmarczyk et al. [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 [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, ΔpH, of the solution. Redox buffer capacity is also involved with the problem of interfacing in CE-MS analysis, and bubbles formation in reaction 2 

$$\text{H}_2\text{O} = \text{O}_2^{2-} + 4\text{H}^+ + 4e^-$$

at the outlet electrode in CE [36-39].

In the paper, a nice proposal of "slyke", as the name for (acid-base, pH) buffer capacity unit, has been raised [40].

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