



Speciation Diagrams in Dynamic Iodide + Dichromate System



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ABSTRACT

The speciation diagrams are suggested as a reasonable tool for explanation of processes occurred during simulated redox titration, where $K_2Cr_2O_7$ solution is added into acidified (H_2SO_4) solution of KI. The related speciation curves $\log[X_i^{z_i}] = f_i(\Phi)$ for all interesting species $X_i^{z_i}$ of the system, and the $E = E(\Phi)$ and $pH = pH(\Phi)$ relationships (Φ -fraction titrated) are plotted and discussed. The calculations made for this purpose are performed in accordance with principles of the Generalized Approach to Electrolytic Systems (GATES) with Generalized Electron Balance (GEB) involved, and realized with use of iterative computer programs offered by MATLAB. The reactions proceeding in this system can be formulated together with their efficiencies, at any stage of the titration. The stoichiometry is considered as the derivative concept when put in context with GATES/GEB.

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1. Introduction

The first attempts made to systematize the thermodynamic knowledge, involved with electrolytic redox systems and related to pairs of species formed by particular elements on different oxidation degrees, were of qualitative nature. A pioneer in the application of chemical thermodynamics to inorganic species was Latimer [1] who presented the results of his classification in the books issued in 1938 [2] and 1952 [3], where potentials at $pH = 0$ and $pH = 14$ for many electrochemical reactions were listed in compact form [4–6].

Later on, Frost [7] and Ebsworth [8] presented some diagrams [9,10], where standard free energies of various species formed by a given element were plotted *versus* the oxidation numbers of the element in these species. On this basis, the stability of particular species was qualitatively evaluated, oxidizing and reducing agents were indicated, and possibilities of disproportionation or comproportionation (synproportionation) reactions were expected. However, the information obtained from a Frost diagram refer to $pH = 0$ and $pH = 14$, as in Latimer schemes.

The Pourbaix diagrams [11,12], introduced in 1945 [13], with areas for predominating species drawn in (pH, E) coordinates, were considered [14] as the most mature form of graphical presentation of redox systems, published in numerous elaborations (books,

papers), issued also in recent years, see e.g. [15,16]. Potentials (E) on the ordinate are expressed in the SHE scale. This way, one can follow the potential changes, and hence the composition of the system for other pH values.

The Pourbaix diagrams were plotted for the species formed by particular elements in aqueous media. Any plot related to redox equilibria was obtained there on the basis of the Nernst function, formulated for the corresponding redox reaction, characterized by the standard potential value. The plots for non-redox reactions are formulated on the basis of equations for dissociation constants or stability constants of complexes, or solubility products of precipitates. The ionic product of water (K_W) is frequently involved in these relations. The complexation equilibria with other ligands were put in context with redox systems only in specific cases, e.g. [17]. In precipitation reactions, hydroxides [18–21] or (rarely) other solid species [22] were involved.

All the schemes presented above refer exclusively to bath (static) systems. This means that the status of the system is essentially defined by total concentration of an element considered, whereas concentrations of other components constituting the system and providing appropriate pH of the solution, i.e., acid or base, are omitted in considerations. In Pourbaix diagram, only a dominant species is indicated for a given pair of pH and E values.

The Pourbaix diagrams are still considered in literature as a valuable tool in reference to corrosion of metals and (passive) dissolution phenomena, for the systems composed of an excess of a solid phase in equilibrium with the solution. However, they are useless when referred to a relatively simple system, represented e.g. by aqueous, C mol/L solution of Br_2 , where pH and E values

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Notations

D	titrand
Φ	fraction titrated (Eq.id=6#1)
$(\Phi_{\text{eq}i}, Y_{\text{eq}i})$	i-th equivalence point ($i = 1,2$); $\Phi_{\text{eq}1} = 1/6$, $\Phi_{\text{eq}2} = 1$
T	titrant
V	volume [mL] of T
V_0	volume [mL] of D, $Y = E, \text{pH}$

result unequivocally from the pre-assumed C-value [23]. In more complex systems, the pH and E values depend on the pre-assumed concentrations of all components of this system. In all instances, the static redox system with defined composition is represented by only one point on the (pH, E) plane.

For obvious reasons, the Pourbaix diagrams are not applicable for dynamic redox systems, realized in titrations. Earlier approaches to redox titrations, based on stoichiometry of a summary redox reaction principle, are totally invalid, when put in context with the Generalized Approach to Electrolytic Systems (GATES) [24–30].

GATES is related to redox or non-redox systems, of any degree of complexity. In redox systems, a distinguishing/key role plays the Generalized Electron Balance (GEB), discovered by Michałowski (1992). GEB is fully compatible with other (charge and concentration) balances related to a redox system in question; the GATES referred to redox systems is denoted as GATES/GEB. Among others, GATES/GEB is related to dynamic systems, represented by a titration, where V mL of the solution, named as titrand (T), is added into V_0 mL of titrand (D), and the D + T mixture of volume $V_0 + V$ mL is obtained; V is considered as a steering variable in such systems. GATES/GEB is based on (verifiable) physicochemical knowledge, involved with equilibrium constants; this knowledge is relatively

extensive for aqueous media, although an extension of GATES/GEB on non-aqueous and binary-solvent media is also possible [31].

Two equivalent Approaches (I and II) to GEB were suggested [24–30]. In particular, the Approach I to GEB [23,32–40], named as the ‘short’ version of GEB, is based on the principle of common pool of electrons, introduced by electron-active elements named (in convention of ‘‘card game’’ [41]) as ‘‘players’’. In this convention, electron-non-active elements are named as ‘‘fans’’, and electrons are considered as ‘‘money’’ transferred between ‘‘players’’; the ‘‘fans’’ accounts are intact, in this convention. The Approach I to GEB needs a knowledge of oxidation degrees for all elements in the species participating the system considered.

This knowledge is not required in the Approach II to GEB; the known composition (chemical formula) of a species and its external charge are quite sufficient for this purpose. A knowledge of the numbers of hydrating (solvating [31]) molecules is not required, in both (I and II) Approaches. Within GATES/GEB, the roles of oxidants and reductants are not ascribed *a priori* to particular components of a system, and to the species formed in this system.

2. The system tested

We consider an interesting example of titration of V_0 mL of D containing KI (C_0 mol/L) + H_2SO_4 (C_{01} mol/L) with V mL of C mol/L $\text{K}_2\text{Cr}_2\text{O}_7$ as T. We apply the term of the fraction titrated [42]

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

providing a kind of normalization in quantitative description of the system tested. We assume $V_0 = 100$, $C_0 = 0.01$, $C = 0.1$ and the value C_{01} will be varied in the calculations made according to iterative computer program MATLAB, presented in Appendix for an algorithm involving GEB, charge and concentration balances, together with a set of relations resulting from the independent equations for the corresponding equilibrium constants. The principles of the calculation procedure are presented e.g. in [24].

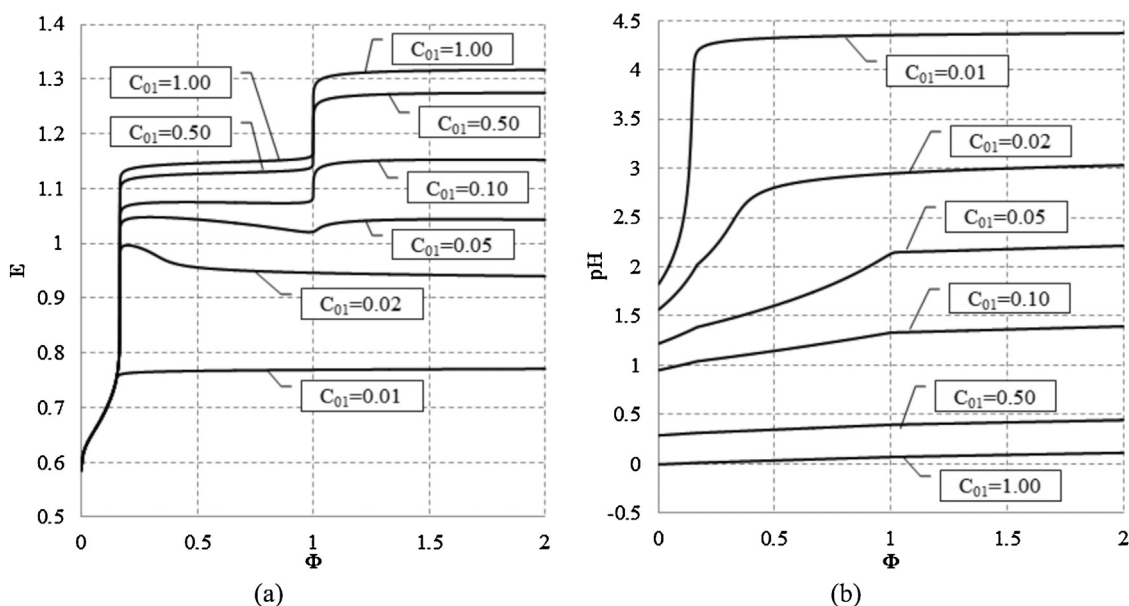


Fig. 1. The plots of (a) $E = E(\Phi)$ and (b) $\text{pH} = \text{pH}(\Phi)$ functions related to the systems obtained after addition of V mL of $C = 0.1$ mol/L $\text{K}_2\text{Cr}_2\text{O}_7$ into $V_0 = 100$ mL of the solution containing KI ($C_0 = 0.01$ mol/L) + H_2SO_4 (C_{01} mol/L); the C_{01} values are indicated at the corresponding curves.

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