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Symproportionation *versus* Disproportionation in Bromine Redox Systems

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A R T I C L E I N F O

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The paper refers to dynamic (titration) redox systems where symproportionation or disproportionation of bromine species occur. The related systems are modeled according to principles assumed in the Generalized Approach to Electrolytic Redox Systems (GATES), with Generalized Electron Balance (GEB) concept involved in the GATES/GEB software. The results obtained from calculations made with use of iterative computer programs prepared according to MATLAB computational software, are presented graphically, as *2D* and *3D* graphs.

1. Introduction

This paper concerns two opposite processes involved with redox reactions, named as disproportionation [1] (dismutation [2]), and symproportionation [3–5] (also known as synproportionation [6], conproportionation [7–10] comproportionation [11,12]) reactions, see [13]. The adjective "proportionate" means "being in proper proportion", or "degree when considered in relation to something else" [14]. Disproportionation is a special type of redox reaction, where a compound/species on an intermediate oxidation number of an element is transformed – simultaneously – to the species with lower and higher oxidation numbers of this element; it means that this element must form the species with at least three different oxidation numbers. For example, bromine forms the species with five (−1, −1/3, 0, 1, 5) oxidation numbers, see Fig. 1; e.g. Br in bromine (Br_2) and BrO^- has intermediate oxidation numbers: 0 and 1, respectively. The term dismutation is referred rather to disproportionation reactions in biological systems, associated with superoxide dismutases (SODs) – the enzymes catalyzing a dismutation of toxic superoxide (O_2^-) radical. Disproportionation of inorganic sulfur species, such as thiosulfate ($S_2O_3^{2-} + H_2O = SO_4^{2-} + HS^- + H^+$) and elemental sulfur ($3\mathbf{S} + 2FeOOH = SO_4^{2-} + 2\mathbf{FeS} + 2H^+$) is involved with bacterial growth [15–18]. It should be noted that the term "disproportionation" is sometimes related not to redox reactions, but to simultaneous ability of a species for acceptance and dissociation of protons (acid-base disproportionation, autoionization) [19,20]. Catalytic effects involved with some disproportionation processes were considered in [21,22]. A disproportionation in some metastable systems can result from a catalytic action [23].

Symproportionation is a process where two reactants containing the same element like Br, with different oxidation numbers, react with formation of the species having intermediate oxidation number(s) of this element (Fig. 1). In further parts of this paper, the symproportionation concept be extended on the case with three reactants formed by the same element participating in the symproportionation.

The disproportionation and symproportionation of the related element can be caused by a compound having none oxidative or reductive properties in defined media, e.g., NaOH [24] or H_2SO_4. Smaller disproportionation or symproportionation effects result from dilution with water [25].

On the basis of GATES/GEB, see [26] and earlier references cited therein, we consider the disproportionation and symproportionation as interdependent phenomena occurred in dynamic redox systems (aqueous media) involved with bromine. The dynamic process is realized according to titrimetric mode, where V mL of titrant (T) is added into V_0 mL of titrand (solution titrated, D) at a given point of the titration, see Table 1. Additivity in the volumes is

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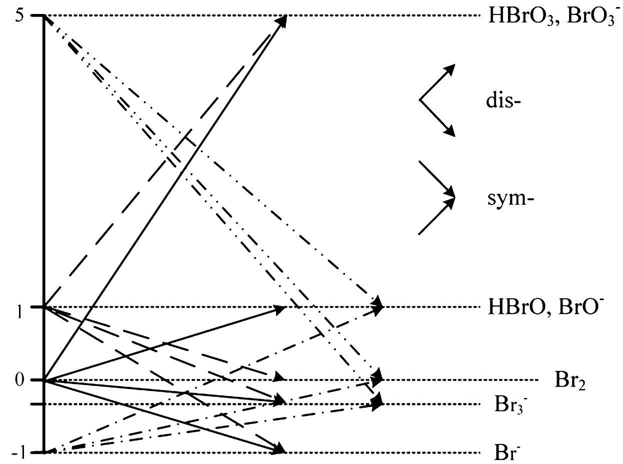

Fig. 1. Schemes of disproportionation and symproportionation of bromine and hypobromite species.

assumed, i.e., the volume of the D+T system thus formed is $V_0 + V$ mL. An impact of different components on equilibria in the D + T system is demonstrated. The processes occurring in more complex D + T systems, will be considered first in context of formation of the appropriate titrand (D). The speciation diagrams obtained from calculations made according to iterative computer programs, are the basis to formulate the reactions occurring on different stages of the relevant processes, along with their relative efficiencies. The calculations are made for pre-assumed concentrations of particular compounds in D and T. The knowledge about maximal solubilities of these compounds in water is taken into account.

The systems with bromine and chlorine species are very grateful subject to considerations, due to the fact that they involve the elements forming the species on many oxidation states. Besides, the effect of acidity, resulting from presence of different components, is clearly marked out here.

2. Formulation of balances

To formulate the balances in a short/compact manner for 9 systems presented in Table 1, we apply the following segments:

$$\alpha = [H^+] - [OH^-] = 10^{-pH} - 10^{pH-14} \quad (1)$$

$$\Omega_{1Br} = (Z\text{-}5)([HBrO_3] + [BrO_3^-]) + (Z\text{-}1)([HBrO] + [BrO^-]) + 2Z[Br_2] + (3Z+1)[Br_3^-] + (Z+1)[Br^-] \quad (2)$$

$$\Omega_{2Br} = [BrO_3^-] + [BrO^-] + [Br_3^-] + [Br^-] \quad (3)$$

$$\Omega_{3Br} = [HBrO_3] + [BrO_3^-] + [HBrO] + [BrO^-] + 2[Br_2] + 3[Br_3^-] + [Br^-] \quad (4)$$

$$\Omega_{2S} = [HSO_4^-] + 2[SO_4^{2-}] \quad (5)$$

$$\Omega_{3S} = [HSO_4^-] + [SO_4^{2-}] \quad (6)$$

The segments (1) – (6) are involved in: GEB, charge and concentration balances specified in Table 1.

Three other Systems (10 – 12) are also considered. The Systems 10 and 11 are used for explanation of a more complex System 12. In

Table 1
Some details and notations involved with D + T systems tested; C – concentration [mol/L] of reagent in titrant (T); C_0, C_{01}, C_{02}, C_{03}–concentrations [mol/L] of NaBr, Br_2, NaBrO and H_2SO_4 in titrand (D), resp.; V_0–volume [mL] of D; V – volume [mL] of T; Z = 35–atomic number for Br.

System no.	D (V_0)	T (V)	GEB	Charge balance	Conc. balances
1	NaBr (C_0)	Br_2 (C)	$\Omega_{1Br} = P_1$	$\alpha - \Omega_{2Br} + R_1 = 0$	$\Omega_{3Br} = Q_1$
2	NaBr (C_0) + H_2SO_4 (C_{03})	Br_2 (C)	$\Omega_{1Br} = P_2$	$\alpha - \Omega_{2Br} - \Omega_{2S} + R_2 = 0$	$\Omega_{3Br} = Q_2$ $\Omega_{3S} = \Sigma$
3	NaBr (C_0)	$KBrO_3$ (C)	$\Omega_{1Br} = P_3$	$\alpha - \Omega_{2Br} + R_3 = 0$	$\Omega_{3Br} = Q_3$
4	NaBr (C_0) + H_2SO_4 (C_{03})	$KBrO_3$ (C)	$\Omega_{1Br} = P_4$	$\alpha - \Omega_{2Br} - \Omega_{2S} + R_4 = 0$	$\Omega_{3Br} = Q_4$ $\Omega_{3S} = \Sigma$
5	NaBr (C_0) + Br_2 (C_{01})	$KBrO_3$ (C)	$\Omega_{1Br} = P_5$	$\alpha - \Omega_{2Br} + R_5 = 0$	$\Omega_{3Br} = Q_5$
6	NaBr (C_0) + Br_2 (C_{01}) + H_2SO_4 (C_{03})	$KBrO_3$ (C)	$\Omega_{1Br} = P_6$	$\alpha - \Omega_{2Br} - \Omega_{2S} + R_6 = 0$	$\Omega_{3Br} = Q_6$ $\Omega_{3S} = \Sigma$
7	NaBr (C_0)	NaBrO (C)	$\Omega_{1Br} = P_7$	$\alpha - \Omega_{2Br} + R_7 = 0$	$\Omega_{3Br} = Q_7$
8	NaBr (C_0) + H_2SO_4 (C_{03})	NaBrO (C)	$\Omega_{1Br} = P_8$	$\alpha - \Omega_{2Br} - \Omega_{2S} + R_8 = 0$	$\Omega_{3Br} = Q_8$ $\Omega_{3S} = \Sigma$
9	NaBr (C_0) + NaBrO (C_{02})	$KBrO_3$ (C)	$\Omega_{1Br} = P_9$	$\alpha - \Omega_{2Br} + R_9 = 0$	$\Omega_{3Br} = Q_9$

$P_1 = P_2 = ((Z+1)C_0V_0 + 2ZCV)/(V_0 + V)$
$P_3 = P_4 = ((Z+1)C_0V_0 + (Z-5)CV)/(V_0 + V)$
$P_5 = P_6 = ((Z+1)C_0V_0 + 2ZC_{01}V_0 + (Z-5)CV)/(V_0 + V)$
$P_7 = P_8 = ((Z+1)C_0V_0 + (Z-1)CV)/(V_0 + V)$
$P_9 = ((Z+1)C_0V_0 + (Z-1)C_{02}V_0 + (Z-5)CV)/(V_0 + V)$

$R_1 = R_2 = C_0V_0/(V_0 + V)$

$Q_1 = Q_2 = (C_0V_0 + 2CV)/(V_0 + V)$
$Q_3 = Q_4 = Q_7 = Q_8 = R_3 = R_4 = R_5 = R_6 = R_7 = R_8 = (C_0V_0 + CV)/(V_0 + V)$
$Q_5 = Q_6 = (C_0V_0 + 2C_{01}V_0 + CV)/(V_0 + V)$
$Q_9 = R_9 = (C_0V_0 + C_{02}V_0 + CV)/(V_0 + V)$

$\Sigma = C_{03}V_0/(V_0 + V)$