

# Generalization of the Reduction Degree

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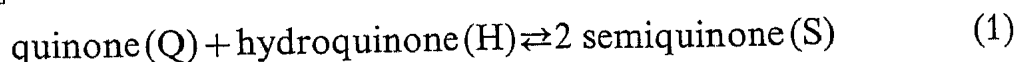
The reduction degree is in many photoredox systems an invariant under irradiation. Therefore it is an important degree of freedom in these systems. We give a general definition of the reduction degree. To illustrate the application and the practical value of this definition, the iron iodine system is discussed.

In vielen Photoredoxsystemen ist der Reduktionsgrad eine Invariante unter Belichtung. Er ist ein wichtiger Freiheitsgrad dieser Systeme. In der vorliegenden Arbeit wird eine allgemeine Definition des Reduktionsgrades gegeben. Die Verwendung und der praktische Nutzen dieser Definition werden am Beispiel des Jod/Eisen-Systems illustriert.

## 1. Introduction

From a mechanistic point of view photoredox systems can be rather complicated. It is therefore worth-while to study those parameters carefully, which only depend on the stoichiometry of the reactions. An important entity of this kind is the reduction degree which we call  $r$ . It is a measure for the number of redox equivalents which are donated to a system relative to a well defined starting position and characterizes this system, whether or not it performs a photoredox reaction under illumination.

The reduction degree  $r$  has been introduced to discuss redox systems of the type [1]:

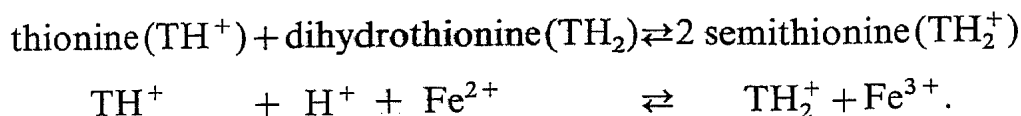


$$r = \frac{[S] + 2[H]}{2 \cdot \{[Q] + [H] + [S]\}}; \quad 0 \leq r \leq 1. \quad (2)$$

A different definition of the oxidation degree or reduction degree is successfully used to describe e.g. redox behaviour of transition metal ions in

zeolites [2], [3]. We have found that the reduction degree — defined in a more systematic way — can be used as an important degree of freedom not only to understand systems at equilibrium but also to describe photoredox systems far from equilibrium [4]. Hereafter we give a general definition for the reduction degree and illustrate its application in a photoredox system which has not been described correctly to this date.

It is useful to introduce first an extension of the definition (2) for the thionine/iron system [5], [6]. The following reactions are considered:



The symbol  $\rho$  is used for the number of redox equivalents of a mole of molecules or fragments relative to an oxidation state of the same species which by definition has a reduction degree of zero. It is reasonable to define  $\rho(\text{TH}^+) = 0$  and  $\rho(\text{Fe}^{3+}) = 0$ . From this follows  $\rho(\text{TH}_2^+) = 1$ ,  $\rho(\text{TH}_2) = 2$ , and  $\rho(\text{Fe}^{2+}) = 1$ .  $\{\text{TH}^+, \text{TH}_2^+, \text{TH}_2\}$  is called independent redox system number 1, and therefore  $\{\text{Fe}^{3+}, \text{Fe}^{2+}\}$  is the independent redox system number 2. By introducing the symbols  $G_1^\circ$  and  $G_2^\circ$  for the total concentrations of the two systems

$$G_1^\circ = [\text{TH}^+] + [\text{TH}_2^+] + [\text{TH}_2]$$

$$G_2^\circ = [\text{Fe}^{3+}] + [\text{Fe}^{2+}]$$

we define:

$$r = \frac{+ \frac{\{\rho(\text{TH}^+) [\text{TH}^+] + \rho(\text{TH}_2^+) [\text{TH}_2^+] + \rho(\text{TH}_2) [\text{TH}_2]\}}{\{\rho(\text{Fe}^{3+}) [\text{Fe}^{3+}] + \rho(\text{Fe}^{2+}) [\text{Fe}^{2+}]\}}}{\rho_{\max}(\text{system 1}) G_1^\circ + \rho_{\max}(\text{system 2}) G_2^\circ}$$

or by inserting the values for  $\rho$ :

$$r = \frac{\{[\text{TH}_2^+] + 2[\text{TH}_2]\} + \{[\text{Fe}^{2+}]\}}{2G_1^\circ + G_2^\circ}.$$

The values of  $r$  lie between 0 and 1.

## 2. Definition

$\rho_{k_i}$  is the number of redox equivalents of a mole of molecules or fragments  $k_i = 1_i, 2_i, \dots, K_i$  relative to an oxidation state of the same species which by definition has a reduction degree of zero. The index  $i = 1, \dots, S$  counts the independent systems.  $d_{k_i}$  is the density of the  $k_i$ -th molecule or fragment. It is reasonable to define  $\rho_i^+$  and  $\rho_i^-$  by the following equations:

$$\rho_i^+ = \text{MAX}(\rho_{1_i}, \rho_{2_i}, \dots, \rho_{K_i}) \\ \rho_i^- = \text{MIN}(\rho_{1_i}, \rho_{2_i}, \dots, \rho_{K_i}). \quad (3)$$

Now it is possible to define the reduction degree in a general way:

$$r^+ = \frac{\sum_i \left( \sum_{k_i=1}^{K_i} \rho_{k_i} d_{k_i} \right)}{\sum_i \rho_i^+ G_i^\circ}; \quad \text{only for } \rho_i^+ > 0 \quad (4)$$

$$r^- = \frac{\sum_i \left( \sum_{k_i=1}^{K_i} \rho_{k_i} d_{k_i} \right)}{\sum_i |\rho_i^-| G_i^\circ}; \quad \text{only for } \rho_i^- < 0. \quad (5)$$

In order to normalize  $r^+$  and  $r^-$  the  $G_i^\circ$  have to be chosen in a way that the following equations are fulfilled for all independent systems  $i$ :

$$1 = : \frac{\sum_{k_i=1}^{K_i} \rho_{k_i} d_{k_i}^+}{\rho_i^+ G_i^\circ} \quad (6)$$

$$-1 = : \frac{\sum_{k_i=1}^{K_i} \rho_{k_i} d_{k_i}^-}{|\rho_i^-| G_i^\circ}$$

$d_{k_i}^+$ ,  $d_{k_i}^-$  are the densities at the highest reduction resp. oxidation state of the system. In this state the following conditions are fulfilled:

$$d_{k_i}^+ = 0 \quad \text{for } \rho_{k_i} < \rho_i^+$$

$$d_{k_i}^- = 0 \quad \text{for } \rho_{k_i} > \rho_i^-.$$

The reduction degrees  $r^+$ ,  $r^-$  can now only have the values:

$$0 \leq r^+ \leq 1 \quad (7)$$

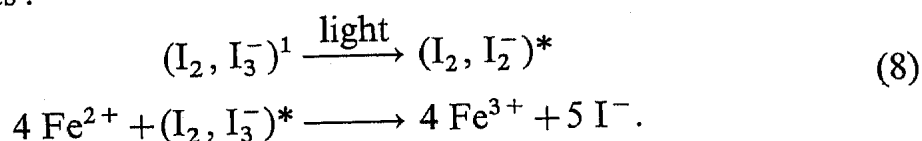
$$-1 \leq r^- \leq 0.$$

The boundary values (0, 1) resp. (-1, 0) may only be reached asymptotically.

### 3. Example

To illustrate the practical value of these definitions, let us discuss the completely reversible iron/iodine system in 0.1 molar sulfuric acid [7]. The following photoreactions and dark reactions have to be considered:

*Photoreactions:*



<sup>1</sup> It seems that  $I_2$  as well as  $I_3^-$  are photoactive. The separate quantum yields are not known [12].

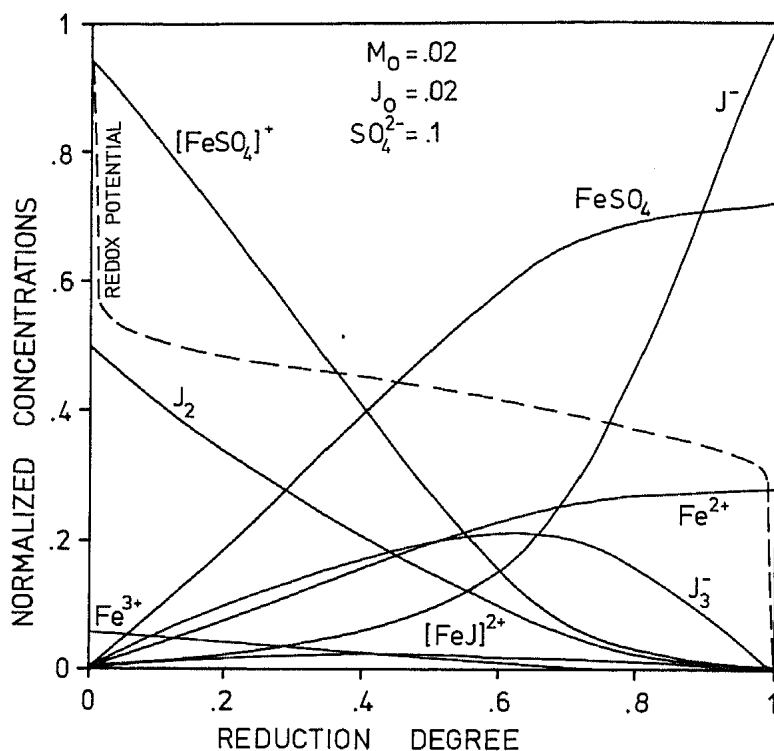
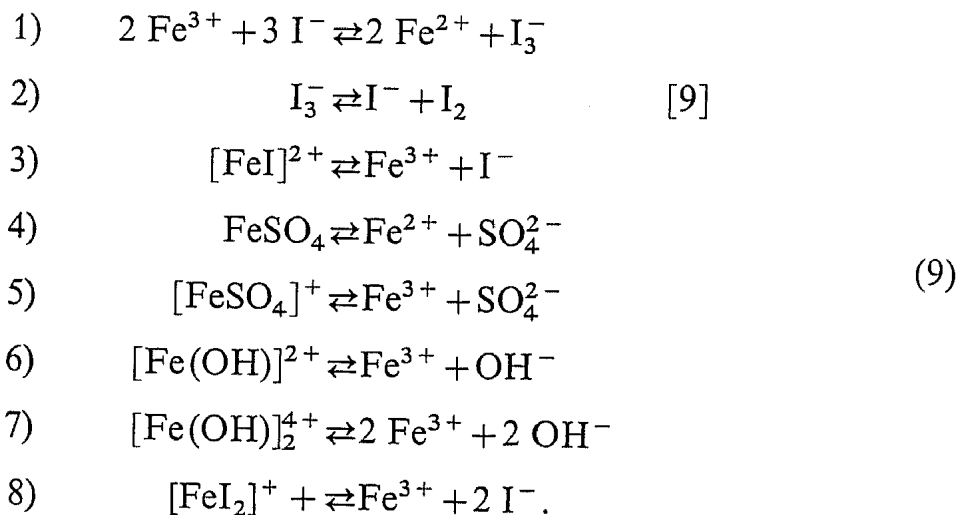


Fig.1. Normalized equilibrium concentrations ( $G_1^0 = 1$ ;  $G_2^0 = 1$ ) in 0.1 molar sulfuric acid versus the reduction degree.  $G_1^0 = I_0$  [mol/l],  $G_2^0 = M^0$  [mol/l]

Dark reactions<sup>2</sup>: [8]



Since  $\text{OH}^-$  and  $\text{SO}_4^{2-}$  do not exchange any redox equivalents, there are only two independent systems:

$$\begin{aligned}
 i=1; \quad & \text{I}^-, \text{I}_2, \text{I}_3^- \\
 i=2; \quad & \text{Fe}^{2+}, \text{Fe}^{3+}. \quad (10)
 \end{aligned}$$

<sup>2</sup> For clearness' sake, we do not consider the solubility of  $\text{I}_2$ . It will be introduced in a paper describing experiments on the iodine/iron system [12].

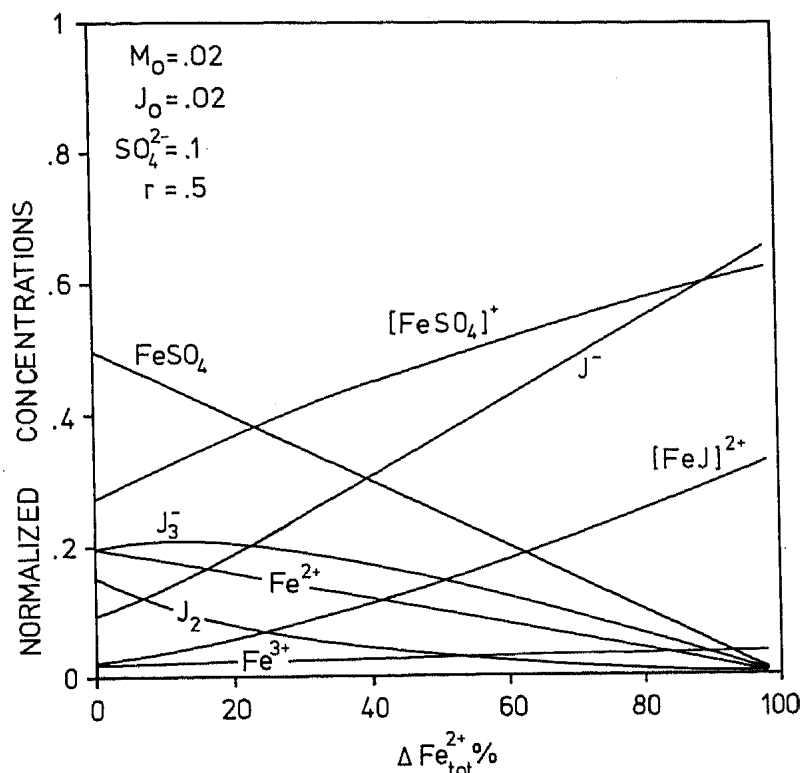


Fig. 2. Normalized concentrations in photostationary states versus the light induced decrease of iron (II) species assuming the reactions 2) to 8) are in equilibrium.  $\Delta Fe_{tot}^{2+} \%$  is defined as the absolute value of

$$\frac{\Delta[Fe^{2+}] + \Delta[FeSO_4]}{[Fe^{2+}]_{eq} + [FeSO_4]_{eq}} \cdot 100$$

$\Delta Fe_{tot}^{2+} \% = 0$  corresponds to the equilibrium position  $r = 0.5$  in Fig. 1

From the definition  $\rho(I_2) = 0$ ,  $\rho(Fe^{3+}) = 0$  follows that  $\rho(I^-) = 1$ ,  $\rho(I_3^-) = 1$ ,  $\rho(Fe^{2+}) = 1$ . Condition (6) can be satisfied with the following values for  $G_1^\circ$  and  $G_2^\circ$ :

$$\begin{aligned} G_1^\circ &= [I^-] + 2[I_2] + 3[I_3^-] + [FeI]^{2+} + 2[FeI_2]^+ \\ G_2^\circ &= [Fe^{2+}] + [Fe^{3+}] + [FeI]^{2+} + [FeI_2]^+ + [FeSO_4] \\ &\quad + [FeSO_4]^+ + [Fe(OH)]^{2+} + 2[Fe(OH)_2]_2^{4+}. \end{aligned} \quad (11)$$

Since  $\rho_1^+$ ,  $\rho_2^+$  are both equal to +1 and  $\rho_1^-$ ,  $\rho_2^-$  are equal to zero, only  $r^+$  is defined:

$$r^+ = \frac{\{[I^-] + [I_3^-] + [FeI]^{2+} + 2[FeI_2]^+\} + \{[Fe^{2+}] + [FeSO_4]\}}{G_1^\circ + G_2^\circ}. \quad (12)$$

Figure 1 shows the equilibrium concentrations of the different species versus the reduction degree. Calculations have been carried out with the help of a method described in an earlier paper [10]. In 0.1 molar sulfuric acid the complexes  $[Fe(OH)]^{2+}$ ,  $[Fe(OH)_2]_2^{4+}$ ,  $[FeI_2]^+$  can be neglected. The

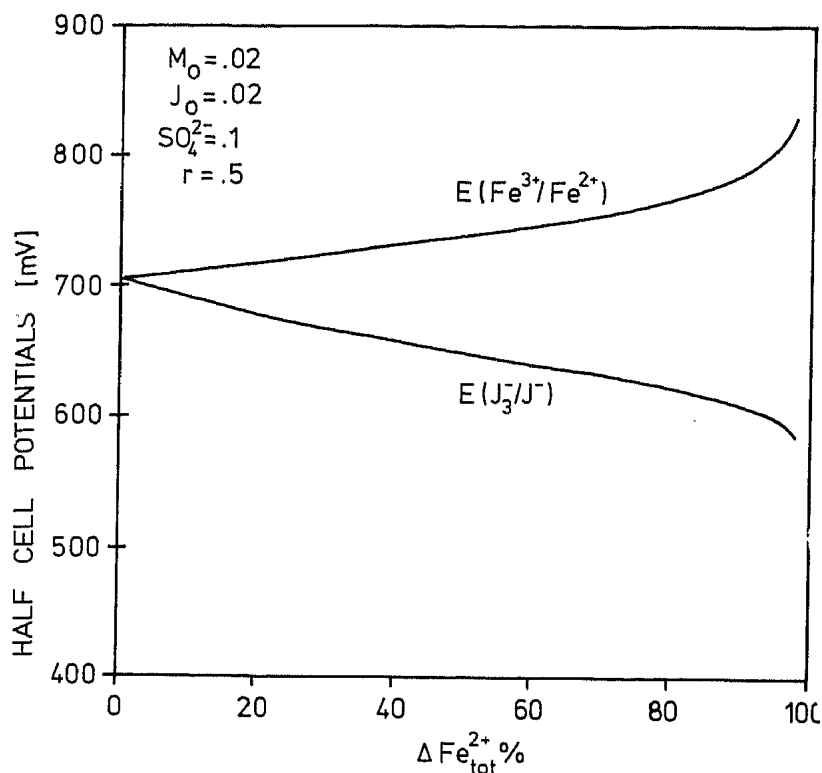


Fig. 3. Half cell potentials in the photostationary states relative to the standard hydrogen electrode, calculated from the concentrations plotted in Figure 2

concentrations in the photostationary states resulting from a reduction degree of  $r^+ = 0.5$  are plotted in Figure 2. It is assumed that in the photostationary states the reactions 2) to 8) are at equilibrium. Reaction 1) is not at equilibrium under illumination.

We wish to point out that the reduction degree is an invariant under irradiation.

Figure 3 finally shows the half cell potentials under irradiation. These half cell potentials can be measured approximately by means of selective electrodes [4], [11], [12].

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