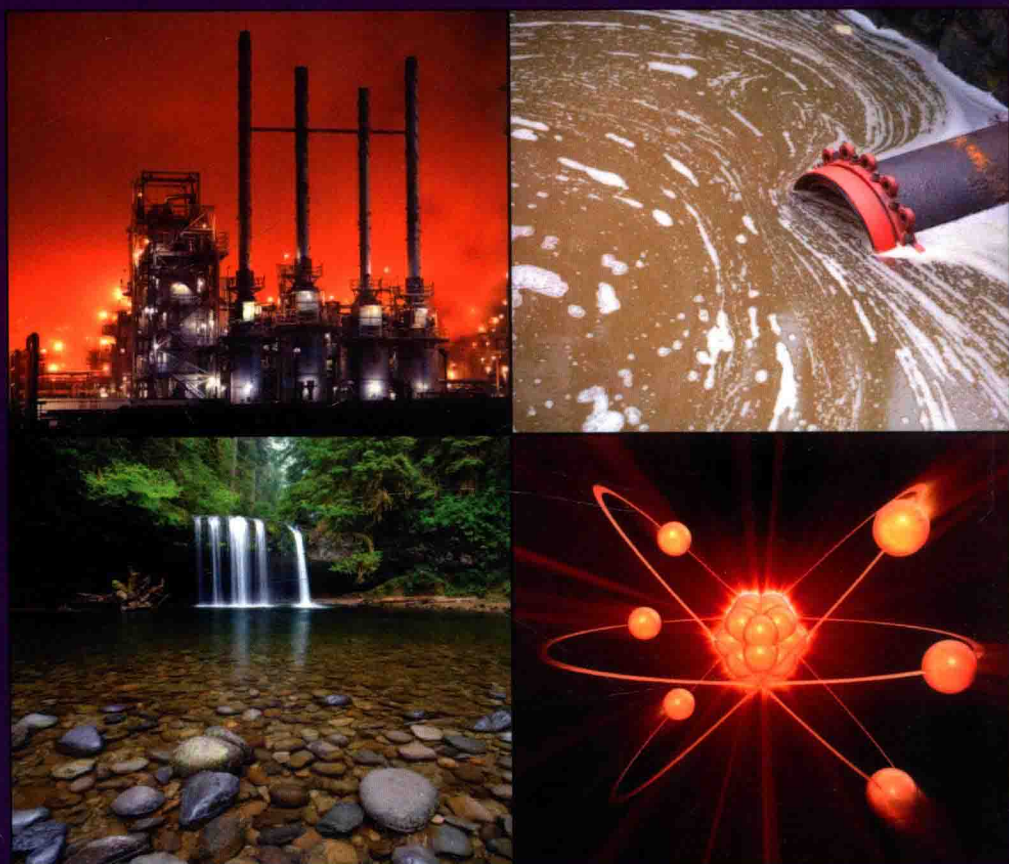


Chemical Oxidation Applications for Industrial Wastewaters

Olcay Tünay, Işık Kabdaşlı, Idil Arslan-Alaton and Tuğba Ölmez-Hancı



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Chemical Oxidation Applications for Industrial Wastewaters

Foreword

This book is intended to cover chemical oxidation applications applied to industrial wastewater treatment. At the first glance, the subject may seem rather specific, however as anybody who is involved in industrial waste treatment thinks about the place of chemical oxidation in industrial wastewater control as well as the recent developments in the field realises the scope of the subject and may be the need for a monograph focused on this subject. The authors devoted at least last two decades to chemical wastewater treatment methods and the applications to industrial wastewaters and they mostly collaborate in research and application. The idea of writing this book was almost spontaneous and unanimous as we discuss the merits of chemical oxidation and its commonplace in industrial wastewater treatment. Then, the process of writing the book has begun.

The book aims to cover to an up-to-date review, discussion and evaluation of the chemical oxidation applications to industrial wastewaters. Within this context, all existing methods and technologies as well as new and developing methods have been evaluated with specific reference to industrial wastewaters and from the stand points of both theoretical background and applicational aspects such as cost and operation. The wide spectrum of the methods employed in the field call for a review of theoretical basis of the chemical oxidation and the applied methods in the field which have been the subject of first chapter. Chapters 2–9 have been devoted to applications to specific industries which have been selected considering the environmental importance and worldwide common use of the industry as well as the role of chemical oxidation in the treatment of wastewaters. In the last chapter, several industrial process wastewaters and municipal landfill leachate have been the subject of review due to increasing use of chemical oxidation application for their wastewater control.

The book is written for graduate level students, researchers and practitioners. However, design aspects, cost and operation information about the processes address a wider audience.

Istanbul, 2010

Olcay Tünay
Işık Kabdaşlı
Idil Arslan-Alaton
Tuğba Ölmez-Hancı

To our families

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Chapter 1

Introduction to redox reactions

1.1 INTRODUCTION

1.1.1 Redox processes

Chemical oxidation is a process in which the oxidation state of an atom is increased. The atom being oxidised may be in the elemental form or in a substance like a molecule or ion. The term “*oxidised*” is also used for the substance containing the oxidised atom. If the oxidation takes place within biological processes the terms biological or biologically-mediated oxidation are used. Chemical reduction is the process by which the oxidation state, the valence, of an atom is reduced. Every oxidation reaction is accompanied by a reduction reaction and these reactions are termed redox reactions.

For inorganic redox reactions, oxidation and reduction are brought about by electron transfer. Oxidation is the loss of electrons and reduction is the gain of electrons by an atom. In the below example:



Sulphide ion is oxidised to elemental sulphur by losing two electrons, while elemental iodine is reduced to iodide ion by gaining two electrons. In the organic

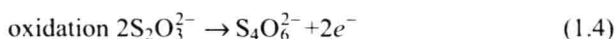
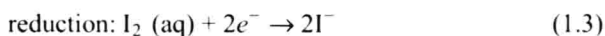
reactions, the mechanism is more complex. An organic reaction oxidation is carried out by replacement of one of the electrons making up the covalent bond between two atoms, by changing one of the atoms in a way for reversing the order of electronegativities of the atoms. If atoms A and B are tied up with a covalent bond and atom A is more electronegative than atom B, replacement of atom B by atom C which is more electronegative than atom A, through breaking the A-B bond and formation of an A-C bond, results in the oxidation of atom A. The basis of this process is expressed by the Pauling rule stating that *"In a covalent bond the charge of an atom is found by assigning each shared pair of electrons completely to the more electronegative of the two atoms sharing them. An electron pair shared by two atoms of the same electronegativity is split between them"* (Stumm and Morgan 1996).

1.1.2 Thermodynamics of redox reactions

A redox reaction is represented by two half-reactions; oxidation and reduction. This representation is quite useful in analysing the redox reactions and defining thermodynamic aspects of the reactions. The half-reactions are *"coupled"*. The redox reaction:



is represented by the following half-reactions:



In the reduction half-reaction the reactant that accepts electrons is termed *"oxidant"*. In the oxidation half-reaction the reactant that donates electrons is termed *"reductant"*. An important definition in redox stoichiometry is *"equivalent weight"*. Equivalent weight is calculated by dividing the formula weights of reductant and oxidant to number of electrons in the half-reactions. In thermodynamics spontaneity of a reaction occurring under constant pressure is determined using Gibbs free energy. The negative free energy change indicates that the redox reaction is spontaneous in the direction it is written. The same approach is applied to half-reactions.

As indicated above half-reactions are hypothetical presentations. A half-reaction cannot occur unless it is combined with another half-reaction to yield a

redox reaction provided that the redox reaction is thermodynamically possible. So the two half-reactions are “coupled”. They are coupled because the free electrons cannot exist in solution and the electrons given off in a half-reaction must be received by a substance taking part in the second half-reaction. On the other hand, they are energetically coupled in that the spontaneity of the reactions is judged by the value of the free energy change of final redox reaction. Free energy change of any half-reaction may be positive indicating it is not spontaneous, but the half-reaction proceeds as long as free energy change of the redox reaction is negative, since the half-reactions are energetically coupled. Electron transfer between the substances is readily carried out in solution. Now assume that the half-reactions (Eq. 1.3) and (Eq. 1.4) are attempted to be realised in two separate containers marked I and II in Figure 1.1. None of the half-reactions, even the one having negative free energy can occur. If electron transfer is provided through electrodes dipped in both containers and they are connected with a conductor wire, the half-reactions still do not occur, because electroneutrality condition cannot be satisfied in both containers. In Container I the lack of electrons causes positive charge accumulation and in Container II negative charges will accumulate. If we provide ion transfer between the containers electroneutrality is satisfied and half-reactions begin to take place and electrons flow through the connecting wire. Electron flow creates electric current whose energy corresponds to free energy change of the total redox reaction. Such a system is named as an electrochemical cell.

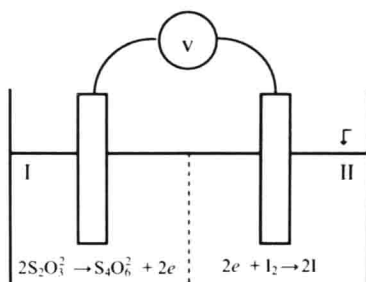


Figure 1.1 Iodine-thiosulphate reaction.

An electrochemical cell (or galvanic cell) is a device for producing an electric current (potential difference) as a result of electrochemical (redox) reactions. A cell consists of two electrodes, an electrolyte (electrolytic conductor) in which electrodes are immersed and a metal conductor by which electrodes are connected. Metal conductor and electrolyte are also called as external circuit and internal

circuit, respectively. The potential difference of the electric current obtained by the operation of the cell is (more precisely the maximum potential difference during reversible operation of the cell) called the electromotive force (*e.m.f.*) The *e.m.f.* of a cell is equal to the algebraic sum of the potential differences (jumps) at the interfacial boundaries (surfaces of electrodes) of the cell. *e.m.f.* of a cell is denoted as E_{cell} , and is defined, in a similar manner to reaction free energy, as:

$$E_{\text{cell}} = E_{\text{ox}} + E_{\text{red}} \quad (1.5)$$

where E_{ox} and E_{red} denote potentials of oxidation and reduction half-reactions, respectively. These potentials are termed electrode potentials of the half-reactions. Electrode potential of a half-reaction is a characteristic of the reaction and related to the free energy of this half-reaction.

A cell produces electricity on its external circuit. This corresponds to the work by the cell on the surroundings. Electrical work is defined as:

$$-w_{\text{el}} = Q \times E \quad (1.6)$$

where w_{el} is the electrical work and Q is the charge which is moved across a potential difference E . Negative sign of w_{el} is due to the convention that the work (energy) transferred to surroundings by the system is taken negative. The charge Q is carried by the electrons. Faraday constant (F) expresses the charge of a mole of electrons and equals 96,490 Coulomb per mole of electrons. n denotes the number of moles of electrons per mole of reaction with the unit (mol/mol). Then total charge, Q , passing through the external circuit is:

$$Q = n \times F \quad (1.7)$$

The electrical work is, therefore:

$$-w_{\text{el}} = n \times F \times E \quad (1.8)$$

On the other hand, the non-expansion work of a reversible electrochemical cell, in other words ΔG equals w_{el} , then:

$$\Delta G = -n \times F \times E \quad (1.9)$$

is the equation that relates free energy to the *e.m.f.* of the cell, or electrode potential of half-reactions. E is measured in volts. Since:

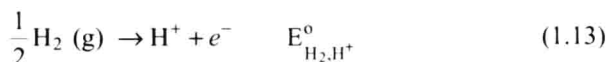
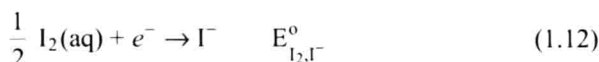
$$\text{Joule} = \text{Coulomb} \times \text{volt} \quad (1.10)$$

the units of ΔG are J/mol, or if two sides of Eq. (1.9) are divided by 4.18 (this is made by assuming that the Faraday constant as 23,060) in cal/mol.

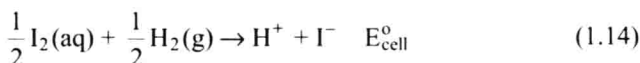
Since individual half-cell reactions do not occur, absolute value of a half-cell potential cannot be determined. However, a half-cell potential can be measured in relation to the potentials of other half-cells. This leads to adopting a reference half-cell reaction and determining the potentials of all other half-reactions against this reference half-reaction. For this purpose, the hydrogen half-cell has been adopted universally as the reference cell. The half-cell reaction:



is assigned the standard potential of 0.000 V under standard conditions (1 atm H_2 pressure, 25°C and $\text{pH} = 0$). This assignment is consistent with $\Delta G_f^\circ = 0$ for $\text{H}_2(\text{g})$ and $\text{H}^+(\text{aq})$. The hydrogen reference electrode under standard conditions is named standard hydrogen electrode and abbreviated SHE. For the cell formed by the below reactions where E° indicates standard conditions:



E_{cell}° is determined by summation of the half-reactions as:



and:

$$E_{\text{cell}}^\circ = E_{\text{I}_2, \text{I}^-}^\circ + E_{\text{H}_2, \text{H}^+}^\circ \quad (1.15)$$

by definition $E_{\text{H}_2, \text{H}^+}^\circ = 0$ and:

$$E_{\text{cell}}^\circ = E_{\text{I}_2, \text{I}^-}^\circ \quad (1.16)$$

Electrode potential of a half-reaction determined against hydrogen reference electrode, under standard conditions, is termed standard electrode potential. In the above given example E_{cell}° is the standard electrode potential of half-reaction $E_{\text{I}_2, \text{I}^-}^\circ$. Direction of the reaction is important for the expression of the electrode

potential. Standard electrode potential is universally adopted to be the potential of a half-reaction written in the direction of reduction. Since $E_{12,1}^{\circ}$ -half-reaction is written in the direction of reduction the value of $E_{12,1}^{\circ}$ is its standard electrode potential. Electrode potentials of some reactions are tabulated in Table 1.1. The superscript in the symbol E° denotes that all the reactions are at standard state. Standard state indicates that reactions are at 1 atm pressure, 25°C temperature while all reactants and products in the reactions in unit activity or 1 molar where it is applicable.

Table 1.1 Standard electrode potentials (Hendricks 2006)

Half-Reaction	E° (Volt)
$H^{+} + e^{-} \rightarrow 1/2 H_2(g)$	0
$Cr_2O_7^{2-} + 14H^{+} + 6e^{-} \rightarrow 2Cr^{3+} + 7H_2O$	+1.33
$O_2(aq) + 4H^{+} + 4e^{-} \rightarrow 2H_2O$	+1.27
$O_2(aq) + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$	+0.40
$Cl_2 + 2e^{-} \rightarrow 2Cl^{-}$	+1.39
$HOCl + 2e^{-} + H^{+} \rightarrow 2Cl^{-} + H_2O$	+1.49
$OCl^{-} + 2e^{-} + H^{+} \rightarrow Cl^{-} + H_2O$	+1.72
$O_3(g) + 2H^{+} + 2e^{-} \rightarrow O_2 + H_2O$	+2.08
$H_2O_2 + 2H^{+} + 2e^{-} \rightarrow 2H_2O$	+1.78
$ClO_2 + 2H_2O + 5e^{-} \rightarrow Cl^{-} + 4OH^{-}$	+0.80
$HSO_5^{-} + 2H^{+} + 2e^{-} \rightarrow HSO_4^{-} + H_2O$	+1.85
$FeO_4^{2-} + 8H^{+} + 3e^{-} \rightarrow Fe^{3+} + 4H_2O$	+2.20

The E value of a reaction is independent of reaction stoichiometry, however, as Eq. (1.9) indicates; the ΔG value is dependent on the stoichiometry. ΔG is an extensive property and its value depends on the amount of the matter. Therefore, ΔG values of reactions are always additives. E value of an oxidation reduction reaction cannot be found by the addition of the E values of the half-reactions yielding the resulting oxidation reduction reaction. E value is an intensive property so is independent of the amount of matter. The simple addition of E values of the half-reaction is justified only for the case where number of electrons in the half-reactions is equal and cancels each other resulting in a cell reaction.

In Eq. (1.9), F and n are positive entities; therefore ΔG and E have reverse signs. A reaction is spontaneous when ΔG is a negative number. Then, redox reactions are spontaneous as their E values are positive, in other words, as they make up a cell and produce electricity. According to this thermodynamic property in actual conditions, the half-reactions determine their direction in order to yield a redox reaction with positive E value. The half-reaction with higher E value