# Oxidative Processes in Water Technology

**Lecture (2 h):** **Thursday** **$14^{15}$ - $16^{00}$, S05 T02 B16**
**Tutorial + Seminar (1h):** **Thursday** **$16^{15}$ - $17^{00}$, S05 T02 B16**

| Subject | Who? | Date | Date Tutorial |
|---|---|---|---|
| Introduction to oxidative processes and course organization | **TS/All** | **12.04.12** | |
| Fundamental reactions I | **CvS** | **19.04.12** | |
| Fundamental reactions II | **CvS** | **26.04.12** | **10.05.12** |
| Fundamental reactions III | **CvS** | **03.05.12** | **24.05.12** |
| Fundamental reactions IV | **CvS** | **10.05.12** | **31.05.12** |
| Applications in water treatment (including disinfection) I | **TS** | **24.05.12** | |
| Applications in water treatment (including disinfection) II | **TS** | **31.05.12** | **14.06.12** |
| Applications in wastewater treatment I | **JT** | **21.06.12** | **21.06.12** |
| Applications in wastewater treatment II | **JT** | **28.06.12** | **28.06.12** |
| Disinfection/transformation by-products: (Eco)toxicological evaluation | **JT** | **05.07.12** | **05.07.12** |
| Economical considerations | **JT** | **12.07.12** | **12.07.12** |
| Wrap-Up | **all** | **19.07.12** | |
| Exam | | **25.07.12** | |

Note that this is a **preliminary timetable** and may be subject of change!

Major **aims** of the course:

- Overview of routine and state-of-the-art oxidative processes used in water and wastewater treatment
- advanced understanding of fundamental transformation processes involved in technical processes
- Evaluation of advantages and drawbacks of oxidative processes for exemplary applications
- Development of criteria for the selection of appropriate technological solutions

- **Organisation**

  The course is given by Prof. Torsten Schmidt (torsten.schmidt@uni-due.de), Prof. Clemens von Sonntag (clemens@vonsonntag.de) and Dr. Jochen Türk (tuerk@iuta.de), and will be supported by the PhD students Dipl.-Chem. Alexandra Beermann (alexandra.beermann@uni-due.de) and M.Sc. Claudia vom Eyser (vomEyser@iuta.de)
- Up to eight groups of students form in the first lecture/tutorial on April 12, at best consisting of not more than 4 students (depending on the number of participants).
- Each group presents in the four tutorials up to June 14 their solution to a specified problem in a problem set handed out in the course. Their approach will be discussed. It is not the primary goal to show the correct result but to learn how to tackle such problems. When forming groups you should try to incorporate people with different levels of expertise and each group should encompass one of the foreign students who have started here with the Master course. By doing so, all of you will benefit most.
- Ca. end of May each group will receive a paper that shall be read in detail and very critically reviewed. The groups have to deliver a written review (ca. 2 pages) to the supporting PhD students and to give a short presentation on the major results discussed in the paper and the points to be criticized in the final four tutorial sessions in June/July indicated in the timetable above.

**Recommended Reading**
We recommend the following review articles for a first overview or in-depth discussion of specific oxidative processes:

U. von Gunten:
Ozonation of drinking water: Part I. Oxidation kinetics and product formation
Water Research 37 (2003) 1443–1467
Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine
Water Research 37 (2003) 1469–1487

U. von Gunten:
The basics of oxidants in water treatment. Part B: ozone reactions
Water Science & Technology—WST 55 (2007) 21-25

C. von Sonntag:
Advanced oxidation processes: mechanistic aspects
Water Science & Technology—WST 58 (2008) 1015-1021

J.J. Pignatello, E. Oliveros, A. MacKay:
Advanced Oxidation Processes for Organic Contaminant Destruction Based on the Fenton Reaction and Related Chemistry
Critical Reviews in Environmental Science and Technology 36 (2006) 1–84

The following textbooks provide a more extensive treatment of parts of the lecture:

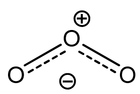
- Urs von Gunten, Clemens von Sonntag:
  Chemistry of Ozone in Water and Wastewater Treatment: From Basic Principles to Applications.
  IWA Publishing, 2012
- Christiane Gottschalk, Judy Ann Libra, Adrian Saupe:
  Ozonation of Water and Waste Water: A Practical Guide to Understanding Ozone and its Applications.
  Wiley-VCH, 2009
- Thomas Oppenländer:
  Photochemical Purification of Water and Air: Advanced Oxidation Processes (AOPs): Principles, Reaction Mechanisms, Reactor Concepts.
  Wiley-VCH, 2002

# Appendix 1: Oxidation States

## Chlorine Oxidation States

| **Oxidation State** | **-I** | **0** | **+I** | **+III** | **+IV** | **+V** | **+VII** |
|---|---|---|---|---|---|---|---|
| **Chem. Formula** | $Cl^-$ | $Cl_2$ | $HOCl/OCl^-$ | $HClO_2/ClO_2^-$ | $ClO_2$ | $HClO_3/ClO_3^-$ | $HClO_4/ClO_4^-$ |
| **Name (if acid/base of both species)** | **Hydrogen chloride/ Chloride** | **Chlorine** | **Hypochlorous acid/ Hypochlorite** | **Chlorous Acid/ Chlorite** | **Chlorine dioxide** | **Chloric acid/ Chlorate** | **Perchloric acid/ Perchlorate** |
| $pK_a$ | **-7** | | **7.5** | **1** | | **-1 to -3** | **-10** |

## Oxygen Oxidation States

| **Formal Oxidation State** | **Chem. Formula** | **Name (if acid/base of both species)** | ***pK<sub></sub>*** |
|---|---|---|---|
| **-2** | $H_2O/OH^-$ | **Water/ Hydroxide** | **15.7** |
| **-1** | $H_2O_2$ | **Hydrogen peroxide** | **11.8** |
| **-1** | $HO^{\bullet}/O^{\bullet -}$ | **Hydroxyl radical/ Oxide radical anion** | **11.8** |
| **-1** | $RO^{\bullet}$ | **Oxyl radical** | |
| **-2/3** | $H_2O_3/HO_3^-$ | | **7** |
| **-1/2** | $HO_2^{\bullet}/O_2^{\bullet -}$ | **Hydroperoxyl radical/ Superoxide radical anion** | **4.8** |
| **-1/2** | $RO_2^{\bullet}$ | **Peroxyl radical** | |
| **-1/3** | $HO_3^{\bullet}/O_3^{\bullet -}$ | **Hydrotrioxyl radical/ Ozonide radical anion** | **-2** |
| **0** | $^3O_2$ | **Triplet oxygen (ground state)** | |
| **0** | $^1O_2$ | **Singlet Oxygen** | |
| **0** | $O_3$ | **Ozone**  | |
| **0** | $O^{\bullet}$ | **Oxygen atom** | |

**R = Organic rest**

**Appendix 2: A few useful relationships (Ref.: Stumm&Morgan 1996)**

**Table 2.6. Basic Relationships for Equilibria: Fixed $T$ and $p$ Systems**

| | |
|---|---|
| 1. Chemical potential of a species | $\mu_i = \mu_i^\circ + RT \ln \{i\} = \mu_i$ $= \mu_i^\circ + RT \ln c_i\gamma_i$ |
| 2. Reference states for $\gamma_i$ | $\gamma_i \to 1$ as $x_i \to 1$ or $x_i \to 0$ ; $\gamma_i \to 1$ as $\sum m_j \to 0$ or $\gamma_i \to 1$ as $m_i \to 0$ |
| 3. Standard states for $c_i$ | $\gamma_i = 1$ and: $x_i = 1$ or $m_i = 1$ |
| 4. Reaction $\sum \nu_i M_i = 0$ | $\Delta H = \sum_i \nu_i \bar{H}_i, \quad \Delta V = \sum_i \nu_i \bar{V}_i,$ $\Delta S = \sum_i \nu_i \bar{S}_i \quad \Delta G = \sum \nu_l \mu_l$ |
| 5. State function relationship | $\Delta G = \Delta H - T\Delta S$ |
| 6. Equilibrium constant | $K = \prod_i \{i\}_{eq}^{\nu_i}$ |
| 7. Reaction quotient | $Q = \prod_i \{i\}^{\nu_i}$ |
| 8. Standard free energy and $K$ | $\Delta G^\circ$ (kJ mol$^{-1}$) $= -5.71 \log K$ at 25°C |
| 9. Free energy and $Q$ | $\Delta G = RT \ln \frac{Q}{K}$ |
| 10. $K$, $m_i$, and $\nu_i$ | $K = \left( \prod_i \left(\frac{m_i}{m^\circ}\right)^{\nu_i} \prod_i \gamma_i^{\nu_i} \right)_{eq}$ |
| 11. $K$ and $T$ | $\log \frac{K_{T_2}}{K_{T_1}} = \frac{\Delta H^\circ}{2.3R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ |
| 12. $K$ and $P$ | $\log \frac{K_{P_2}}{K_{P_1}} = -\frac{\Delta V^\circ (P_2 - P_1)}{2.3RT}$ |

A simple help with large logarithms:

$\ln 10^x = x \ln 10$