

# Water Chemistry

Lecture (2 h):

Wednesday 08<sup>15</sup> - 10<sup>00</sup>, S05 T00 B59

Tutorial+Exercise (2h):

Monday 12<sup>15</sup> - 14<sup>00</sup>, S03 V00 E59

Subject	Date	Date Tutorial
Introduction/Concepts/Organization	19.10.	
Essentials in Equilibrium and Kinetics of aquatic systems	26.10.	31.10.
<i>Case Study Introduction</i>		09.11.
Useful Tools	02.11.	09.11.
Aquatic Chemistry of Surfaces and Colloids	07.11.**	14.11.
Advanced Sorption	16.11.	21.11.
Transformation reactions: Substitution and Elimination	23.11.	28.11.
Photochemistry	30.11.	05.12.
<i>Mile Stone I: Concept</i>		05.12.*
<i>Mile Stone II: Relevant Processes</i>		11.01.*
<i>Case Study Presentation and Discussion</i>	25.01./ 30.01. (12-16)	
<i>Final Discussion and Wrap up</i>	01.02.	
<b>Exam</b>	.02./04.	

\* individual group appointments with advising PhD student

\*\* this lecture takes place on Monday!

Major **aims** of the course:

- Qualitative and quantitative understanding of processes dominating natural aquatic systems
- Fundamentals for evaluation of the fate of pollutants in natural and technical systems
- Realization of (necessary) simplifications and plausibility control of assumptions and results
- Realizing a small-scale project in a very limited timeframe: learning how to organize project tasks in a group, how to present and discuss results

**Organisation**

- The course is given by Prof. Schmidt (torsten.schmidt@uni-due.de) and the PhD students Nerea Lorenzo Parodi (nerea.lorenzo-parodi@uni-due.de) and Sarah Willach (sarah.willach@uni-due.de), both former Water Science students.
- We will gather contact data of all participants on October 19. We will then form up to 8 groups of students by incorporating people with different levels of expertise and backgrounds in each group. By doing so, all of you will benefit most.
- Each group presents in the tutorial on Monday 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.

**Environmental case studies (second half of the term)**

In November, each group will be given a past environmental case study to work on over the semester. In these case studies you should learn to apply the knowledge and skills acquired during your past courses in the area of water chemistry. The situation will be similar to typical future project tasks as an environmental consultant. Firstly, you need to understand the problem to be addressed, gather a few sources of information and judge required time to be spend on the project. You also need to split tasks among group members. You are required to put together these information into a concept of your further work and submit it to the responsible PhD student prior to milestone 1 (deadline 05.12.16, 1 page). On December 07 or upon individual appointment around this date your group will discuss the submitted concept with the PhD student. For this and the following mile stone discussions attendance of all group members is compulsory! Otherwise, this will heavily affect your final case study grading. Based on this discussion you will set out to work on the topic. You need to decide which environmental processes are relevant in a particular situation and which you may neglect based on an appropriate evaluation. You will also need to handle uncertainties in data, make adequate assumptions for unknowns etc. The results of your work are summarized in a short report (max. 5 pages) that is submitted to the responsible PhD student prior to milestone 2 (deadline 09.01.17). On January 11 or upon individual appointment each group will discuss the submitted report with the PhD student. Based on this discussion each group will prepare a short presentation. The last two tutorials will be used to introduce the subjects and findings with these presentations. An important aspect of your work is that science is not necessarily free of subjective judgment. To demonstrate this, each subject will be given to two groups that start from the same situation/problem but requires different viewpoints (e.g., industry representative vs. environmental NGO). In all cases you work as experts for such groups. Since you do not want to compromise your good reputation you

need to base all your statements and judgements on good science. However, you will see that interpretation may differ to some extent.

The case studies will be substantially taken into account for the final grade. The criteria which will be taken into account for the grading are:

- Participation in Milestone I & II report and meeting (attendance is compulsory)
- Participation in final presentation and subsequent discussion
- Attendance during all other presentations and participation in the corresponding discussions

Each participant will be graded individually according to the commitment to his/her case study. However, you also need to pass the exam with a minimum of 50 %!

Preliminary Subject list:

1. PCB contamination of Hudson river
2. Benzene pollution of Songhua river, PRC
3. Drinking water pollution by chlorinated solvents: Woburn case
4. Drinking water pollution: hexavalent chromium/Erin Brockovich
5. Atrazine in Greifensee

## Recommended Reading

The course is covered to a large extent by any of the aquatic chemistry textbooks cited below:

- Howard, A. G., 1998: Aquatic Environmental Chemistry, Oxford University Press, Oxford (very brief introductory material, only sufficient for repetition of bachelor course contents, cheap)
- Jensen, J. N., 2003: A Problem-solving Approach to Aquatic Chemistry, Wiley, NY
- Benjamin, M.M., 2002: Water Chemistry, McGraw-Hill, New York
- Schwarzenbach, R.P., Gschwend, P.M. and D. Imboden, 2003: Environmental Organic Chemistry, Wiley, NY
- Stumm, W. and J.J. Morgan, 1996: Aquatic Chemistry, Wiley, NY (*the* authoritative textbook but not well suited for learning purposes and a bit weak/outdated on environmental organic chemistry for which the Schwarzenbach is a much better choice)
- Brezonik, P. L., Arnold, W.A., 2011: Water Chemistry, Oxford University Press, Oxford (a very interesting newly introduced textbook that surely is worth having a look at)

**Please be aware that this is a Master level course that requires some basic knowledge in chemistry. If you lack the fundamentals make sure to compensate for these gaps as soon as possible after the lecture series started. To that end, you may also use the lecture slides of the bachelor level course on water chemistry provided at [https://www.uni-due.de/water-science/2951wc\\_16.php](https://www.uni-due.de/water-science/2951wc_16.php), which are almost completely in English.**

**Otherwise you will not benefit much from the offered lectures, tutorials and case studies.**

## Exam

The exam will be organized as an open book exam. You may bring any material except for:

1. Mobile phones/laptops/tablets etc. If these are not switched off, this will be taken as an attempt to cheat and you will immediately fail.
2. (Presolved) old exams. If these are noticed they will be immediately seized, regardless of further notices you may require.

**We highly recommend to bring following things to the exam:**

- **periodic table of elements**
- **the appendix of this handout**
- **a pocket calculator**

**Syllabus (might change to some extent depending on your background)****Retro of thermodynamics, chemical equilibrium and kinetics**

- Units and scales
- Thermodynamics
- Chemical equilibrium
- Speciation diagrams
- Reaction rates, reaction orders (0<sup>th</sup>, 1<sup>st</sup>, 2<sup>nd</sup> order)
- Pseudo-first-order kinetics
- Effect of temperature (Arrhenius equation)

**Useful Tools**

- Thermodynamic cycle
- Mass balance equations
- Single-parameter Linear Free Energy Relationships (LFERs)
- Poly-parameter LFERs
- Steady-state systems

**Aquatic Chemistry of Surfaces and Colloids**

- Surface chemistry
- Surface charge
- Surface potential
- Layer theory
- Electrostatic interactions: Ion Exchange II
- Sorption of organic ions
- Surface complexation
- Colloids
- Colloidal material in the environment
- Colloidal contaminant transport

**Advanced Sorption**

- Sorption processes
- Role of organic matter: partitioning
- Role of surfaces (minerals, carbonaceous materials): adsorption
- Sorption isotherms
- Determination of sorption parameters
- Dissolved organic carbon (DOC)

**Transformation reactions**

- Reaction mechanisms: Nucleophilic substitution
- A special case: Hydrolysis (water as a nucleophile)
- Reaction mechanisms: Elimination
- Acid and base catalysis
- Hammett relationships

**Photochemistry**

- Basics of Photochemistry
- Quantum yield
- Light attenuation in natural water bodies
- Direct and indirect photolysis
- Reactive species in indirect photolysis

Appendix 1: Thermodynamic Data

App.1 Standard-State Thermodynamic Data

Species	$\Delta G_f^\circ$ (kJ/mol)	$\Delta H_f^\circ$ (kJ/mol)	$S^\circ$ (J/mol · K)	Source
KCl (sylvite)	-408.6	-436.5	82.6	5
KAlSi <sub>3</sub> O <sub>8</sub>	-3742.9	-3681.1	214.22	2
(microcline feldspar)				
KAl <sub>3</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub> (muscovite mica)	-5608.4	-5984.4	305.3	2
Mg <sup>2+</sup>	-456.1	-468.6	-138.1	1
	-454.8	-466.85	-138.1	2
Mg(OH) <sub>2</sub> (brucite)	-833.51	-924.54	63.18	2
MgCO <sub>3</sub> (magnesite)	-1012.1	-1095.8	65.7	2
Mg <sub>2</sub> SiO <sub>4</sub> (forsterite)	-2056.7	-2175.7	95.2	6
MgSiO <sub>3</sub> (enstatite)	-1459.9	-1546.8	67.8	6
Mg <sub>3</sub> Si <sub>2</sub> O <sub>7</sub> (OH) <sub>4</sub> (chrysotile, serpentine)	-4037.8	-4365.6	221.3	2
Mg <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> (talc)	-5523.7	-5903.5	260.7	7
Mg <sub>5</sub> Al <sub>2</sub> Si <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub> (chlorite)	-8207.8	-8857.4	465.3	6
Mg <sub>6</sub> Si <sub>4</sub> O <sub>15</sub> (OH) <sub>2</sub> · 6H <sub>2</sub> O (sepiolite)	-9251.6	-10116.9	613.4	6
Mn (metal)	0	0	32.0	2
Mn <sup>2+</sup>	-228.1	-220.75	-73.6	2
MnO	-362.90	-385.22	59.71	2
Mn(OH) <sub>2</sub> (pyrochroite)	-616.5			8
MnO(OH) (manganite)	-133.3			8
Mn <sub>2</sub> O <sub>3</sub> (hausmannite)	-1283.2	-1387.8	155.6	2
Mn <sub>2</sub> O <sub>4</sub> (bixbyite)	-881.1	-959.0	110.5	2
MnO <sub>2</sub> (pyrolusite)	-465.14	-520.3	53.06	2
MnO <sub>2</sub> (barnesite)	-453.1			8
MnCO <sub>3</sub> (rhodochrosite)	-816.7	-894.1	85.8	2
MnS (alabandite)	-218.0	-213.8	78.2	4
MnSiO <sub>3</sub> (rhodonite)	-1243.1	-1319.2	102.5	4
N <sub>2</sub> (g)	0	0	191.6	2
NH <sub>3</sub> (g)	-16.45	-46.11	192.5	2
NH <sub>3</sub> (aq)	-26.50	-80.29	111.3	2
NH <sub>4</sub> <sup>+</sup>	-79.31	-132.51	113.4	2
NO <sub>2</sub> <sup>-</sup>	-108.74	-205.0	146.4	2
Na <sup>+</sup>	-261.92	-240.29	58.4	1
	-261.91	-240.12	59.0	2
NaCl (halite)	-384.14	-411.15	72.1	2
NaHCO <sub>3</sub> (nahcolite)	-851.9	-947.7	102.1	9
NaHCO <sub>3</sub> · Na <sub>2</sub> CO <sub>3</sub> · 2H <sub>2</sub> O (trona)	-2386.6			9
Na <sub>2</sub> SO <sub>4</sub> (thenardite)	-1269.8	-1387.8	149.6	5
Na <sub>2</sub> SO <sub>4</sub> · 10H <sub>2</sub> O (mirabilite)	-3646.4	-4327.1	592.0	5
NaSi <sub>3</sub> O <sub>7</sub> (OH) <sub>3</sub> (magadite)	-6651.9			10
NaAlSi <sub>3</sub> O <sub>8</sub> (albite)	-3711.5	-3935.1	207.4	2
NaAlSi <sub>3</sub> O <sub>8</sub> · H <sub>2</sub> O (analcite)	-3082.6	-3300.8	234.3	2

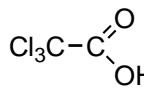
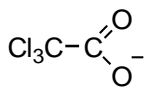
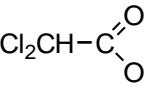
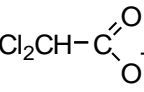
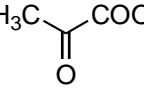
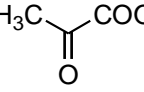
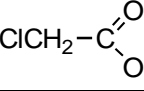
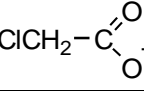
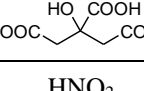
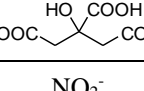
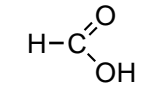
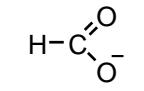
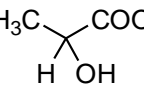
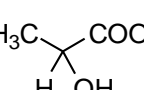
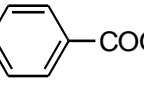
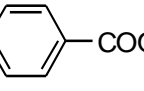
Standard-State Thermodynamic Data App.1

Species	$\Delta G_f^\circ$ (kJ/mol)	$\Delta H_f^\circ$ (kJ/mol)	$S^\circ$ (J/mol · K)	Source
Na <sub>0.33</sub> Al <sub>2.33</sub> Si <sub>3.67</sub> O <sub>10</sub> (OH) <sub>2</sub> (Na-beidellite)	-5382			7
O <sub>2</sub> (g)	0	0	205.1	2
S (rhomboh)	0	0	31.8	2
H <sub>2</sub> S (g)	-33.56	-20.63	205.8	2
H <sub>2</sub> S (aq)	-27.83	-39.7	121	2
SO <sub>2</sub> (g)	-300.2	-296.8	248.1	2
HS <sup>-</sup>	12.08	-17.6	62.8	2
S <sup>2-</sup>	85.8	33.1	-14.6	2
HSO <sub>4</sub> <sup>-</sup>	-755.91	-887.34	131.8	2
SO <sub>4</sub> <sup>2-</sup>	-744.53	-909.27	20.1	2
SiO <sub>2</sub> (quartz)	-856.64	-910.94	41.84	2
SiO <sub>2</sub> (amorph)	-849.28	-902.07	46.9	7
H <sub>4</sub> SiO <sub>4</sub> (aq)	-1308.1	-1439.5	180	7
Si <sup>2+</sup>	-563.83	-550.90	-31.5	11
SiCO <sub>3</sub> (strontianite)	-1144.73	-1225.77	97.2	11
SiSO <sub>4</sub> (celestite)	-1340.9	-1453.1	117.	2

- SOURCES
1. Nordstrom et al. (1984)
  2. Wagman et al. (1982)
  3. Haas et al. (1981)
  4. Busenberg and Plummer (1986)
  5. Robie et al. (1978)
  6. Helgeson et al. (1978)
  7. Adjusted by the author for consistency with other values.
  8. Bricker (1965)
  9. Garrels and Christ (1965)
  10. Calculated from Bricker (1969)
  11. Busenberg et al. (1984)

Source: Diever, 1988

## Appendix 2: Dissociation constants of acids

Acid	HA	A <sup>-</sup>	K <sub>a</sub>	pK <sub>a</sub>
Hydroiodic acid	HI	I <sup>-</sup>	10 <sup>11</sup>	-11
Perchloric acid	HClO <sub>4</sub>	ClO <sub>4</sub> <sup>-</sup>	10 <sup>10</sup>	-10
Hydrobromic acid	HBr	Br <sup>-</sup>	10 <sup>9</sup>	-9
Hydrochloric acid	HCl	Cl <sup>-</sup>	10 <sup>7</sup>	-7
Chloric acid	HClO <sub>3</sub>	ClO <sub>3</sub> <sup>-</sup>	10 <sup>3</sup>	-3
Sulfuric acid	H <sub>2</sub> SO <sub>4</sub>	HSO <sub>4</sub> <sup>-</sup>	10 <sup>2</sup>	-2
Nitric acid	HNO <sub>3</sub>	NO <sub>3</sub> <sup>-</sup>	10	-1
Hydronium-Ion (H <sup>+</sup> <sub>(aq)</sub> )	H <sub>3</sub> O <sup>+</sup>	H <sub>2</sub> O	1	0.0
Trichloroacetic acid			2.0•10 <sup>-1</sup>	0.70
Oxalic acid	HOOC-COOH	HOOC-COO <sup>-</sup>	5.9•10 <sup>-2</sup>	1.23
Dichloroacetic acid			3.32•10 <sup>-2</sup>	1.48
Sulfurous acid	H <sub>2</sub> SO <sub>3</sub>	HSO <sub>3</sub> <sup>-</sup>	1.5•10 <sup>-2</sup>	1.81
Hydrogensulfate ion	HSO <sub>4</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	1.2•10 <sup>-2</sup>	1.92
Phosphoric acid	H <sub>3</sub> PO <sub>4</sub>	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	7.5•10 <sup>-3</sup>	2.12
Glycinium ion	H <sub>3</sub> N <sup>+</sup> -COOH	H <sub>3</sub> N <sup>+</sup> -COO <sup>-</sup>	4.0•10 <sup>-3</sup>	2.4
Pyruvic acid			3.24•10 <sup>-3</sup>	2.49
Malonic acid	HOOC-CH <sub>2</sub> -COOH	HOOC-CH <sub>2</sub> -COO <sup>-</sup>	1.49•10 <sup>-3</sup>	2.83
Chloroacetic acid			1.36•10 <sup>-3</sup>	2.87
Citric acid			7.45•10 <sup>-4</sup>	3.13
Nitrous acid	HNO <sub>2</sub>	NO <sub>2</sub> <sup>-</sup>	4.6•10 <sup>-4</sup>	3.34
Hydrofluoric acid	HF	F <sup>-</sup>	3.5•10 <sup>-4</sup>	3.45
Formic acid			1.8•10 <sup>-4</sup>	3.75
Lactic acid			1.4•10 <sup>-4</sup>	3.86
Benzoic acid			6.46•10 <sup>-5</sup>	4.19

Acid	HA	A <sup>-</sup>	K <sub>a</sub>	pK <sub>a</sub>
Ascorbic acid (vitamin C)			$6.3 \cdot 10^{-5}$	4.2
Succinic acid			$6.21 \cdot 10^{-5}$	4.21
Dihydrogencitrate ion			$4.0 \cdot 10^{-5}$	4.4
Anilinium ion			$2.3 \cdot 10^{-5}$	4.63
Acetic acid			$1.8 \cdot 10^{-5}$	4.75
1-Butanoic acid			$1.5 \cdot 10^{-5}$	4.82
Propionic acid (propanoic acid)			$1.4 \cdot 10^{-5}$	4.87
Pyridinium ion			$5.6 \cdot 10^{-6}$	5.25
Hydrogenmalonate ion			$2.03 \cdot 10^{-6}$	5.69
Hydrogencitrate ion			$2.0 \cdot 10^{-6}$	5.7
Carbonic acid	$\text{H}_2\text{CO}_3$	$\text{HCO}_3^-$	$4.3 \cdot 10^{-7}$	6.37
Hydrogen sulfide	$\text{H}_2\text{S}$	$\text{HS}^-$	$9.1 \cdot 10^{-8}$	7.04
Dihydrogenphosphate ion	$\text{H}_2\text{PO}_4^-$	$\text{HPO}_4^{2-}$	$6.2 \cdot 10^{-8}$	7.21
Hydrazinium ion	$\text{H}_2\text{N}-\text{NH}_3^+$	$\text{H}_2\text{N}-\text{NH}_2$	$5.9 \cdot 10^{-9}$	8.23
Boric acid	$\text{B}(\text{OH})_3$	$\text{B}(\text{OH})_4^-$	$7.2 \cdot 10^{-10}$	9.14
Ammonium ion	$\text{NH}_4^+$	$\text{NH}_3$	$5.6 \cdot 10^{-10}$	9.25
Hydrogen cyanide	$\text{HCN}$	$\text{CN}^-$	$4.9 \cdot 10^{-10}$	9.31
Trimethylammonium ion			$1.6 \cdot 10^{-10}$	9.81
Phenol			$1.3 \cdot 10^{-10}$	9.89
Bicarbonate ion	$\text{HCO}_3^-$	$\text{CO}_3^{2-}$	$4.8 \cdot 10^{-11}$	10.32
Hydrogen peroxide	$\text{H}_2\text{O}_2$	$\text{HOO}^-$	$2.4 \cdot 10^{-12}$	11.62
Hydrogenphosphate ion	$\text{HPO}_4^{2-}$	$\text{PO}_4^{3-}$	$2.2 \cdot 10^{-13}$	12.67
Water	$\text{H}_2\text{O}$	$\text{HO}^-$	$1.0 \cdot 10^{-14}$	14.0



### Appendix 3: List of oxidation states in common compounds (Ref.: Pankow 1991)

Molecule or Ion	Name	Oxidation States
O <sub>2</sub>	molecular, elemental oxygen	O(0)
H <sub>2</sub> O <sub>2</sub>	hydrogen peroxide	O(-I), H(I)
H <sub>2</sub> O	water	O(-II), H(I)
OH <sup>-</sup>	hydroxide	O(-II), H(I)
H <sup>+</sup>	proton	H(I)
HOCl	molecular hypochlorous acid	Cl(I), O(-II), H(I)
OCl <sup>-</sup>	hypochlorite ion	Cl(I), O(-II)
Cl <sub>2</sub>	molecular, elemental chlorine	Cl(0)
HCl	molecular hydrochloric acid	Cl(-I), H(I)
Cl <sup>-</sup>	chloride ion	Cl(-I)
H <sub>2</sub> CO <sub>3</sub> *	carbonic acid	C(IV), O(-II), H(I)
HCO <sub>3</sub> <sup>-</sup>	bicarbonate ion	C(IV), O(-II), H(I)
CO <sub>3</sub> <sup>2-</sup>	carbonate ion	C(IV), O(-II)
HCOO <sup>-</sup>	formate ion	C(II), O(-II), H(I)
CH <sub>3</sub> -CH <sub>2</sub> -OH	ethanol	C(-II), O(-II), H(I)
C <sub>(s)</sub>	elemental carbon, e.g. graphite or diamond	C(0)
CH <sub>2</sub> O	formaldehyde	C(0)
C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	glucose	C(0)
CH <sub>3</sub> -CH <sub>3</sub>	ethane	C(-III)
CH <sub>4</sub>	methane	C(-IV)
H <sub>2</sub> SO <sub>4</sub>	molecular sulfuric acid	S(VI), O(-II), H(I)
HSO <sub>4</sub> <sup>-</sup>	bisulfate	S(VI), O(-II), H(I)
SO <sub>4</sub> <sup>2-</sup>	sulfate	S(VI), O(-II)
S <sub>8(s)</sub>	molecular, elemental sulfur	S(0)
H <sub>2</sub> S	hydrogen sulfide	S(-II), H(I)
HS <sup>-</sup>	bisulfide	S(-II), H(I)
S <sup>2-</sup>	sulfide	S(-II)
HNO <sub>3</sub>	molecular nitric acid	N(V), O(-II), H(I)
NO <sub>3</sub> <sup>-</sup>	nitrate	N(V), O(-II)
HNO <sub>2</sub>	molecular nitrous acid	N(III), O(-II), H(I)
NO <sub>2</sub> <sup>-</sup>	nitrite	N(III), O(-II)
N <sub>2</sub>	molecular, elemental nitrogen	N(0)
NH <sub>3</sub>	ammonia	N(-III), H(I)
NH <sub>4</sub> <sup>+</sup>	ammonium	N(-III), H(I)

Appendix 4: Equilibrium constants for environmentally relevant redox processes (Ref.: Pankow 1991)

TABLE 19.2. Data for selected redox reactions at 25°C/1 atm in order of increasing  $pe^0$  and  $E_H^0$ . (Data from Bard et al. (1985) and Stumm and Morgan (1981).) The reducing strength of the RED species tends to increase towards the top of the table, and the oxidizing strength of the OX species tends to increase towards the bottom of the table.

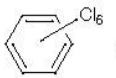
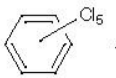
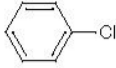
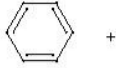
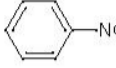
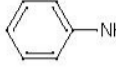
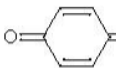
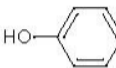
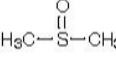
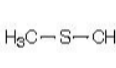
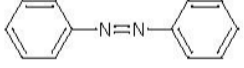

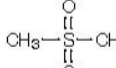
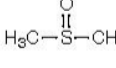
Reduction Half Reaction	$\log K$	$pe^0$	$pe^0(W)$	$E_H^0$
OX + ne = RED	$\frac{\{RED\}}{\{OX\}\{e^-\}^n}$	$\frac{1}{n} \log K$	$pe^0 - \frac{pe^0}{n} 7$	$0.05916 pe^0$
Na <sup>+</sup> + e <sup>-</sup> = Na <sub>(s)</sub>	-46.0	-46.0	-46.0	-2.71
Zn <sup>2+</sup> + 2e <sup>-</sup> = Zn <sub>(s)</sub>	-26.0	-13.0	-13.0	-0.76
FeCO <sub>3(s)</sub> + 2e <sup>-</sup> = Fe <sub>(s)</sub> + CO <sub>3</sub> <sup>2-</sup>	-25.58	-12.79	-12.79	-0.76
Fe <sup>2+</sup> + 2e <sup>-</sup> = Fe <sub>(s)</sub>	-14.9	-7.45	-7.45	-0.44
CO <sub>2(g)</sub> + H <sup>+</sup> + 2e <sup>-</sup> = HCOO <sup>-</sup>	-9.66	-4.83	-8.33	-0.29
CO <sub>2(g)</sub> + 4H <sup>+</sup> + 4e <sup>-</sup> = CH <sub>2</sub> O + H <sub>2</sub> O	-4.8	-1.2	-8.2	-0.071
CO <sub>2(g)</sub> + 4H <sup>+</sup> + 4e <sup>-</sup> = $\frac{1}{6}C_6H_{12}O_6$ (glucose) + H <sub>2</sub> O	-0.8	-0.2	-7.2	-0.012
2H <sup>+</sup> + 2e <sup>-</sup> = H <sub>2(g)</sub>	0.0	0.0	-7.0	0.00
N <sub>2(g)</sub> + 6H <sup>+</sup> + 6e <sup>-</sup> = 2NH <sub>3</sub>	9.5	1.58	-5.42	0.093
S <sub>(s)</sub> + 2H <sup>+</sup> + 2e <sup>-</sup> = H <sub>2</sub> S	4.8	2.4	-4.6	0.14
Cu <sup>2+</sup> + e <sup>-</sup> = Cu <sup>+</sup>	2.7	2.7	2.7	0.16
HCOO <sup>-</sup> + 3H <sup>+</sup> + 2e <sup>-</sup> = CH <sub>2</sub> O + H <sub>2</sub> O	5.64	2.82	-7.68	0.17
CO <sub>2(g)</sub> + 8H <sup>+</sup> + 8e <sup>-</sup> = CH <sub>4(g)</sub> + 2H <sub>2</sub> O	23.0	2.87	-4.13	0.17
AgCl <sub>(s)</sub> + e <sup>-</sup> = Ag <sub>(s)</sub> + Cl <sup>-</sup>	3.7	3.7	3.7	0.22
CH <sub>2</sub> O + 2H <sup>+</sup> + 2e <sup>-</sup> = CH <sub>3</sub> OH	8.0	4.0	-3.0	0.24
SO <sub>4</sub> <sup>2-</sup> + 9H <sup>+</sup> + 8e <sup>-</sup> = HS <sup>-</sup> + 4H <sub>2</sub> O	34.0	4.25	-3.63	0.25
Hg <sub>2</sub> Cl <sub>2(s)</sub> + 2e <sup>-</sup> = 2Hg <sub>(l)</sub> + 2Cl <sup>-</sup>	9.06	4.53	4.53	0.268
N <sub>2(g)</sub> + 8H <sup>+</sup> + 6e <sup>-</sup> = 2NH <sub>4</sub> <sup>+</sup>	28.1	4.68	-4.65	0.28
SO <sub>4</sub> <sup>2-</sup> + 10H <sup>+</sup> + 8e <sup>-</sup> = H <sub>2</sub> S + 4H <sub>2</sub> O	41.0	5.13	-3.62	0.30
Cu <sup>2+</sup> + 2e <sup>-</sup> = Cu <sub>(s)</sub>	11.4	5.7	5.7	0.34
HSO <sub>4</sub> <sup>-</sup> + 7H <sup>+</sup> + 6e <sup>-</sup> = S <sub>(s)</sub> + 4H <sub>2</sub> O	34.2	5.7	-2.47	0.34
SO <sub>4</sub> <sup>2-</sup> + 8H <sup>+</sup> + 6e <sup>-</sup> = S <sub>(s)</sub> + 4H <sub>2</sub> O	36.2	6.03	-3.3	0.36

TABLE 19.2. (continued)

Reduction Half Reaction	$\log K$	$pe^0$	$pe^0(W)$	$E_H^0$
OX + ne = RED	$\frac{\{RED\}}{\{OX\}\{e^-\}^n}$	$\frac{1}{n} \log K$	$pe^0 - \frac{pe^0}{n} 7$	$0.05916 pe^0$
CH <sub>2</sub> O + 4H <sup>+</sup> + 4e <sup>-</sup> = CH <sub>4(g)</sub> + H <sub>2</sub> O	27.8	6.94	-0.06	0.41
Cu <sup>+</sup> + e <sup>-</sup> = Cu <sub>(s)</sub>	8.8	8.8	8.8	0.52
CH <sub>3</sub> OH + 2H <sup>+</sup> + 2e <sup>-</sup> = CH <sub>4(g)</sub> + H <sub>2</sub> O	19.8	9.88	2.88	0.58
Fe <sup>3+</sup> + e <sup>-</sup> = Fe <sup>2+</sup>	13.0	13.0	13.0	0.77
Ag <sup>+</sup> + e <sup>-</sup> = Ag <sub>(s)</sub>	13.5	13.5	13.5	0.80
NO <sub>3</sub> <sup>-</sup> + 7H <sup>+</sup> + 6e <sup>-</sup> = NH <sub>3</sub> + 2H <sub>2</sub> O	81.5	13.58	5.41	0.80
NO <sub>3</sub> <sup>-</sup> + 2H <sup>+</sup> + 2e <sup>-</sup> = NO <sub>2</sub> <sup>-</sup> + H <sub>2</sub> O	28.3	14.15	7.15	0.84
NO <sub>3</sub> <sup>-</sup> + 10H <sup>+</sup> + 8e <sup>-</sup> = NH <sub>4</sub> <sup>+</sup> + 3H <sub>2</sub> O	119.2	14.9	6.15	0.88
NO <sub>3</sub> <sup>-</sup> + 8H <sup>+</sup> + 6e <sup>-</sup> = NH <sub>4</sub> <sup>+</sup> + 2H <sub>2</sub> O	90.8	15.14	5.82	0.90
MnO <sub>2(s)</sub> + HCO <sub>3</sub> <sup>-</sup> + 3H <sup>+</sup> + 2e <sup>-</sup> = MnCO <sub>3(s)</sub> + 2H <sub>2</sub> O	25.8	15.9	5.4	0.94
(α)FeOOH <sub>(s)</sub> + HCO <sub>3</sub> <sup>-</sup> + 2H <sup>+</sup> + e <sup>-</sup> = FeCO <sub>3(s)</sub> + 2H <sub>2</sub> O	13.15	13.15	-0.85	0.78
(α)FeOOH <sub>(s)</sub> + 3H <sup>+</sup> + e <sup>-</sup> = Fe <sup>2+</sup> + 2H <sub>2</sub> O	13.5	13.5	-7.5	0.80
(am)Fe(OH) <sub>3</sub> + 3H <sup>+</sup> + e <sup>-</sup> = Fe <sup>2+</sup> + 3H <sub>2</sub> O	16.2	16.2	-4.8	0.96
O <sub>2(g)</sub> + 4H <sup>+</sup> + 4e <sup>-</sup> = 2H <sub>2</sub> O	83.1	20.78	13.78	-1.23
NO <sub>3</sub> <sup>-</sup> + 6H <sup>+</sup> + 5e <sup>-</sup> = $\frac{1}{2}N_2(g)$ + 3H <sub>2</sub> O	105.3	21.05	12.65	1.25
MnO <sub>2(s)</sub> + 4H <sup>+</sup> + 2e <sup>-</sup> = Mn <sup>2+</sup> + 2H <sub>2</sub> O	43.6	21.8	7.8	1.29
Fe <sup>3+</sup> + CO <sub>3</sub> <sup>2-</sup> + e <sup>-</sup> = FeCO <sub>3(s)</sub>	23.68	23.68	23.68	1.40
Cl <sub>2</sub> + 2e <sup>-</sup> = 2Cl <sup>-</sup>	47.2	23.6	23.6	1.40
HOCl + H <sup>+</sup> + e <sup>-</sup> = $\frac{1}{2}Cl_2$ + H <sub>2</sub> O	26.9	26.9	19.9	1.59
ClO <sup>-</sup> + 2H <sup>+</sup> + 2e <sup>-</sup> = Cl <sup>-</sup> + H <sub>2</sub> O	57.8	28.9	21.8	1.71
H <sub>2</sub> O <sub>2</sub> + 2H <sup>+</sup> + 2e <sup>-</sup> =	59.6	29.80	22.80	1.76

## Appendix 5: Equilibrium constants for redox reactions of selected environmentally relevant organic compounds (Ref.: Schwarzenbach et al. 2002)

**Table 14.3** Standard Reduction Potentials and Average Standard Free Energies of Reaction (per Electron Transferred) at 25°C of Some Organic Redox Couples in Aqueous Solution (The reactions are ordered in decreasing  $E_H^0(W)$  values.)<sup>a</sup>

Halfreaction		$E_H^0$ (V)	$E_H^0(W)^b$ (V)	$\Delta_r G_H^0(W)/n^c$ (kJ·mol <sup>-1</sup> )
Oxidized Species	Reduced Species			
(1) $\text{CCl}_3\text{---CCl}_3 + 2e^-$	= $\text{Cl}_2\text{C=CCl}_2 + 2\text{Cl}^-$	+ 0.95	+ 1.13	- 109.0
(2) $\text{CBr}_4 + \text{H}^+ + 2e^-$	= $\text{CHBr}_3 + \text{Br}^-$	+ 0.89	+ 0.83	- 80.1
(3) $\text{CCl}_4 + \text{H}^+ + 2e^-$	= $\text{CHCl}_3 + \text{Cl}^-$	+ 0.79	+ 0.67	- 64.7
(4) $\text{CHBr}_3 + \text{H}^+ + 2e^-$	= $\text{CH}_2\text{Br}_2 + \text{Br}^-$	+ 0.67	+ 0.61	- 58.9
(5) $\text{Cl}_2\text{C=CCl}_2 + \text{H}^+ + 2e^-$	= $\text{Cl}_2\text{C=CHCl} + \text{Cl}^-$	+ 0.70	+ 0.58	- 56.0
(6) $\text{CHCl}_3 + \text{H}^+ + 2e^-$	= $\text{CH}_2\text{Cl}_2 + \text{Cl}^-$	+ 0.68	+ 0.56	- 54.0
(7)  + $\text{H}^+ + 2e^-$	=  + $\text{Cl}^-$	+ 0.68	+ 0.56	- 54.0
(8)  + $\text{H}^+ + 2e^-$	=  + $\text{Cl}^-$	+ 0.54	+ 0.42	- 40.5
(9)  + $6\text{H}^+ + 6e^-$	=  + $2\text{H}_2\text{O}$	+ 0.83	+ 0.42	- 40.5
(10)  + $2\text{H}^+ + 2e^-$	= 	+ 0.70	+ 0.28	- 27.0
(11)  + $2\text{H}^+ + 2e^-$	=  + $\text{H}_2\text{O}$	+ 0.57	+ 0.16	- 15.4
(12)  + $4\text{H}^+ + 4e^-$	= 2 	+ 0.31	- 0.10	+ 9.7
(13)  + $2\text{H}^+ + 2e^-$	=  + $\text{H}_2\text{O}$	+ 0.17	- 0.24	+ 23.2
(14) $\text{R---S---S---R} + 2\text{H}^+ + 2e^-$ (cystine)	= $2\text{R---SH}$ (cysteine)	+ 0.02	- 0.39	+ 37.6

<sup>a</sup> Estimated from thermodynamic data Dean (1985); Vogel et al. (1987); Krop et al. (1994); Roberts et al. (1996); Totten and Roberts (2001). <sup>b</sup>  $[\text{H}^+] = 10^{-7}$ ,  $\{\text{Cl}^-\} = 10^{-3}$ ,  $\{\text{Br}^-\} = 10^{-5}$ . <sup>c</sup>  $n$  = number of electrons transferred.

**Appendix 6: Cation exchange capacities (CEC) of various environmental materials found in the colloidal size fraction (Ref.: van Loon/Duffy 2005)**

<b>Material</b>	<b>CEC range (average) /cmol(+) kg<sup>-1</sup></b>
Kaolinite	3-15 (8)
Halloysite	4-10 (8)
Montmorillonite	80-150 (100)
Chlorite	10-40 (25)
Vermiculite	100-150 (125)
Hydrous iron and aluminium oxides	Ca. 4
Feldspar	1-2 (2)
Quartz	1-2 (2)
Organic matter	150-500 (200)

## Appendix 7: 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	$\mu_i = \mu_i^\circ + RT \ln \{i\} = \mu_i^\circ + RT \ln c_i \gamma_i$
2. Reference states for $\gamma_i$	$\gamma_i \rightarrow 1$ as $x_i \rightarrow 1$ or $x_i \rightarrow 0$ $\gamma_i \rightarrow 1$ as $\sum m_j \rightarrow 0$ or $\gamma_i \rightarrow 1$ as $m_i \rightarrow 0$
3. Standard states for $c_i$	$\gamma_i = 1$ and: $x_i = 1$ or $m_i = 1$
4. Reaction $\sum \nu_i M_i = 0$	$\Delta H = \sum \nu_i \bar{H}_i, \Delta V = \sum \nu_i \bar{V}_i,$ $\Delta S = \sum \nu_i \bar{S}_i \quad \Delta G = \sum \nu_i \mu_i$
5. State function relationship	$\Delta G = \Delta H - T \Delta S$
6. Equilibrium constant	$K = \prod_i \{i\}_{\text{eq}}^{\nu_i}$ $Q = \prod_i \{i\}^{\nu_i}$
7. Reaction quotient	
8. Standard free energy and $K$	$\Delta G^\circ \text{ (kJ mol}^{-1}\text{)} = -5.71 \log K \text{ at } 25^\circ\text{C}$
9. Free energy and $Q$	$\Delta G = RT \ln \frac{Q}{K}$
10. $K, m_i,$ and $\nu_i$	$K = \left( \prod_i \left( \frac{m_i}{m^\circ} \right)^{\nu_i} \prod_i \gamma_i^{\nu_i} \right)_{\text{eq}}$
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:

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