Water Chemistry

Lecture (2 h): **Wednesday 08^{15} - 10^{00}, S05 T00 B59**
Tutorial+Exercise (2h): **Monday 12^{15} - 14^{00}, S03 V00 E59**

Subject	**Date**	**Date Tutorial**
Introduction/Concepts/Organization	**10.10.**	**24.10.**
Essentials in Equilibrium and Kinetics of aquatic systems	**17.10.**	**05.11.**
Case Study Introduction		***24.10.***
Useful Tools	**22.10.****	**12.11.**
Mile Stone I: Concept		**16.11.***
Aquatic Chemistry of Surfaces and Colloids	**31.10.**	**14.11.**
Advanced Sorption	**07.11.**	**19.11.**
Transformation reactions: Substitution and Elimination	**28.11.**	**03.12.**
Photochemistry	**05.12.**	**10.12.**
Mile Stone II: Relevant Processes		**10.12.***
Case Study Presentation and Discussion		***14.01./21.01.***
Final Discussion and Wrap up	**30.01.**	
Exam	**TBA**	

* 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 Vanessa Wirzberger (vanessa.wirzberger@uni-due.de), both former Water Science students.
- We will gather contact data of all participants on October 10th. 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.
- Latecomers are asked to contact the responsible PhD students as soon as possible in order to asses if they can still participate in the study course. The last day to register for the groups will be November 5th.
- 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 October, 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 16.11.18, 1 page). On November 19th 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 10.12.18). On December 17th 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.

Once both sides have presented their arguments, the question and answer session will be open. There, you are encouraged to ask questions to the other group regarding their presentation. Furthermore, the audience will also be able to pose questions to try to make up their mind and decide which group presented the strongest arguments. Remember, try to answer the questions in a concise manner, otherwise, you will be stopped, and we will move on to the next question. Once the questions are answered, the audience will be asked which group defended their case better, by asking a topic-related question.

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:

- Milestone I & II reports, final report and presentation
- 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. Glyphosate in Europe
3. Drinking water pollution with lead in Flint
4. Benzene pollution of Songhua River

Required Background

Please be aware that this is a **Master level course that requires some basic knowledge in chemistry**.

Required background encompasses:

- Physical Chemistry:
  Thermodynamics, chemical equilibrium, mass balance equations, kinetics
- Organic Chemistry:
  Functional groups, Reaction mechanisms
- Water Chemistry:
  - Ions in aqueous solution (Acid/base, Dissolution, Complexation)
  - Redox chemistry
  - Fundamentals of phase transfer (sorption, air-water)

If you lack the fundamentals make sure to **compensate for these gaps before or 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,
which are almost completely in English (same password, if as an external student you want to prepare in advance, contact the PhD students for the PW) or you can use any textbook (recommended readings for Water Chemistry below).
With a German speaking background you may also use a Moodle course at the Ruhr University Bochum for self-testing at
https://moodle.ruhr-uni-bochum.de/m/course/view.php?id=1304.

Without preparation you will not benefit much from the offered lectures, tutorials and case studies.

Recommended Reading for the course

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, 2017: Environmental Organic Chemistry, Wiley, NY
- Stumm, W. and J.J. Morgan, 1996: Aquatic Chemistry, Wiley, NY (*the* authorative 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)

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 notes 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^{th}, 1^{st}, 2^{nd} 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)

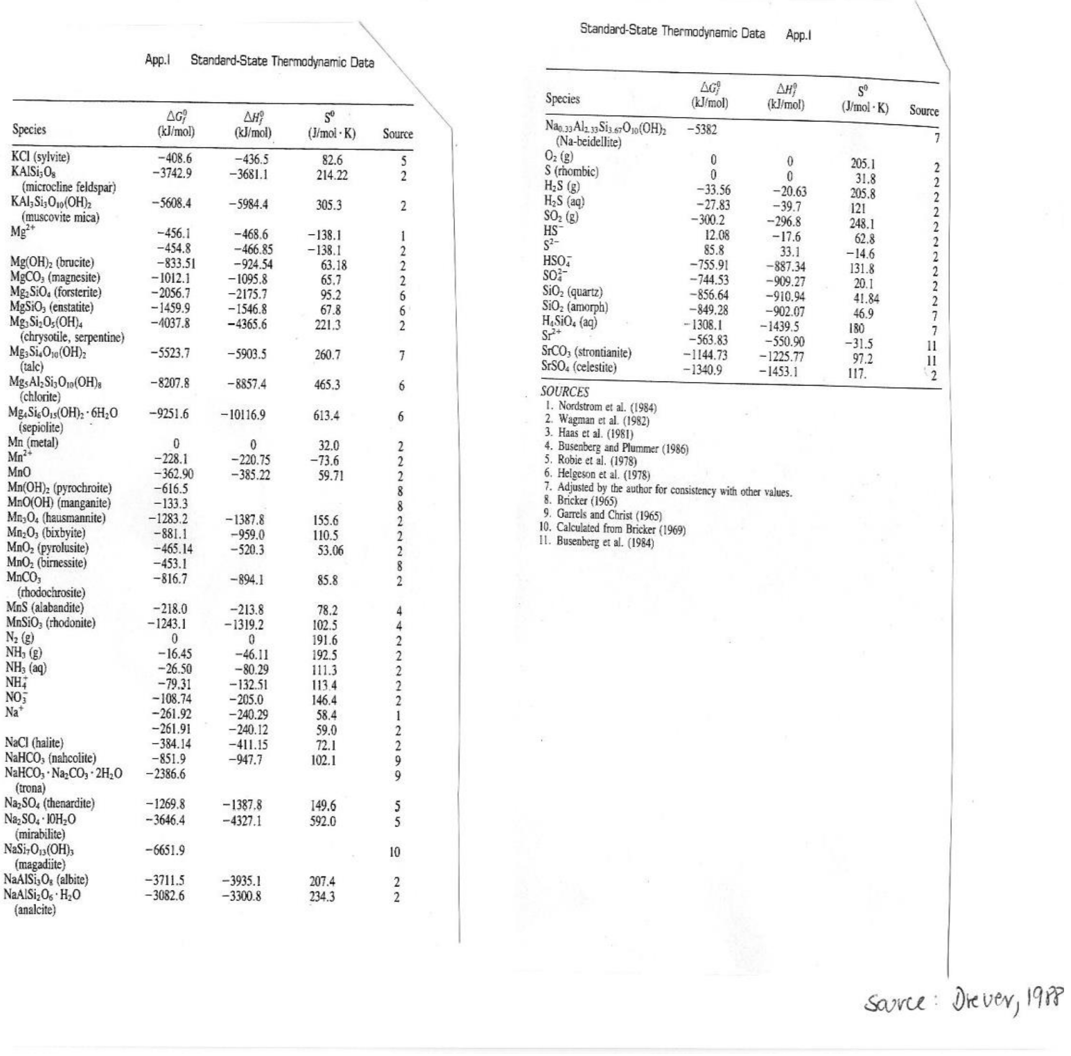
Transformation reactions

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.I Standard-State Thermodynamic Data

Species	ΔG_f^0 (kJ/mol)	ΔH_f^0 (kJ/mol)	S^0 (J/mol · K)	Source
KCl (sylvite)	−408.6	−436.5	82.6	5
$KAlSi_3O_8$ (microcline feldspar)	−3742.9	−3681.1	214.22	2
$KAl_3Si_3O_{10}(OH)_2$ (muscovite mica)	−5608.4	−5984.4	305.3	2
Mg^{2+}	−456.1	−468.6	−138.1	1
	−454.8	−466.85	−138.1	2
$Mg(OH)_2$ (brucite)	−833.51	−924.54	63.18	2
$MgCO_3$ (magnesite)	−1012.1	−1095.8	65.7	2
Mg_2SiO_4 (forsterite)	−2056.7	−2175.7	95.2	6
$MgSiO_3$ (enstatite)	−1459.9	−1546.8	67.8	6
$Mg_3Si_2O_5(OH)_4$ (chrysotile, serpentine)	−4037.8	−4365.6	221.3	2
$Mg_3Si_4O_{10}(OH)_2$ (talc)	−5523.7	−5903.5	260.7	7
$Mg_5Al_2Si_3O_{10}(OH)_8$ (chlorite)	−8207.8	−8857.4	465.3	6
$Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$ (sepiolite)	−9251.6	−10116.9	613.4	6
Mn (metal)	0	0	32.0	2
Mn^{2+}	−228.1	−220.75	−73.6	2
MnO	−362.90	−385.22	59.71	2
$Mn(OH)_2$ (pyrochroite)	−616.5			8
MnO(OH) (manganite)	−133.3			8
Mn_3O_4 (hausmannite)	−1283.2	−1387.8	155.6	2
Mn_2O_3 (bixbyite)	−881.1	−959.0	110.5	2
MnO_2 (pyrolusite)	−465.14	−520.3	53.06	2
MnO_2 (birnessite)	−453.1			8
$MnCO_3$ (rhodochrosite)	−816.7	−894.1	85.8	2
MnS (alabandite)	−218.0	−213.8	78.2	4
$MnSiO_3$ (rhodonite)	−1243.1	−1319.2	102.5	4
N_2 (g)	0	0	191.6	2
NH_3 (g)	−16.45	−46.11	192.5	2
NH_3 (aq)	−26.50	−80.29	111.3	2
NH_4^+	−79.31	−132.51	113.4	2
NO_3^-	−108.74	−205.0	146.4	2
Na^+	−261.92	−240.29	58.4	1
	−261.91	−240.12	59.0	2
NaCl (halite)	−384.14	−411.15	72.1	2
$NaHCO_3$ (nahcolite)	−851.9	−947.7	102.1	9
$NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$ (trona)	−2386.6			9
Na_2SO_4 (thenardite)	−1269.8	−1387.8	149.6	5
$Na_2SO_4 \cdot 10H_2O$ (mirabilite)	−3646.4	−4327.1	592.0	5
$NaSi_7O_{13}(OH)_3$ (magadiite)	−6651.9			10
$NaAlSi_3O_8$ (albite)	−3711.5	−3935.1	207.4	2
$NaAlSi_2O_6 \cdot H_2O$ (analcite)	−3082.6	−3300.8	234.3	2

Standard-State Thermodynamic Data App.I

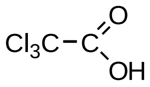
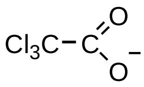
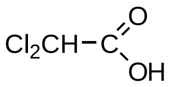
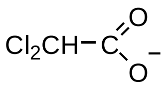
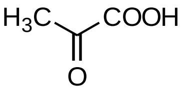
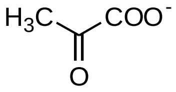
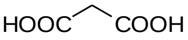
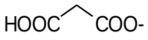
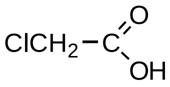
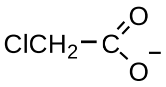
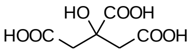
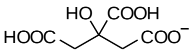
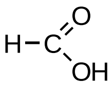
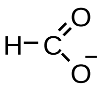
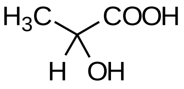
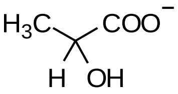
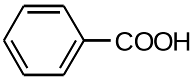
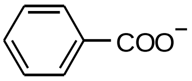
Species	ΔG_f^0 (kJ/mol)	ΔH_f^0 (kJ/mol)	S^0 (J/mol · K)	Source
$Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$ (Na-beidellite)	−5382			7
O_2 (g)	0	0	205.1	2
S (rhombic)	0	0	31.8	2
H_2S (g)	−33.56	−20.63	205.8	2
H_2S (aq)	−27.83	−39.7	121	2
SO_2 (g)	−300.2	−296.8	248.1	2
HS^-	12.08	−17.6	62.8	2
S^{2-}	85.8	33.1	−14.6	2
HSO_4^-	−755.91	−887.34	131.8	2
SO_4^{2-}	−744.53	−909.27	20.1	2
SiO_2 (quartz)	−856.64	−910.94	41.84	2
SiO_2 (amorph)	−849.28	−902.07	46.9	7
H_4SiO_4 (aq)	−1308.1	−1439.5	180	7
Sr^{2+}	−563.83	−550.90	−31.5	11
$SrCO_3$ (strontianite)	−1144.73	−1225.77	97.2	11
$SrSO_4$ (celestite)	−1340.9	−1453.1	117.	2

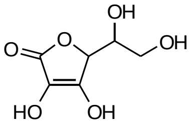
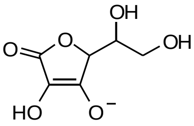
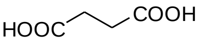
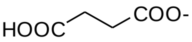
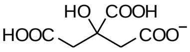
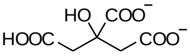
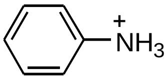
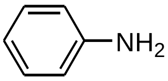
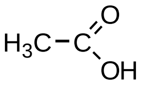
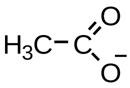
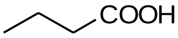
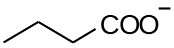
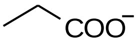
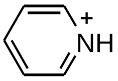
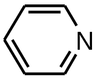
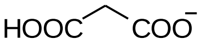
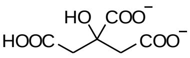
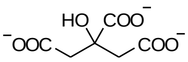
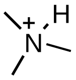
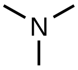
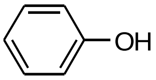
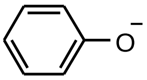
SOURCES

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)

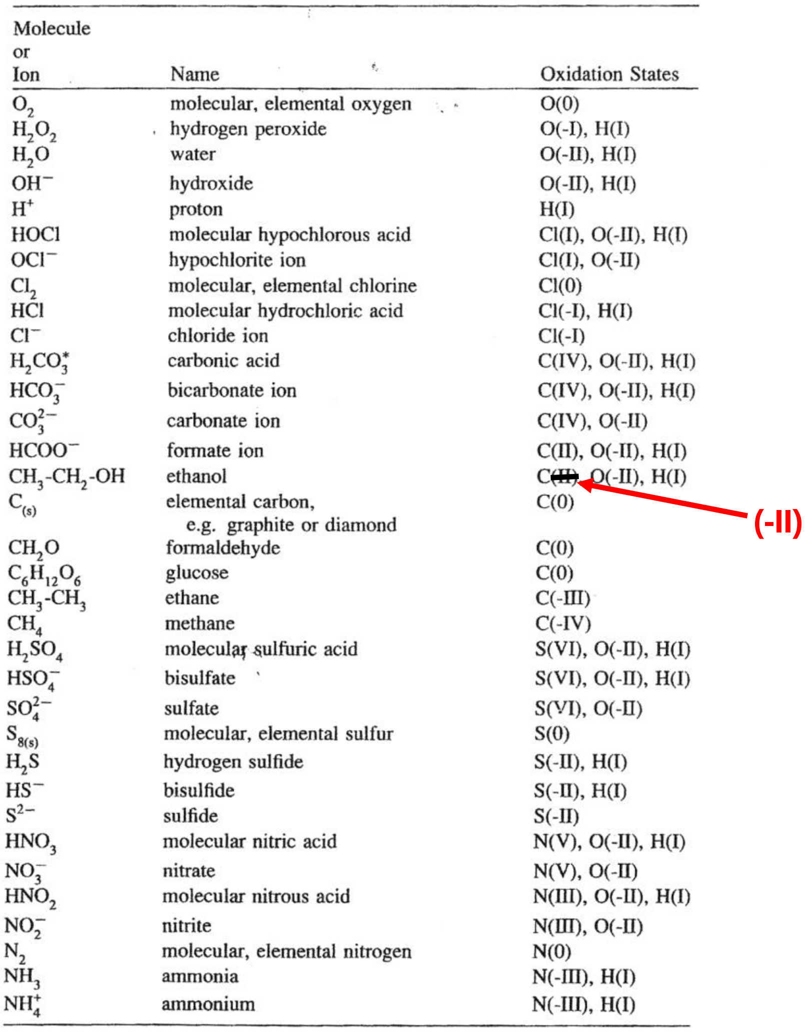
Source: Drever, 1988

Appendix 2: Dissociation constants of acids

Acid	**HA**	**A⁻**	K_a	pK_a
Hydroiodic acid	HI	I^-	10^{11}	-11
Perchloric acid	$HClO_4$	ClO_4^-	10^{10}	-10
Hydrobromic acid	HBr	Br^-	10^9	-9
Hydrochloric acid	HCl	Cl^-	10^7	-7
Chloric acid	$HClO_3$	ClO_3^-	10^3	-3
Sulfuric acid	H_2SO_4	HSO_4^-	10^2	-2
Nitric acid	HNO_3	NO_3^-	10	-1
Hydronium-Ion ($H^+_{(aq)}$)	H_3O^+	H_2O	1	0.0
Trichloroacetic acid			$2.0 \bullet 10^{-1}$	0.70
Oxalic acid	$HOOC-COOH$	$HOOC-COO^-$	$5.9 \bullet 10^{-2}$	1.23
Dichloroacetic acid			$3.32 \bullet 10^{-2}$	1.48
Sulfurous acid	H_2SO_3	HSO_3^-	$1.5 \bullet 10^{-2}$	1.81
Hydrogensulfate ion	HSO_4^-	SO_4^{2-}	$1.2 \bullet 10^{-2}$	1.92
Phosphoric acid	H_3PO_4	$H_2PO_4^-$	$7.5 \bullet 10^{-3}$	2.12
Glycinium ion	$H_3\overset{+}{N}-COOH$	$H_3\overset{+}{N}-COO^-$	$4.0 \bullet 10^{-3}$	2.4
Pyruvic acid			$3.24 \bullet 10^{-3}$	2.49
Malonic acid			$1.49 \bullet 10^{-3}$	2.83
Chloroacetic acid			$1.36 \bullet 10^{-3}$	2.87
Citric acid			$7.45 \bullet 10^{-4}$	3.13
Nitrous acid	HNO_2	NO_2^-	$4.6 \bullet 10^{-4}$	3.34
Hydrofluoric acid	HF	F^-	$3.5 \bullet 10^{-4}$	3.45
Formic acid			$1.8 \bullet 10^{-4}$	3.75
Lactic acid			$1.4 \bullet 10^{-4}$	3.86
Benzoic acid			$6.46 \bullet 10^{-5}$	4.19

Acid	**HA**	**A^-**	**K_a**	**pK_a**
Ascorbic acid (vitamin C)			$6.3 \bullet 10^{-5}$	4.2
Succinic acid			$6.21 \bullet 10^{-5}$	4.21
Dihydrogencitrate ion			$4.0 \bullet 10^{-5}$	4.4
Anilinium ion			$2.3 \bullet 10^{-5}$	4.63
Acetic acid			$1.8 \bullet 10^{-5}$	4.75
1-Butanoic acid			$1.5 \bullet 10^{-5}$	4.82
Propionic acid (propanoic acid)			$1.4 \bullet 10^{-5}$	4.87
Pyridinium ion			$5.6 \bullet 10^{-6}$	5.25
Hydrogenmalonate ion			$2.03 \bullet 10^{-6}$	5.69
Hydrogencitrate ion			$2.0 \bullet 10^{-6}$	5.7
Carbonic acid	H_2CO_3	HCO_3^-	$4.3 \bullet 10^{-7}$	6.37
Hydrogen sulfide	H_2S	HS^-	$9.1 \bullet 10^{-8}$	7.04
Dihydrogenphosphate ion	$H_2PO_4^-$	HPO_4^{2-}	$6.2 \bullet 10^{-8}$	7.21
Hydrazinium ion	$H_2N-\overset{+}{N}H_3$	H_2N-NH_2	$5.9 \bullet 10^{-9}$	8.23
Boric acid	$B(OH)_3$	$B(OH)_4^-$	$7.2 \bullet 10^{-10}$	9.14
Ammonium ion	$NH_{4,}^{+}$	NH_3	$5.6 \bullet 10^{-10}$	9.25
Hydrogen cyanide	HCN	CN^-	$4.9 \bullet 10^{-10}$	9.31
Trimethylammonium ion			$1.6 \bullet 10^{-10}$	9.81
Phenol			$1.3 \bullet 10^{-10}$	9.89
Bicarbonate ion	HCO_3^-	CO_3^{2-}	$4.8 \bullet 10^{-11}$	10.32
Hydrogen peroxide	H_2O_2	HOO^-	$2.4 \bullet 10^{-12}$	11.62
Hydrogenphosphate ion	HPO_4^{2-}	PO_4^{3-}	$2.2 \bullet 10^{-13}$	12.67
Water	H_2O	HO^-	$1.0 \bullet 10^{-14}$	14.0

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



Molecule or Ion	Name	Oxidation States
O_2	molecular, elemental oxygen	O(0)
H_2O_2	hydrogen peroxide	O(-I), H(I)
H_2O	water	O(-II), H(I)
OH^-	hydroxide	O(-II), H(I)
H^+	proton	H(I)
HOCl	molecular hypochlorous acid	Cl(I), O(-II), H(I)
OCl^-	hypochlorite ion	Cl(I), O(-II)
Cl_2	molecular, elemental chlorine	Cl(0)
HCl	molecular hydrochloric acid	Cl(-I), H(I)
Cl^-	chloride ion	Cl(-I)
$H_2CO_3^*$	carbonic acid	C(IV), O(-II), H(I)
HCO_3^-	bicarbonate ion	C(IV), O(-II), H(I)
CO_3^{2-}	carbonate ion	C(IV), O(-II)
$HCOO^-$	formate ion	C(II), O(-II), H(I)
CH_3-CH_2-OH	ethanol	C~~(II),~~ O(-II), H(I) (-II)
$C_{(s)}$	elemental carbon, e.g. graphite or diamond	C(0)
CH_2O	formaldehyde	C(0)
$C_6H_{12}O_6$	glucose	C(0)
CH_3-CH_3	ethane	C(-III)
CH_4	methane	C(-IV)
H_2SO_4	molecular sulfuric acid	S(VI), O(-II), H(I)
HSO_4^-	bisulfate	S(VI), O(-II), H(I)
SO_4^{2-}	sulfate	S(VI), O(-II)
$S_{8(s)}$	molecular, elemental sulfur	S(0)
H_2S	hydrogen sulfide	S(-II), H(I)
HS^-	bisulfide	S(-II), H(I)
S^{2-}	sulfide	S(-II)
HNO_3	molecular nitric acid	N(V), O(-II), H(I)
NO_3^-	nitrate	N(V), O(-II)
HNO_2	molecular nitrous acid	N(III), O(-II), H(I)
NO_2^-	nitrite	N(III), O(-II)
N_2	molecular, elemental nitrogen	N(0)
NH_3	ammonia	N(-III), H(I)
NH_4^+	ammonium	N(-III), H(I)

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

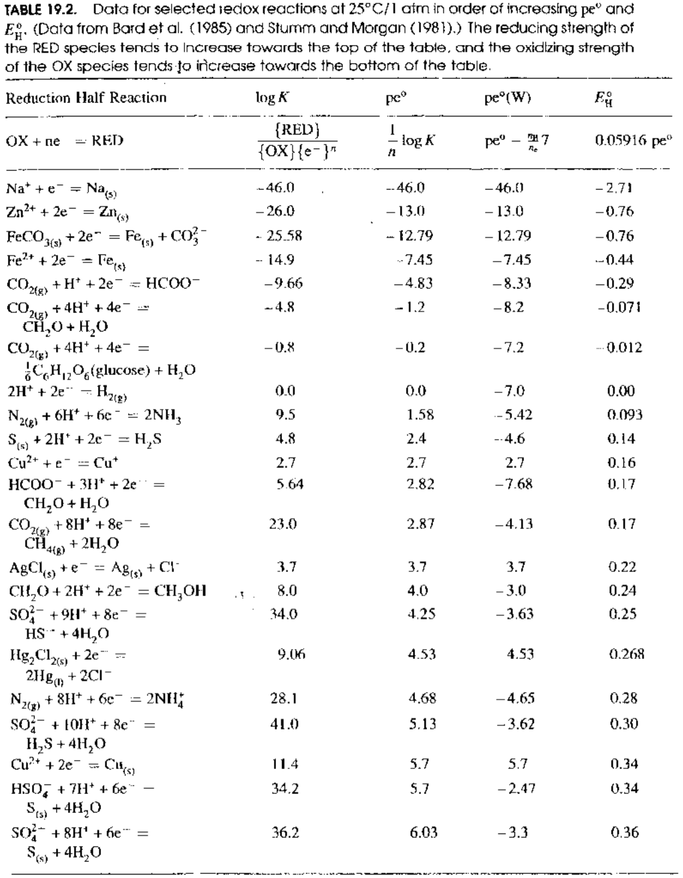


TABLE 19.2. Data for selected redox reactions at 25°C/1 atm in order of increasing pe° and E_H°. (Data from Bard et al. (1985) and Stumm and Morgan (1981).) The reducing strength of the RED species tends to increase towards the top of the table, and the oxidizing strength of the OX species tends to increase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

Reduction Half Reaction	log K	pe°	pe°(W)	E_H°
OX + ne = RED	$\frac{\{RED\}}{\{OX\}\{e^-\}^n}$	$\frac{1}{n}\log K$	$pe^\circ - \frac{n_H}{n_e}7$	0.05916 pe°
$Na^+ + e^- = Na_{(s)}$	−46.0	−46.0	−46.0	−2.71
$Zn^{2+} + 2e^- = Zn_{(s)}$	−26.0	−13.0	−13.0	−0.76
$FeCO_{3(s)} + 2e^- = Fe_{(s)} + CO_3^{2-}$	−25.58	−12.79	−12.79	−0.76
$Fe^{2+} + 2e^- = Fe_{(s)}$	−14.9	−7.45	−7.45	−0.44
$CO_{2(g)} + H^+ + 2e^- = HCOO^-$	−9.66	−4.83	−8.33	−0.29
$CO_{2(g)} + 4H^+ + 4e^- =$ $CH_2O + H_2O$	−4.8	−1.2	−8.2	−0.071
$CO_{2(g)} + 4H^+ + 4e^- =$ $\frac{1}{6}C_6H_{12}O_6(\text{glucose}) + H_2O$	−0.8	−0.2	−7.2	−0.012
$2H^+ + 2e^- = H_{2(g)}$	0.0	0.0	−7.0	0.00
$N_{2(g)} + 6H^+ + 6e^- = 2NH_3$	9.5	1.58	−5.42	0.093
$S_{(s)} + 2H^+ + 2e^- = H_2S$	4.8	2.4	−4.6	0.14
$Cu^{2+} + e^- = Cu^+$	2.7	2.7	2.7	0.16
$HCOO^- + 3H^+ + 2e^- =$ $CH_2O + H_2O$	5.64	2.82	−7.68	0.17
$CO_{2(g)} + 8H^+ + 8e^- =$ $CH_{4(g)} + 2H_2O$	23.0	2.87	−4.13	0.17
$AgCl_{(s)} + e^- = Ag_{(s)} + Cl^-$	3.7	3.7	3.7	0.22
$CH_2O + 2H^+ + 2e^- = CH_3OH$	8.0	4.0	−3.0	0.24
$SO_4^{2-} + 9H^+ + 8e^- =$ $HS^- + 4H_2O$	34.0	4.25	−3.63	0.25
$Hg_2Cl_{2(s)} + 2e^- =$ $2Hg_{(l)} + 2Cl^-$	9.06	4.53	4.53	0.268
$N_{2(g)} + 8H^+ + 6e^- = 2NH_4^+$	28.1	4.68	−4.65	0.28
$SO_4^{2-} + 10H^+ + 8e^- =$ $H_2S + 4H_2O$	41.0	5.13	−3.62	0.30
$Cu^{2+} + 2e^- = Cu_{(s)}$	11.4	5.7	5.7	0.34
$HSO_4^- + 7H^+ + 6e^- =$ $S_{(s)} + 4H_2O$	34.2	5.7	−2.47	0.34
$SO_4^{2-} + 8H^+ + 6e^- =$ $S_{(s)} + 4H_2O$	36.2	6.03	−3.3	0.36

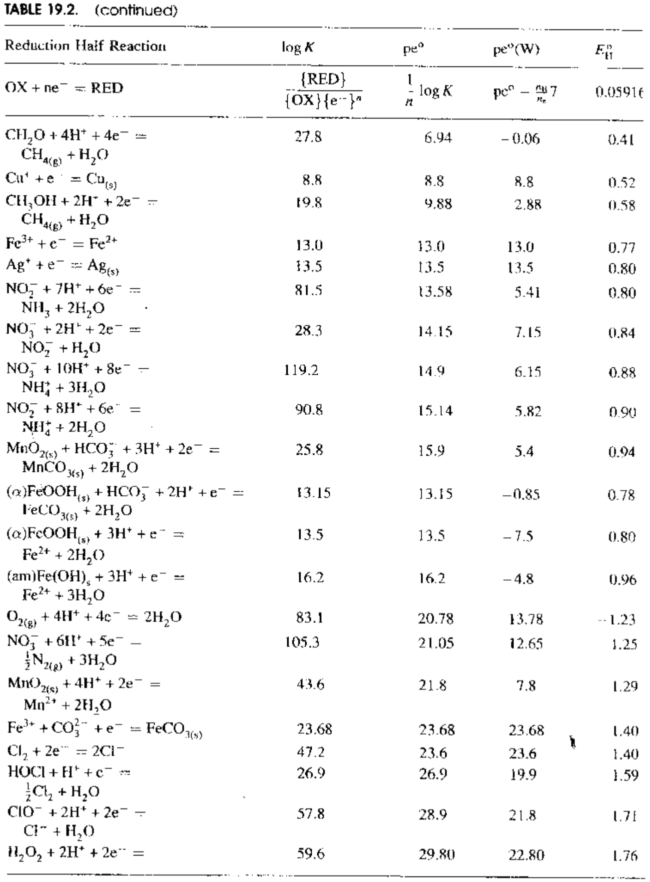


TABLE 19.2. (continued)

Reduction Half Reaction	log K	pe°	pe°(W)	E_H°
$OX + ne^- = RED$	$\frac{\{RED\}}{\{OX\}\{e^-\}^n}$	$\frac{1}{n}\log K$	$pe^\circ - \frac{n_H}{n_e}7$	0.0591
$CH_2O + 4H^+ + 4e^- =$ $CH_{4(g)} + H_2O$	27.8	6.94	−0.06	0.41
$Cu^+ + e^- = Cu_{(s)}$	8.8	8.8	8.8	0.52
$CH_3OH + 2H^+ + 2e^- =$ $CH_{4(g)} + H_2O$	19.8	9.88	2.88	0.58
$Fe^{3+} + e^- = Fe^{2+}$	13.0	13.0	13.0	0.77
$Ag^+ + e^- = Ag_{(s)}$	13.5	13.5	13.5	0.80
$NO_2^- + 7H^+ + 6e^- =$ $NH_3 + 2H_2O$	81.5	13.58	5.41	0.80
$NO_3^- + 2H^+ + 2e^- =$ $NO_2^- + H_2O$	28.3	14.15	7.15	0.84
$NO_3^- + 10H^+ + 8e^- =$ $NH_4^+ + 3H_2O$	119.2	14.9	6.15	0.88
$NO_2^- + 8H^+ + 6e^- =$ $NH_4^+ + 2H_2O$	90.8	15.14	5.82	0.90
$MnO_{2(s)} + HCO_3^- + 3H^+ + 2e^- =$ $MnCO_{3(s)} + 2H_2O$	25.8	15.9	5.4	0.94
$(\alpha)FeOOH_{(s)} + HCO_3^- + 2H^+ + e^- =$ $FeCO_{3(s)} + 2H_2O$	13.15	13.15	−0.85	0.78
$(\alpha)FeOOH_{(s)} + 3H^+ + e^- =$ $Fe^{2+} + 2H_2O$	13.5	13.5	−7.5	0.80
$(am)Fe(OH)_s + 3H^+ + e^- =$ $Fe^{2+} + 3H_2O$	16.2	16.2	−4.8	0.96
$O_{2(g)} + 4H^+ + 4e^- = 2H_2O$	83.1	20.78	13.78	1.23
$NO_3^- + 6H^+ + 5e^- =$ $\frac{1}{2}N_{2(g)} + 3H_2O$	105.3	21.05	12.65	1.25
$MnO_{2(s)} + 4H^+ + 2e^- =$ $Mn^{2+} + 2H_2O$	43.6	21.8	7.8	1.29
$Fe^{3+} + CO_3^{2-} + e^- = FeCO_{3(s)}$	23.68	23.68	23.68	1.40
$Cl_2 + 2e^- = 2Cl^-$	47.2	23.6	23.6	1.40
$HOCl + H^+ + e^- =$ $\frac{1}{2}Cl_2 + H_2O$	26.9	26.9	19.9	1.59
$ClO^- + 2H^+ + 2e^- =$ $Cl^- + H_2O$	57.8	28.9	21.8	1.71
$H_2O_2 + 2H^+ + 2e^- =$	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)

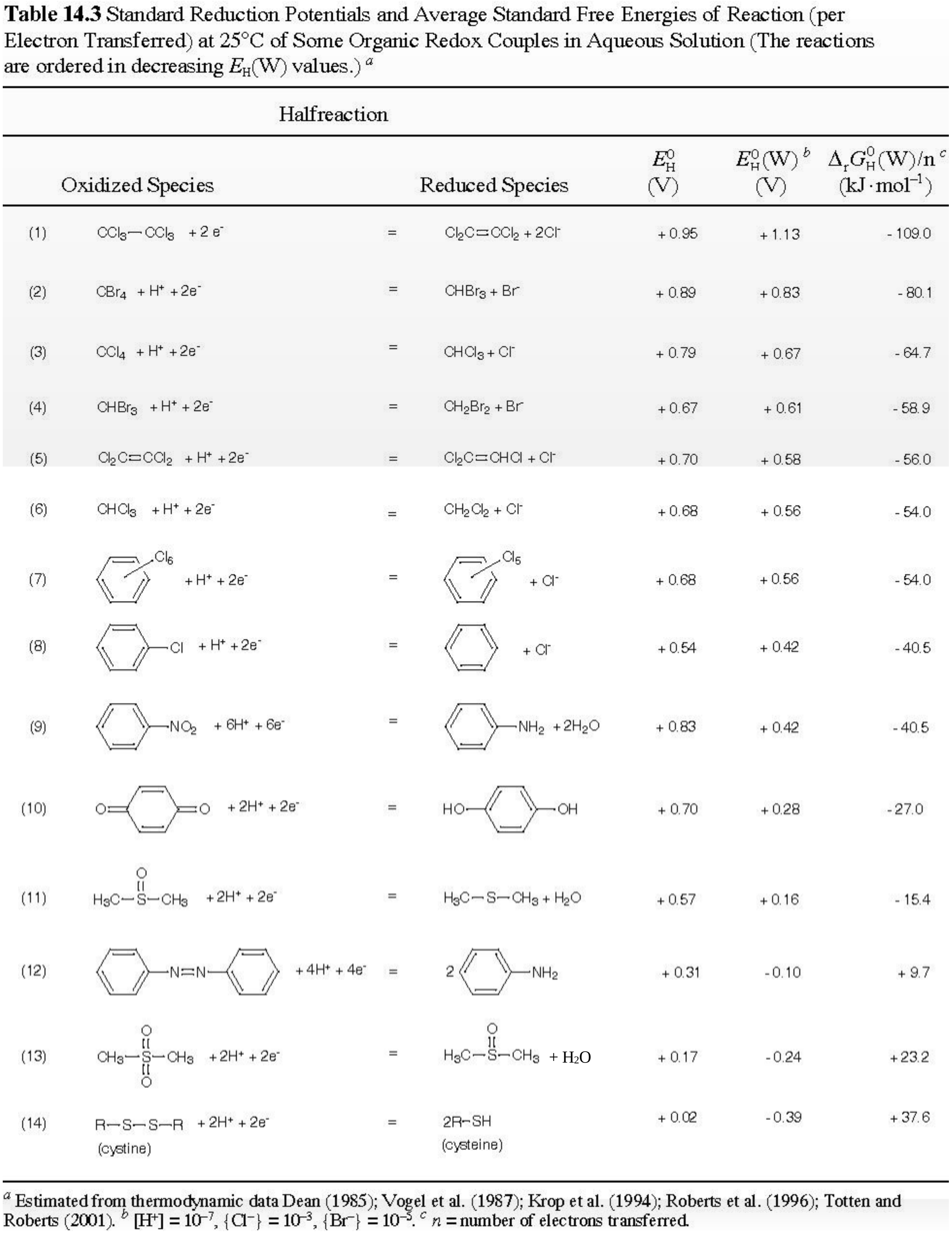


Table 14.3 Standard Reduction Potentials and Average Standard Free Energies of Reaction (per Electron Transferred) at 25°C of Some Organic Redox Couples in Aqueous Solution (The reactions are ordered in decreasing $E_H(W)$ values.) [a]

Halfreaction						
	Oxidized Species		Reduced Species	E_H^0 (V)	$E_H^0(W)$ [b] (V)	$\Delta_r G_H^0(W)/n$ [c] (kJ·mol^{-1})
(1)	$CCl_3—CCl_3$ + 2 e$^-$	=	$Cl_2C{=}CCl_2 + 2Cl^-$	+ 0.95	+ 1.13	- 109.0
(2)	CBr_4 + H$^+$ + 2e$^-$	=	$CHBr_3 + Br^-$	+ 0.89	+ 0.83	- 80.1
(3)	CCl_4 + H$^+$ + 2e$^-$	=	$CHCl_3 + Cl^-$	+ 0.79	+ 0.67	- 64.7
(4)	$CHBr_3$ + H$^+$ + 2e$^-$	=	$CH_2Br_2 + Br^-$	+ 0.67	+ 0.61	- 58.9
(5)	$Cl_2C{=}CCl_2$ + H$^+$ + 2e$^-$	=	$Cl_2C{=}CHCl + Cl^-$	+ 0.70	+ 0.58	- 56.0
(6)	$CHCl_3$ + H$^+$ + 2e$^-$	=	$CH_2Cl_2 + Cl^-$	+ 0.68	+ 0.56	- 54.0
(7)	Cl_6 + H$^+$ + 2e$^-$	=	Cl_5 + Cl$^-$	+ 0.68	+ 0.56	- 54.0
(8)	—Cl + H$^+$ + 2e$^-$	=	+ Cl$^-$	+ 0.54	+ 0.42	- 40.5
(9)	—NO$_2$ + 6H$^+$ + 6e$^-$	=	—NH$_2$ + 2H$_2$O	+ 0.83	+ 0.42	- 40.5
(10)	O= =O + 2H$^+$ + 2e$^-$	=	HO— —OH	+ 0.70	+ 0.28	- 27.0
(11)	$H_3C-\overset{O}{\overset{\|}{S}}-CH_3$ + 2H$^+$ + 2e$^-$	=	$H_3C—S—CH_3 + H_2O$	+ 0.57	+ 0.16	- 15.4
(12)	—N=N— + 4H$^+$ + 4e$^-$	=	2 —NH$_2$	+ 0.31	- 0.10	+ 9.7
(13)	$CH_3-\underset{O}{\underset{\|}{\overset{O}{\overset{\|}{S}}}}-CH_3$ + 2H$^+$ + 2e$^-$	=	$H_3C-\overset{O}{\overset{\|}{S}}-CH_3$ + H$_2$O	+ 0.17	- 0.24	+ 23.2
(14)	R—S—S—R + 2H$^+$ + 2e$^-$ (cystine)	=	2R—SH (cysteine)	+ 0.02	- 0.39	+ 37.6

[a] Estimated from thermodynamic data Dean (1985); Vogel et al. (1987); Krop et al. (1994); Roberts et al. (1996); Totten and Roberts (2001). [b] $[H^+] = 10^{-7}$, $\{Cl^-\} = 10^{-3}$, $\{Br^-\} = 10^{-3}$. [c] 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)

Material	**CEC range (average) /cmol(+) kg^{-1}**
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)

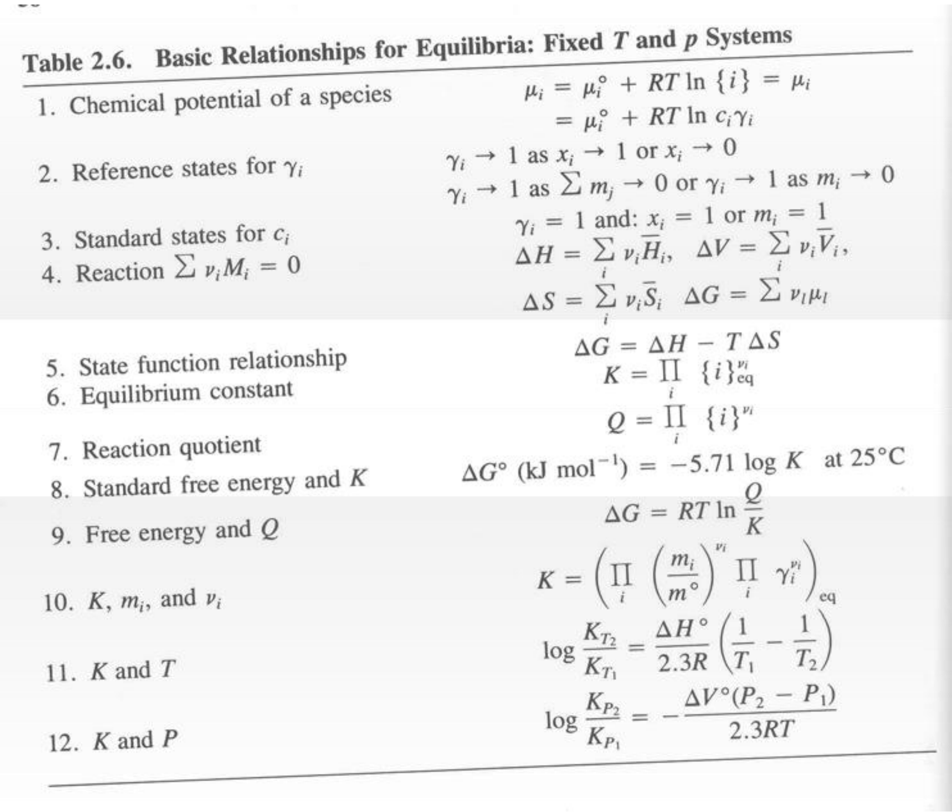


Table 2.6. Basic Relationships for Equilibria: Fixed T and p Systems

1. Chemical potential of a species	$\mu_i = \mu_i^\circ + RT \ln \{i\} = \mu_i$ $= \mu_i^\circ + RT \ln c_i \gamma_i$
2. Reference states for γ_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 $\sum \nu_i M_i = 0$	$\Delta H = \sum_i \nu_i \overline{H}_i, \quad \Delta V = \sum_i \nu_i \overline{V}_i,$ $\Delta S = \sum_i \nu_i \overline{S}_i \quad \Delta G = \sum \nu_l \mu_l$
5. State function relationship	$\Delta G = \Delta H - T\,\Delta S$
6. Equilibrium constant	$K = \prod_i \{i\}_{\mathrm{eq}}^{\nu_i}$
7. Reaction quotient	$Q = \prod_i \{i\}^{\nu_i}$
8. Standard free energy and K	ΔG° (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 ν_i	$K = \left(\prod_i \left(\frac{m_i}{m^\circ} \right)^{\nu_i} \prod_i \gamma_i^{\nu_i} \right)_{\mathrm{eq}}$
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:

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