

Wasserchemie

Vorlesung (2 h): **Dienstag** **8¹⁵ - 10⁰⁰, MG 272**
Übung (2h): **Mittwoch** **12³⁰ - 14³⁰, MG 272**

Thema	VL	Übung
Konzepte/Organisation/Einführung in die Wasserchemie I	08.04.	
Konzepte/Organisation/Einführung in die Wasserchemie II	09.04.	
Chemisches Gleichgewicht/Verteilung in wässrigen Systemen I	15.04	
Chemisches Gleichgewicht/Verteilung in wässrigen Systemen II	22.04	23.04. DK
		30.04. DK
Säure-Base-Chemie in wässrigen Systemen I	06.05.	
		14.05. DK
Säure-Base-Chemie in wässrigen Systemen II	20.05.	
Luft-Wasser-Verteilung/Henry-Konstante	27.05.	28.05.
Kalk-Kohlensäure-System	03.06.	04.06. DK
Auflösung und Fällung	10.06.	11.06.
Komplexierung	17.06.	18.06.
Sorption Einführung	24.06.	25.06.
Redoxchemie I	01.07.	02.07.
Redoxchemie II	08.07.	09.07.
Kinetik Einführung (<i>Wiederholung/Case Study</i>)	15.07.	16.07. (DK)

Wesentliche **Ziele** der Veranstaltung:

- Qualitatives und quantitatives Verständnis von Prozessen, die die Chemie natürlicher wässriger Systeme bestimmt
- Grundlagen der Beurteilung des Verhaltens von Schadstoffen in natürlichen und technischen Systemen
- Erkennen von möglichen Vereinfachungen komplexer Systeme und der Überprüfung der getroffenen Annahmen

Organisation

- Gruppen á 5 Studenten zur Diskussion bilden, Gruppeneinteilung an torsten.schmidt@uni-due.de
- Jede Gruppe stellt in der Übung am Mittwoch ihre Aufgabe entsprechend Übungszettel und den Lösungsweg vor, anschließend Diskussion (es geht **nicht** primär um das richtige Ergebnis!). Bei der Gruppeneinteilung bitte darauf achten, dass möglichst leistungsgemischte Gruppen entstehen, davon profitieren alle am meisten.

Vorlesungs-Inhalte**Einführung/Konzepte/Organisation**

Artikel: K. Roth (2007) Chem. Unserer Zeit 41: 118-126

Literatur

Wassereigenschaften

Wasserressourcen/Hydrologischer Kreislauf

Wassermarkt

Wasser und Pseudowissenschaften

Nomenklatur, Definitionen, Maßeinheiten

Wichtige Klassen an Umweltchemikalien

Chemisches Gleichgewicht/Verteilung in wässrigen Systemen I+II

Freie Energie G (Gibbs Free Energy) und chemisches Potential μ

Gleichgewichtskonstanten K und Reaktionsquotienten Q

Aktivitäten a und Aktivitätskoeffizienten γ

Fugazität f

Ionenstärke I

Standard- und Referenzzustand

Umgang mit chemischen Gleichgewichten

Algebraische Lösungen

Graphische Lösungen

Numerische Lösungen

Temperaturabhängigkeit von K: van't Hoff-Beziehung

Lineare freie Energiebeziehungen

Säure-Base-Chemie in wässrigen Systemen /Titration, Puffer

Artikel: D. K. Nordstrom et al. (2000) Environ. Sci. Technol. 34: 254-258

Titrationen

Puffer

pH als Mastervariable

Speziationsdiagramme

Protonenbilanz

Elektroneutralitätsbilanz

Organische Säuren und Basen: Übersicht

Hammett-Beziehungen

Verteilung organischer Säuren und Basen

Luft-Wasser-Verteilung/Henry-Konstante

Artikel: H. P. H. Arp, T. C. Schmidt (2004) Environ. Sci. Technol. 38: 5405-5412

Raoult'sches und Henry-Gesetz

Thermodynamischer Zyklus: der Umgang mit Massenbilanzen
Bestimmung von Luft-Wasser-Verteilungskonstanten
Regenwasser, „saurer Regen“

Kalk-Kohlensäure-System

Artikel: T. Clarke (2001) Nature 409: 544-545
Geschlossenes vs. Offenes System
Alkalinität

Auflösung und Fällung

Artikel: C. F. Harvey et al. (2002) Science 298: 1602-1606
Löslichkeitsprodukte
Carbonate
Hydroxide
Wasserhärte

Komplexierung

Artikel: F.M.M. Morel, M.M. Price (2003) Science 300: 944-947
Konzept der Komplexierung
Natürliche und anthropogene Liganden
Komplexbildungskonstanten, Brutto-Konstanten, Hydrolysekonstanten
Aquo-Komplexe
Komplexometrie
Oberflächenkomplexierung

Sorption

Artikel: H. K. Karapanagioti et al. (2000) Environ. Sci. Technol. 34, 406-414
Sorptionprozesse
Rolle des organischen Materials: Verteilung
Rolle von Oberflächen (Mineralien, Aktivkohle): Adsorption
Ionenaustausch
Sorptionisothermen
Bestimmung von Sorptionsparametern
Gelöster organischer Kohlenstoff

Redoxchemie

Artikel: F. Scholz, U. Schröder (2003) Nature Biotechnol. 21: 1152-1153
(Thermodynamik, Nernst-Gleichung, Elektrodenpotential, SHE)
Pe-Konzept
Vergleich Redox- und Säure-Base-Reaktionen
Redox-Leitern
Messungen des Redox-Potentials
Redox-Reaktionen in der Mikrobiologie

Reaktionskinetik in der aquatischen Chemie

Artikel: H. Song and E. R. Carraway (2005) Environ. Sci. Technol. 39, 6237-6245
Reaktionsraten, Reaktionsordnung (0., 1., 2. Ordnung)
Kinetik pseudo-erster Ordnung
Temperatureinfluss (Arrhenius-Gleichung)

Literatur

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, cheap)

Jensen, J. N., 2003: A Problem-solving Approach to Aquatic Chemistry, Wiley, NY (closest to the lecture concept)

Benjamin, M.M., 2002: Water Chemistry, McGraw-Hill, New York

(Morel, F.M.M. and J.G. Hering, 1993: Principles and Applications of Aquatic Chemistry, Wiley, NY)

(Pankow, J.F., 1991: Aquatic Chemistry Concepts, Lewis, Chelsea(MI))

Sigg, L. and W. Stumm, 1996: Aquatische Chemie, VDF/Teubner, Zürich (in German!)

Stumm, W. and J.J. Morgan, 1996: Aquatic Chemistry, Wiley, NY (*the* authoritative textbook but not well suited for learning purposes)

Appendix 1: Thermodynamic Data

App.1 Standard-State Thermodynamic Data

Species	ΔG_f° (kJ/mol)	ΔH_f° (kJ/mol)	S° (J/mol · K)	Source
KCl (sylvite)	-408.6	-436.5	82.6	5
KAlSi ₃ O ₈ (microcline feldspar)	-3742.9	-3681.1	214.22	2
KAl ₃ Si ₃ O ₁₀ (OH) ₂ (muscovite mica)	-5608.4	-5984.4	305.3	2
Mg ²⁺	-456.1	-468.6	-138.1	1
Mg(OH) ₂ (brucite)	-454.8	-466.85	-138.1	2
MgCO ₃ (magnesite)	-833.51	-924.54	63.18	2
Mg ₂ SiO ₄ (forsterite)	-1012.1	-1095.8	65.7	2
MgSiO ₃ (enstatite)	-2056.7	-2175.7	95.2	6
Mg ₃ Si ₂ O ₇ (OH) ₂ (chrysotile, serpentine)	-1459.9	-1546.8	67.8	6
Mg ₃ Si ₂ O ₇ (OH) ₂ (talc)	-4037.8	-4365.6	221.3	2
Mg ₃ Al ₂ Si ₂ O ₁₀ (OH) ₂ (chlorite)	-5523.7	-5903.5	260.7	7
Mg ₃ Al ₂ Si ₂ O ₁₀ (OH) ₂ (chlorite)	-8207.8	-8857.4	465.3	6
Mg ₃ Si ₃ O ₁₀ (OH) ₂ · 6H ₂ O (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 ₃ O ₄ (hausmannite)	-1283.2	-1387.8	155.6	2
Mn ₂ O ₃ (bixbyite)	-881.1	-959.0	110.5	2
MnO ₂ (pyrolusite)	-465.14	-520.3	53.06	2
MnO ₂ (birmessite)	-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
NaCl (halite)	-261.91	-240.12	59.0	2
NaHCO ₃ (nahcolite)	-384.14	-411.15	72.1	2
NaHCO ₃ · Na ₂ CO ₃ · 2H ₂ O (trona)	-851.9	-947.7	102.1	9
Na ₂ SO ₄ (thenardite)	-2386.6			9
Na ₂ SO ₄ · 10H ₂ O (mirabilite)	-1269.8	-1387.8	149.6	5
NaSi ₃ O ₈ (OH) ₂ (magadite)	-3646.4	-4327.1	592.0	5
NaAlSi ₃ O ₈ (albite)	-6651.9			10
NaAlSi ₃ O ₈ · H ₂ O (amalcite)	-3711.5	-3935.1	207.4	2
	-3082.6	-3300.8	234.3	2

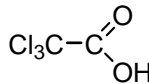
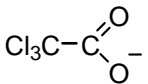
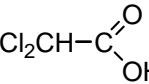
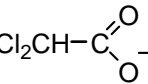
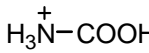
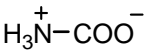
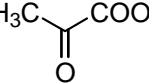
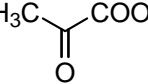
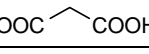
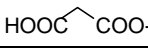
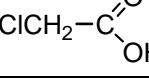
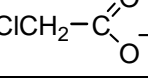
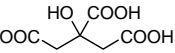
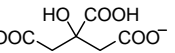
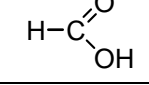
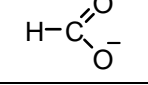
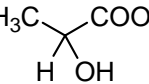
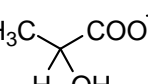
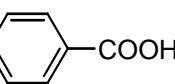
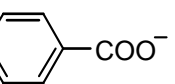
Standard-State Thermodynamic Data App.1

Species	ΔG_f° (kJ/mol)	ΔH_f° (kJ/mol)	S° (J/mol · K)	Source
Na ₂₃ Al ₁₂ Si ₁₄ AsO ₁₀ (OH) ₂ (Na-beidelite)	-5382			7
O ₂ (g)	0	0	205.1	2
S (rhombic)	0	0	31.8	2
H ₂ S (g)	-33.56	-20.63	205.8	2
H ₂ S (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 ₄ SiO ₄ (aq)	-1308.1	-1439.5	180	7
Si ⁴⁺	-563.83	-550.90	-31.5	11
SiCO ₃ (strontianite)	-1144.73	-1225.77	97.2	11
SiSO ₄ (celestite)	-1340.9	-1453.1	117.	2

- SOURCES
- Nordstrom et al. (1984)
 - Wagman et al. (1982)
 - Hess et al. (1981)
 - Busenberg and Plummer (1986)
 - Robie et al. (1978)
 - Helgeson et al. (1978)
 - Adjusted by the author for consistency with other values.
 - Bricker (1965)
 - Garrels and Christ (1965)
 - Calculated from Bricker (1969)
 - Busenberg et al. (1984)

Source: Dreyer, 1978

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 ₂ SO ₄	HSO ₄ ⁻	10 ²	-2
Nitric acid	HNO ₃	NO ₃ ⁻	10	-1
Hydronium-Ion (H ⁺ _(aq))	H ₃ O ⁺	H ₂ O	1	0.0
Trichloroacetic acid			2.0•10 ⁻¹	0.70
Oxalic acid	HOOC-COOH	HOOC-COO ⁻	5.9•10 ⁻²	1.23
Dichloroacetic acid			3.32•10 ⁻²	1.48
Sulfurous acid	H ₂ SO ₃	HSO ₃ ⁻	1.5•10 ⁻²	1.81
Hydrogensulfate ion	HSO ₄ ⁻	SO ₄ ²⁻	1.2•10 ⁻²	1.92
Phosphoric acid	H ₃ PO ₄	H ₂ PO ₄ ⁻	7.5•10 ⁻³	2.12
Glycinium ion			4.0•10 ⁻³	2.4
Pyruvic acid			3.24•10 ⁻³	2.49
Malonic acid			1.49•10 ⁻³	2.83
Chloroacetic acid			1.36•10 ⁻³	2.87
Citric acid			7.45•10 ⁻⁴	3.13
Nitrous acid	HNO ₂	NO ₂ ⁻	4.6•10 ⁻⁴	3.34
Hydrofluoric acid	HF	F ⁻	3.5•10 ⁻⁴	3.45
Formic acid			1.8•10 ⁻⁴	3.75
Lactic acid			1.4•10 ⁻⁴	3.86
Benzoic acid			6.46•10 ⁻⁵	4.19

Ascorbic acid (vitamin C)			$6.3 \cdot 10^{-5}$	4.2
Acid	HA	A⁻	K_a	pK_a
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	H_2CO_3	HCO_3^-	$4.3 \cdot 10^{-7}$	6.37
Hydrogen sulfide	H_2S	HS^-	$9.1 \cdot 10^{-8}$	7.04
Dihydrogenphosphate ion	H_2PO_4^-	HPO_4^{2-}	$6.2 \cdot 10^{-8}$	7.21
Hydrazinium ion	$\text{H}_2\text{N}^+\text{-NH}_3$	$\text{H}_2\text{N-NH}_2$	$5.9 \cdot 10^{-9}$	8.23
Boric acid	B(OH)_3	B(OH)_4^-	$7.2 \cdot 10^{-10}$	9.14
Ammonium ion	NH_4^+	NH_3	$5.6 \cdot 10^{-10}$	9.25
Hydrogen cyanide	HCN	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	HCO_3^-	CO_3^{2-}	$4.8 \cdot 10^{-11}$	10.32
Hydrogen peroxide	H_2O_2	HOO^-	$2.4 \cdot 10^{-12}$	11.62
Hydrogenphosphate ion	HPO_4^{2-}	PO_4^{3-}	$2.2 \cdot 10^{-13}$	12.67
Water	H_2O	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 ₂	molecular, elemental oxygen	O(0)
H ₂ O ₂	hydrogen peroxide	O(-I), H(I)
H ₂ O	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 ₂ CO 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)
C _(s)	elemental carbon, e.g. graphite or diamond	C(0)
CH ₂ O	formaldehyde	C(0)
C ₆ H ₁₂ O ₆	glucose	C(0)
CH ₃ -CH ₃	ethane	C(-III)
CH ₄	methane	C(-IV)
H ₂ SO 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 ₂ S	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.

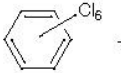
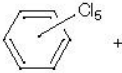
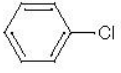
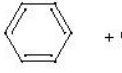
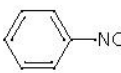
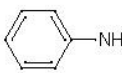
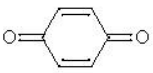
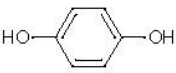
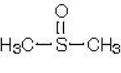
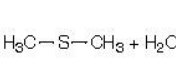
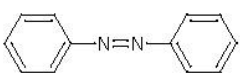
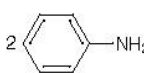
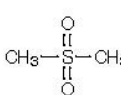
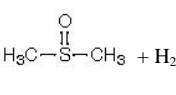
Reduction Half Reaction	$\log K$	pe°	$pe^\circ(W)$	E_H°
OX + ne ⁻ = RED	$\frac{\{RED\}}{\{OX\}\{e^-\}^n}$	$\frac{1}{n} \log K$	$pe^\circ - \frac{pe^\circ}{n} \cdot 7$	0.05916 pe°
Na ⁺ + e ⁻ = Na _(s)	-46.0	-46.0	-46.0	-2.71
Zn ²⁺ + 2e ⁻ = Zn _(s)	-26.0	-13.0	-13.0	-0.76
FeCO _{3(s)} + 2e ⁻ = Fe _(s) + 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 ₂ O + H ₂ O	-4.8	-1.2	-8.2	-0.071
CO _{2(g)} + 4H ⁺ + 4e ⁻ = $\frac{1}{6}C_6H_{12}O_6$ (glucose) + H ₂ O	-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 ₂ S	4.8	2.4	-4.6	0.14
Cu ²⁺ + e ⁻ = Cu ⁺	2.7	2.7	2.7	0.16
HCOO ⁻ + 3H ⁺ + 2e ⁻ = CH ₂ O + H ₂ O	5.64	2.82	-7.68	0.17
CO _{2(g)} + 8H ⁺ + 8e ⁻ = CH _{4(g)} + 2H ₂ O	23.0	2.87	-4.13	0.17
AgCl _(s) + e ⁻ = Ag _(s) + Cl ⁻	3.7	3.7	3.7	0.22
CH ₂ O + 2H ⁺ + 2e ⁻ = CH ₃ OH	8.0	4.0	-3.0	0.24
SO ₄ ²⁻ + 9H ⁺ + 8e ⁻ = HS ⁻ + 4H ₂ O	34.0	4.25	-3.63	0.25
Hg ₂ Cl _{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 ₂ S + 4H ₂ O	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 ₂ O	34.2	5.7	-2.47	0.34
SO ₄ ²⁻ + 8H ⁺ + 6e ⁻ = S _(s) + 4H ₂ O	36.2	6.03	-3.3	0.36

TABLE 19.2. (continued)

Reduction Half Reaction	$\log K$	pe°	$pe^\circ(W)$	E_H°
OX + ne ⁻ = RED	$\frac{\{RED\}}{\{OX\}\{e^-\}^n}$	$\frac{1}{n} \log K$	$pe^\circ - \frac{pe^\circ}{n} \cdot 7$	0.05916
CH ₂ O + 4H ⁺ + 4e ⁻ = CH _{4(g)} + H ₂ O	27.8	6.94	-0.06	0.41
Cu ⁺ + e ⁻ = Cu _(s)	8.8	8.8	8.8	0.52
CH ₂ OH + 2H ⁺ + 2e ⁻ = CH _{4(g)} + H ₂ O	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 ₃ ⁻ + 7H ⁺ + 6e ⁻ = NH ₃ + 2H ₂ O	81.5	13.58	5.41	0.80
NO ₃ ⁻ + 2H ⁺ + 2e ⁻ = NO ₂ ⁻ + H ₂ O	28.3	14.15	7.15	0.84
NO ₃ ⁻ + 10H ⁺ + 8e ⁻ = NH ₄ ⁺ + 3H ₂ O	119.2	14.9	6.15	0.88
NO ₃ ⁻ + 8H ⁺ + 6e ⁻ = NH ₄ ⁺ + 2H ₂ O	90.8	15.14	5.82	0.90
MnO _{2(s)} + HCO ₃ ⁻ + 3H ⁺ + 2e ⁻ = MnCO _{3(s)} + 2H ₂ O	25.8	15.9	5.4	0.94
(α)FeOOH _(s) + HCO ₃ ⁻ + 2H ⁺ + e ⁻ = FeCO _{3(s)} + 2H ₂ O	13.15	13.15	-0.85	0.78
(α)FeOOH _(s) + 3H ⁺ + e ⁻ = Fe ²⁺ + 2H ₂ O	13.5	13.5	-7.5	0.80
(am)Fe(OH) ₃ + 3H ⁺ + e ⁻ = Fe ²⁺ + 3H ₂ O	16.2	16.2	-4.8	0.96
O _{2(g)} + 4H ⁺ + 4e ⁻ = 2H ₂ O	83.1	20.78	13.78	-1.23
NO ₃ ⁻ + 6H ⁺ + 5e ⁻ = $\frac{1}{2}N_{2(g)}$ + 3H ₂ O	105.3	21.05	12.65	1.25
MnO _{2(s)} + 4H ⁺ + 2e ⁻ = Mn ²⁺ + 2H ₂ O	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 ₂ O	26.9	26.9	19.9	1.59
ClO ⁻ + 2H ⁺ + 2e ⁻ = Cl ⁻ + H ₂ O	57.8	28.9	21.8	1.71
H ₂ O 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 $E_{\text{H}}^{\circ}(\text{W})$ values.)^a

Halfreaction		E_{H}° (V)	$E_{\text{H}}^{\circ}(\text{W})$ ^b (V)	$\Delta_{\text{r}}G_{\text{H}}^{\circ}(\text{W})/n$ ^c (kJ·mol ⁻¹)
Oxidized Species	Reduced Species			
(1) $\text{CCl}_3-\text{CCl}_3 + 2e^-$	= $\text{Cl}_2\text{C}=\text{CCl}_2 + 2\text{Cl}^-$	+ 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) $\text{Cl}_2\text{C}=\text{CCl}_2 + \text{H}^+ + 2e^-$	= $\text{Cl}_2\text{C}=\text{CHCl} + \text{Cl}^-$	+ 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)  + $\text{H}^+ + 2e^-$	=  + Cl^-	+ 0.68	+ 0.56	- 54.0
(8)  + $\text{H}^+ + 2e^-$	=  + 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)  + $2\text{H}^+ + 2e^-$	=  + H_2O	+ 0.57	+ 0.16	- 15.4
(12)  + $4\text{H}^+ + 4e^-$	= 2 	+ 0.31	- 0.10	+ 9.7
(13)  + $2\text{H}^+ + 2e^-$	=  + H_2O	+ 0.17	- 0.24	+ 23.2
(14) $\text{R}-\text{S}-\text{S}-\text{R} + 2\text{H}^+ + 2e^-$ (cystine)	= $2\text{R}-\text{SH}$ (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 $[\text{H}^+] = 10^{-7}$, $\{\text{Cl}^-\} = 10^{-3}$, $\{\text{Br}^-\} = 10^{-5}$. ^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	$\gamma_i \rightarrow 1$ 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 $\sum \nu_i M_i = 0$	$\Delta H = \sum_i \nu_i \bar{H}_i$, $\Delta V = \sum_i \nu_i \bar{V}_i$, $\Delta S = \sum_i \nu_i \bar{S}_i$ $\Delta G = \sum_i \nu_i \mu_i$
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	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	$K = \left(\prod_i \left(\frac{m_i}{m^\circ} \right)^{\nu_i} \prod_i \gamma_i^{\nu_i} \right)_{\text{eq}}$
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	$\log \frac{K_{P_2}}{K_{P_1}} = -\frac{\Delta V^\circ (P_2 - P_1)}{2.3RT}$