1 Theoretical Background

1.1 Equilibrium reactions

1.1.1 Introduction

Chemical reactions determine occurrence, distribution, and behavior of aquatic species in water. The aquatic species is defined as organic and inorganic substances dissolved in water in contrast to colloids (1-1000 nm) and particles (> 1000 nm). This definition embraces free anions and cations sensu strictu as well as complexes (chapter 1.1.5.1). The term complex applies to negatively charged species such as OH^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}, NO_3^-, PO_4^{3-}, positively charged species such as $ZnOH^+$, CaH_2PO4^+, $CaCl^+$, and zero charged species such as $CaCO_3^0$, $FeSO_4^0$ or $NaHCO_3^0$ as well as organic ligands. Table 1 provides a summary of relevant inorganic elements and examples of their dissolved species.

Table 1 Selected inorganic elements and examples of aquatic species

Elements	
Major elements (>5mg/L)	
Calcium (Ca)	Ca^{2+}, $CaCO_3^0$, $CaHCO_3^+$, $CaOH^+$, $CaSO_4^0$, $CaHSO_4^+$, $Ca(CH_3COO)_2^0$, $CaB(OH)_4^+$, $Ca(CH_3COO)^+$, $CaCl^+$, $CaCl_2^0$, CaF^+, $CaH_2PO_4^+$, $CaHPO_4^0$, $CaNO_3^+$, $CaP_2O_7^{2-}$, $CaPO_4^-$
Magnesium (Mg)	Mg^{2+}, $MgCO_3^0$, $MgHCO_3^+$, $MgOH^+$, $MgSO_4^0$, $MgHSO_4^+$
Sodium (Na)	Na^+, $NaCO_3^-$, $NaHCO_3^0$, $NaSO_4^-$, $NaHPO_4^-$, NaF^0
Potassium (K)	K^+ , KSO_4^-, $KHPO_4^-$
Carbon (C)	HCO_3^-, CO_3^{2-}, $CO_{2(g)}$, $CO_{2(aq)}$, $Me^ICO_3^-$, $Me^IHCO_3^0$, $Me^{II}CO_3^0$, $Me^{II}HCO_3^+$, $Me^{III}CO_3^+$
Sulfur (S)	SO_4^{2-}, $H_2S_{(g/aq)}$, HS^-, and metal sulfide complexes, $Me^{(2)}S0_4^0$, $Me^{(2)}HSO_4^+$ and further sulfate complexes with uni- or multi-valent metals
Chlorine (Cl)	Cl^-, $CaCl^+$, $CaCl_2^0$ and further chloro-complexes with uni- or multi-valent metals
Nitrogen (N)	NO_3^-, NO_2^-, $NO_{(g/aq)}$, $NO_{2(g/aq)}$, $N_2O_{(g/aq)}$, $NH_{3(g/aq)}$, $HNO_{2(g/aq)}$, NH_4^+, $Me^{II}NO_3^+$
Silicon (Si)	$H_4SiO_4^0$, $H_3SiO_4^-$, $H_2SiO_4^{2-}$, SiF_6^{2-}, $UO_2H_3SiO_4^+$
Minor elements (0,1-5 mg/L)	
Boron (B)	$B(OH)_3^0$, $BF_2(OH)_2^-$, BF_3OH^-, BF_4^-
Fluorine (F)	F^-, AgF^0, AlF^{2+}, AlF_2^+, AlF_3^0, AlF_4^-, AsO_3F^{2-}, $BF_2(OH)_2$, BF_3OH^-, BF_4^-, BaF^+, CaF^+, CuF^+, FeF^+, FeF^{2+}, FeF_2^+, $H_2F_2^0$, $H_2PO_3F^0$, $HAsO_3F^-$, HF^0, HF_2, HPO_3F^-, MgF^+, MnF^+, NaF^0, PO_3F^{2-}, PbF^+, PbF_2^0, $Sb(OH)_2F^0$, SiF_6^-, SnF^+, SnF_2^0, SnF_3^-, SrF^+, ThF^{3+}, ThF_2^{2+}, ThF_3^+,

	ThF_4^0, UF^{3+}, UF_2^{2+}, UF_3^+, UF_4^0, UF_5^-, UF_6^{2-}, UO_2F^+, $UO_2F_2^0$, $UO_2F_3^-$, $UO_2F_4^{2-}$, ZnF^+
Iron (Fe)	Fe^{2+}, Fe^{3+}, $Fe(OH)_3^-$, $FeSO4^0$, $FeH_2PO_4^+$, $Fe(OH)_2^0$, $FeHPO_4^0$, $Fe(HS)_2^0$, $Fe(HS)_3^-$, $FeOH^{2+}$, $FePO_4^+$, $FeSO_4^+$, $FeCl^{2+}$, $FeCl_2^+$, $FeCl_3^0$, $Fe(OH)_2^+$, $Fe(OH)_3^0$, $Fe(OH)_4^-$, $FeH_2PO_4^{2+}$, FeF^{2+}, FeF_2^+, FeF_3^0, $Fe(SO_4)_2^-$, $Fe_2(OH)_2^{4+}$, $Fe_3(OH)_4^{5+}$
Strontium (Sr)	Sr^{2+}, $SrCO_3^0$, $SrHCO_3^+$, $SrOH^+$, $SrSO_4^0$
Trace elements (<0,1 mg/L)	
Lithium (Li)	Li^+, $LiSO_4^-$, $LiOH^0$, $LiCl^0$, $LiCH_3COO^0$, $Li(CH_3COO)_2^-$
Beryllium	BeO_2^{2-}, $Be(CH_3COO)_2^0$, $BeCH_3COO^+$
Aluminum (Al)	Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$, $Al(OH)_4^-$, AlF^{2+}, AlF_2^+, AlF_3^0, AlF_4, $AlSO_4^+$, $Al(SO_4)_2^-$, $Al(OH)_3^0$
Phosphor (P)	PO_4^{3-},HPO_4^{2-}, $H_2PO_4^-$, $H_3PO_4^0$, $MgPO_4^-$, $MgHPO_4^0$, $MgH_2PO_4^+$ (dito Ca, Fe^{II}), $NaHPO_4^-$, $KHPO_4^-$, $Fe^{III}H_2PO_4^{2+}$, $UHPO_4^{2+}$, $U(HPO_4)_2^0$, $U(HPO_4)_3^{2-}$, $U(HPO_4)_4^{4-}$, $UO_2HPO_4^0$, $UO_2(HPO_4)_2^{2-}$, $UO_2H_2PO_4^+$, $UO_2(H_2PO_4)_2^0$, $UO_2(H_2PO_4)_3^-$, $CrH_2PO_4^{2+}$, $CrO_3H_2PO_4^-$, $CrO_3HPO_4^{2-}$
Chromium (Cr)	Cr^{3+}, $Cr(OH)^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3^0$, $Cr(OH)_4^-$, CrO_2^-, $CrBr^{2+}$, $CrCl^{2+}$, $CrCl_2^+$, $CrOHCl_2^0$, CrF^{2+}, CrI^{2+}, $Cr(NH_3)_6^{3+}$, $Cr(NH_3)_5OH^{2+}$, $Cr(NH_3)_4(OH)_2^+$, $Cr(NH_3)_6Br^{2+}$, $CrNO_3^{2+}$, $CrH_2PO_4^{2+}$, $CrSO_4^+$, $CrOHSO_4^0$, $Cr_2(OH)_2(SO_4)_2^0$, CrO_4^{2-}, $HCrO_4^-$, $H_2CrO_4^0$, $Cr_2O_7^{2-}$, CrO_3Cl^-, $CrO_3H_2PO_4^-$, $CrO_3HPO_4^{2-}$, $CrO_3SO_4^{2-}$, $NaCrO_4^-$, $KCrO_4^-$
Manganese (Mn)	Mn^{2+}, $MnCl^+$, $MnCl_2^0$, $MnCl_3^-$, $MnOH^+$, $Mn(OH)_3^-$, MnF^+, $MnSO_4^0$, $Mn(NO_3)_2^0$, $MnHCO_3^+$
Cobalt (Co)	Co^{3+}, $Co(OH)_2^0$, $Co(OH)_4^-$, $Co_4(OH)_4^{4+}$,$Co_2(OH)_3^+$, $Co(CH_3COO)^+$, $Co(CH_3COO)_2^0$, $Co(CH_3COO)_3^-$, $CoCl^+$, $CoHS^+$, $Co(HS)_2^0$, $CoNO_3^+$,$CoBr_2^0$, CoI_2^0, $CoS_2O_3^0$, $CoSO_4^0$, $CoSeO_4^0$
Nickel (Ni)	Ni^{2+}, $Ni(CH_3COO)_2^0$, $Ni(CH_3COO)_3^-$, $Ni(NH_3)_2^{2+}$, $Ni(NH_3)_6^{2+}$, $Ni(NO_3)_2^0$, $Ni(OH)_2^0$, $Ni(OH)_3^-$, Ni_2OH^{3+}, $Ni_4(OH)_4^{4+}$, $NiBr^+$, $Ni(CH_3COO)^+$, $NiCl^+$, $NiHP_2O_7^-$, $NiNO_3^+$, $NiP_2O_7^{2-}$, $NiSO_4^0$, $NiSeO_4^0$
Silver (Ag)	Ag^+, $Ag(CH_3COO)_2^-$, $Ag(CO_3)_2^{2-}$, $Ag(CH_3COO)^0$, $AgCO_3^-$, $AgCl^0$, $AgCl_2^-$, $AgCl_3^{2-}$, $AgCl_4^{3-}$, AgF^0, $AgNO_3^0$
Copper (Cu)	Cu^+, $CuCl_2^-$, $CuCl_3^{2-}$, $Cu(S_4)_2^{3-}$, Cu^{2+}, $Cu(CH_3COO)^+$, $CuCO_3^0$, $Cu(CO_3)_2^{2-}$, $CuCl^+$, $CuCl_2^0$, $CuCl_3^-$, $CuCl_4^{2-}$, CuF^+, $CuOH^+$, $Cu(OH)_2^0$, $Cu(OH)_3^-$, $Cu(OH)_4^{2-}$, $Cu2(OH)_2^{2+}$, $CuSO_4^0$, $Cu(HS)_3^-$, $CuHCO_3^+$
Zinc (Zn)	Zn^{2+}, $ZnCl^+$, $ZnCl_2^0$, $ZnCl_3^-$, $ZnCl_4^{2-}$, ZnF^+, $ZnOH^+$, $Zn(OH)_2^0$, $Zn(OH)_3^-$, $Zn(OH)_4^{2-}$, $ZnOHCl^0$, $Zn(HS)_2^0$, $Zn(HS)_3^-$, $ZnSO_4^0$, $Zn(SO_4)_2^{2-}$, $ZnBr^+$, $ZnBr_2^0$, ZnI^+, ZnI_2^0, $ZnHCO_3^+$, $ZnCO3^0$, $Zn(CO_3)_2^{2-}$
Arsenic (As)	$H_3AsO_3^0$, $H_2AsO_3^-$, $HAsO_3^{2-}$, AsO_3^{3-}, $H_4AsO_3^+$, $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}, AsO_3F^{2-}, $HAsO_3F^-$
Selenium (Se)	Se^{2-}, HSe^-, H_2Se^0, $MnSe^0$, Ag_2Se^0, $AgOH(Se)_2^{4-}$, $HSeO_3^-$, SeO_3^{2-}, $H_2SeO_3^0$, $FeHSeO_3^{2+}$, $AgSeO_3^-$, $Ag(SeO_3)_2^{3-}$, $Cd(SeO_3)_2^{2-}$, SeO_4^{2-}, $HSeO_4^-$, $MnSeO_4^0$, $NiSeO_4^0$, $CdSeO_4^0$, $ZnSeO_4^0$, $Zn(SeO_4)_2^{2-}$
Bromine (Br)	Br^-, $ZnBr^+$, $ZnBr_2^0$, $CdBr^+$, $CdBr_2^0$,$PbBr^+$, $PbBr_2^0$, $NiBr^+$, $AgBr^0$, $AgBr_2^-$, $AgBr_3^{2-}$ (as well as Tl-, Hg- and Cr-complexes)
Molybdenum (Mo)	Mo^{6+}, $H_2MoO_4^0$, $HMoO_4^-$ and MoO_4^{2-}, $Mo(OH)_6^0$, $MoO(OH)_5^-$, MoO_2^{2+} , $MoO_2S_2^{2-}$, $MoOS_3^{2-}$
Cadmium (Cd)	Cd^{2+} , $CdCl^+$, $CdCl_2^0$, $CdCl_3^-$, CdF^+, CdF_2^0, $Cd(CO_3)_3^{4-}$, $CdOH^+$, $Cd(OH)_2^0$, $Cd(OH)_3^-$, $Cd(OH)_4^{2-}$, $Cd2OH^{3+}$, $CdOHCl^0$, $CdNO_3^+$, $CdSO_4^0$, $CdHS^+$, $Cd(HS)_2^0$, $Cd(HS)_3^-$, $Cd(HS)_4^2$, $CdBr^+$, $CdBr_2^0$, CdI^+,

	CdI_2^0, $CdHCO_3^+$, $CdCO_3^0$, $Cd(SO_4)_2^{2-}$
Antimony (Sb)	$Sb(OH)_3^0$, $HSbO_2^0$, $SbOF^0$, $Sb(OH)_2F^0$, SbO^+, SbO_2^-, $Sb(OH)_2^+$, $Sb_2S_4^{2-}$, $Sb(OH)_6^-$, SbO_3^-, SbO_2^+, $Sb(OH)_4^-$
Barium (Ba)	Ba^{2+}, $BaOH^+$, $BaCO3^0$, $BaHCO_3^+$, $BaNO_3^-$, BaF^-, $BaCl^+$, $BaSO_4^0$, $BaB(OH)_4^+$, $Ba(CH_3COO)_2^0$
Mercury (Hg)	Hg^{2+}, $Hg(OH)_2^0$, $HgBr^+$, $HgBr_2^0$, $HgBr_3^-$, $HgBr_4^{2-}$, $HgBrCl^0$, $HgBrI^0$, $HgBrI_3^{2-}$, $HgBr_2I_2^{2-}$, $HgBr_3I^{2-}$, $HgBrOH^0$, $HgCl^+$, $HgCl2^0$, $HgCl_3^-$, $HgCl_4^{2-}$, $HgClI^0$, $HgClOH^0$, HgF^+, HgI^+, HgI_2^0, HgI_3^-, HgI_4^{2-}, $HgNH_3^{2+}$, $Hg(NH_3)_2^{2+}$, $Hg(NH_3)_3^{2+}$, $Hg(NH_3)_4^{2+}$, $HgNO_3^+$, $Hg(NO_3)_2^0$, $HgOH^+$, $Hg(OH)_3^-$, HgS_2^{2-}, $Hg(HS)_2^0$, $HgSO_4^0$
Thallium (Tl)	Tl^+, $Tl(OH)_3^0$, $TlOH^0$, TlF^0, $TlCl^0$, $TlCl_2^-$, $TlBr^0$, $TlBr_2^-$, $TlBrCl^-$, TlI^0, TlI_2^-, $TlIBr^-$, $TlSO_4^-$, $TlNO_3^0$, $TlNO_2^0$, $TlHS^0$, $Tl2HS^+$, $Tl_2OH(HS)_3^{2-}$, $Tl_2(OH)_2(HS)_2^{2-}$, Tl^{3+}, $TlOH^{2+}$, $Tl(OH)_2^+$, $Tl(OH)_4^-$, $TlCl^{2+}$, $TlCl_2^+$, $TlCl_3^0$, $TlCl_4^-$, $TlBr^{2+}$, $TlBr_2^+$, $TlBr_3^0$, $TlBr_4^-$, TlI_4^-, $TlNO_3^{2+}$, $TlOHCl^+$
Lead (Pb)	Pb^{2+}, $PbCl^+$, $PbCl_2^0$, $PbCl_3^-$, $PbCl_4^{2-}$, $Pb(CO_3)_2^{2-}$, PbF^+, PbF_2^0, PbF_3^-, PbF_4^{2-}, $PbOH^+$, $Pb(OH)_2^0$, $Pb(OH)_3^-$, Pb_2OH^{3+}, $PbNO_3^+$, $PbSO_4^0$, $Pb(HS)_2^0$, $Pb(HS)_3^-$, $Pb3(OH)_4^{2+}$, $PbBr^+$, $PbBr_2^0$, PbI^+, PbI_2^0, $PbCO_3^0$, $Pb(OH)_4^{2-}$, $Pb(SO_4)_22^-$, $PbHCO_3^+$
Thorium (Th)	Th^{4+} , $Th(H_2PO_4)_2^{2+}$, $Th(HPO_4)_2^0$, $Th(HPO_4)_3^{2-}$, $Th(OH)_2^{2+}$, $Th(OH)^{3+}$, $Th(OH)_4^0$, $Th(SO_4)_2^0$, $Th(SO_4)_3^{2-}$, $Th(SO_4)_4^{4-}$, $Th_2(OH)_2^{6+}$, $Th_4(OH)_8^{8+}$, $Th_6(OH)_{15}^{9+}$, $ThCl^{3+}$, $ThCl_2^{2+}$, $ThCl_3^+$, $ThCl_4^0$, ThF^{3+} , ThF_2^{2+} , ThF_3^+ , ThF_4^0 , $ThH_2PO_4^{3+}$, $ThH_3PO_4^{4+}$, $ThHPO_4^{2+}$, $ThOH^{3+}$, $ThSO_4^{2+}$
Radium (Ra)	Ra^{2+}, $RaOH^+$, $RaCl^+$, $RaCO_3^0$, $RaHCO_3^+$, $RaSO_4^0$, $RaCH_3COO^+$
Uranium (U)	U^{4+}, UOH^{3+}, $U(OH)_2^{2+}$, $U(OH)_3^+$, $U(OH)_4^0$, $U(OH)_5^-$, $U6(OH)_{15}^{9+}$, UF^{3+}, UF_2^{2+}, F_3^+, UF_4^0, UF_5^-, UF_6^{2-}, UCl^{3+}, USO_4^{2+}, $U(SO_4)_2^0$, $UHPO_4^{2+}$, $U(HPO_4)_2^0$, $U(HPO_4)_3^{2-}$, $U(HPO4)_4^{4-}$, UO_2OH^+, $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_3(OH)_5^+$, $UO_2CO_3^0$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, UO_2^{2+}, UO_2F^+, $UO_2F_2^0$, $UO_2F_3^-$, $UO_2F_4^{2-}$, UO_2Cl^+, $UO_2SO_4^0$, $UO_2(SO_4)_2^{2-}$, $UO_2HPO_4^0$, $UO_2(HPO_4)_2^{2-}$, $UO_2H_2PO_4^+$, $UO_2(H_2PO_4)_2^0$, $UO_2(H_2PO_4)_3^-$, $UO_2H_3SiO_4^+$

Besides inorganic species there are a number of significant organic (Table 2) and biotic substances (Table 3) in water that are of great importance for water quality.

Table 2 Selected organic substances (plus-sign in brackets means that geogene formation in traces is possible, only the typical concentration range is indicated)

Substance	geogene	anthropogene	typical range of concentration
Humic matter	+	-	mg/L
aliphatic carbons: oil, fuel	+	+	mg/L
Phenols	+	+	mg/L
BTEX (benzene, toluene, ethylbenzene, xylene)	(+)	+	µg/L
PAHs (polycyclic aromatic hydrocarbons)	(+)	+	µg/L
PCBs (polychlorinated biphenyls)	-	+	µg/L

Substance	geogene	anthropogene	typical range of concentration
CFC´s (Chlorofluorocarbons)	-	+	ng/L
Dioxins, furans	(+)	+	pg/L
pesticides	(+)	+	ng/L
hormones	(+)	+	pg/L
pharmaceuticals	-	+	pg/L

Table 3 Organisms in groundwater

	size
Virus	10 - 1000 nm
Prokaryotes	
Bacteria	500 - 5.000 nm
Archaea (methaneogenous, extreme halophiles, extreme thermophiles)	100 - 15.000 nm
Eukaryotes	
Protozoa (Foraminifera, Radiolaria, Dinoflagellata)	> 3 µm
Yeast (anaerob)	~20 µm
Fungi (aerob)	
Fish (Brotulidae, Amblyopsidae, Astyanax Jordani, Caecobarbus Geertsi)	mm… cm

Interactions of the different species among themselves (chapter 1.1.5), with gases (chapter 1.1.3), and solid phases (minerals) (chapter 1.1.4.) as well as transport (chapter 1.3) and decay processes (biological decomposition, radioactive decay) are fundamental in determining the hydrogeochemical composition of ground and surface water.

Hydrogeochemical reactions involving only a single phase are called homogeneous, whereas heterogeneous reactions occur between two or more phases such as gas and water, water and solids, or gas and solids. In contrast to open systems, closed systems can only exchange energy, not constituents, with the environment.

Chemical reactions can be described by thermodynamics (chapter 1.1.2) and kinetics (chapter 1.2). Reactions expressed by the mass-action law (chapter 1.1.2.1), are thermodynamically reversible and independent of time. In contrast, kinetic processes are time dependent reactions. Thus, models that take into account kinetics can describe irreversible reactions such as decay processes that require finite amounts of time and cannot be reversed under a given set of conditions.

1.1.2 Thermodynamic fundamentals

1.1.2.1 Mass action law

In principle, any chemical equilibrium reaction can be described by the mass-action law.

$$aA + bB \leftrightarrow cC + dD \qquad \text{Eq. (1.)}$$

$$K = \frac{\{C\}^c \cdot \{D\}^d}{\{A\}^a \cdot \{B\}^b} \qquad \text{Eq. (2.)}$$

With a, b, c, d = number of moles of the reactants A, B, and the end products C, D, respectively for the given reaction, (1);
K = thermodynamic equilibrium or dissociation constant (general name)

In particular, the term K is defined in relation to the following types of reactions using the mass-action law:

- Dissolution/ Precipitation (chapter 1.1.4.1)
  K_S= solubility product constant
- Sorption (chapter 1.1.4.2)
  K_d=distribution coefficient
  K_x=selectivity coefficient
- Complex formation /destruction of complexes (chapter 1.1.5.1)
  K= complexation constant, stability constant
- Redox reaction (chapter 1.1.5.2)
  K= stability constant

If one reverses reactants and products in a reaction equation, then the solubility constant is K'=1/K. Hence it is important always to convey the reaction equation with the constant.

Furthermore, it must be clearly stated, if one deals with a conditional constant, being valid for one type of standard state, or with an infinite dilution constant, another type of standard state (i.e. T=25°C and ionic strength I=0). The latter might be calculated from the former. Standard temperature conditions can be calculated using the van't Hoff equation (Eq. 3), whereas the following equation (Eq. 4) can be applied to determine the effect of pressure:

$$\log(K_r) = \log(K_0) + \frac{H^0{}_r}{2.303 \cdot R} \cdot \frac{T_K - T_{K_0}}{T_K \cdot T_{K_0}} \qquad \text{Eq. (3.)}$$

with K_r = equilibrium constant at temperature
K_0 = equilibrium constant at standard temperature
T_K = temperature in degrees Kelvin
T_{K_0} = temperature in Kelvin, at which the standard enthalpy $H^0{}_r$ was estimated
R = ideal gas constant (8.315 J/K mol)

$$\ln K(P) = \ln K(S) - \frac{\Delta V(T)}{T \cdot R \cdot \beta} \cdot \ln \frac{\sigma(P)}{\sigma(S)} \qquad \text{Eq. (4.)}$$

with K(P) equilibrium constant at pressure P
K(S) equilibrium constant at saturation vapor pressure

$\Delta V(T)$ = volume change of the dissociation reaction at temperature T and saturation water pressure S

ß =coefficient of the isothermal compressibility of water at T and P

σ (P) = density of water at pressure P

σ (S) = density of water at saturation water pressure conditions

Fig. 1 shows the dependence of calcite dissolution on different pressure and temperature conditions.

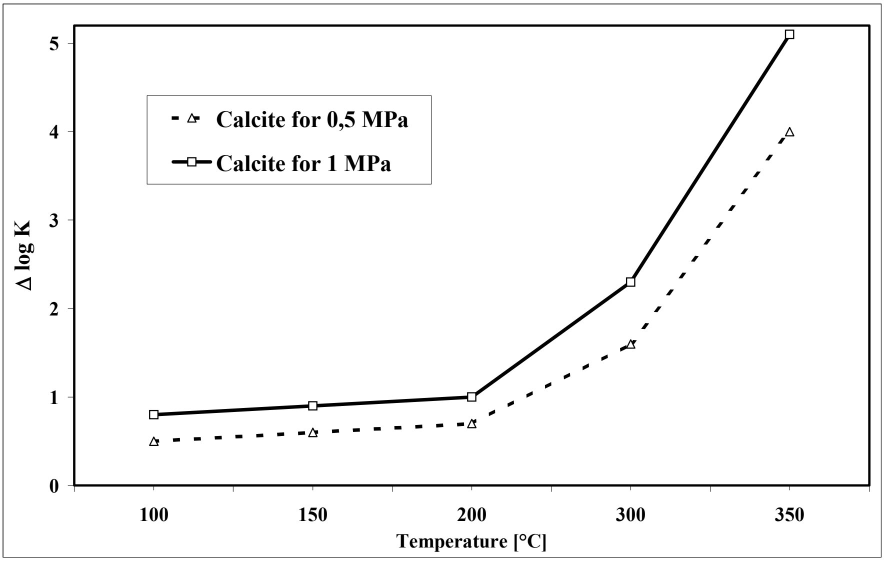


Fig. 1 Influence of pressure and temperature on the solubility of calcite (after Kharaka et al. 1988)

If a process consists of a series of subsequent reactions, as for instance the dissociation of H_2CO_3 to HCO_3^- and to CO_3^{2-}, then the stability (dissociation) constants are numbered in turn (e.g. K_1 and K_2).

1.1.2.2 Gibbs free energy

A system at constant temperature and pressure is at disequilibrium until all of its Gibbs free energy, G, is used up. In the equilibrium condition the Gibbs free energy equals zero.

The Gibbs free energy is a measure of the probability that a reaction occurs. It is composed of the enthalpy, H, and the entropy, S^0 (Eq. 5). The enthalpy can be described as the thermodynamic potential, which ensues $H = U + p*V$, where U is the internal energy, p is the pressure, and V is the volume. The entropy, according to classical definitions, is a measure of molecular order of a thermodynamic system and the irreversibility of a process, respectively.

$$G = H - S^0 \cdot T \qquad \text{Eq. (5.)}$$

with T = temperature in Kelvin

A positive value for G means that additional energy is required for the reaction to happen, and a negative value that the process happens spontaneously thereby releasing energy.

The change in free energy of a reaction is directly related to the change in energy of the activities of all reactants and products under standard conditions.

$$G = G^0 + R \cdot T \cdot \ln \frac{\{C\}^c \cdot \{D\}^d}{\{A\}^a \cdot \{B\}^b} \qquad \text{Eq. (6.)}$$

with R = ideal gas constant
G^0 = standard Gibbs free energy at 25°C and 100 kPa

G^0 equals G, if all reactants occur with unit activity, and thus the argument of the logarithm in Eq. 6 being 1 and consequently the logarithm becoming zero.

For equilibrium conditions it follows:

$$G = 0 \qquad \text{and} \qquad G^0 = - R \cdot T \cdot \ln K \qquad \text{Eq. (7.)}$$

Accordingly G provides a forecast of the direction in which the reaction aA + bB ↔ cC + dD proceeds. If G <0, the reaction to the right hand side will dominate, for G>0 it is the other way round.

1.1.2.3 Gibbs phase rule

The Gibbs phase rule states the number of the degrees of freedom that results from the number of components and phases, coexisting in a system.

$$F = C - P + 2 \qquad \text{Eq. (8.)}$$

with F = number of degrees of freedom
C = number of components
P = number of phases

The number 2 in the Eq. 8 arises from the two independent variables, pressure and temperature. Phases are limited, physically and chemically homogeneous, mechanically separable parts of a system. Components are defined as simple chemical entities or units that comprise the composition of a phase.

In a system, where the number of phases and the number of components are equal, there are two degrees of freedom, meaning that two variables can be varied independently (e.g. temperature and pressure). If the number of the degrees of freedom is zero, then temperature and pressure are constant and the system is invariant.

In a three-phase system including a solid and a liquid as well as a gas, the Gibbs phase rule is modified to:

$$F = C' - N - P + 2 \qquad \text{Eq. (9.)}$$

with F = number of the degrees of freedom
C′ = number of different chemical species
N = number of possible equilibrium reactions (species, charge balance, stoichiometric relations)-
P = number of phases

1.1.2.4 Activity

For the mass-action law, the quantities of substances are represented as activities, a_i, and not as concentrations, c_i, with respect to a species, i.

$$a_i = f_i \cdot c_i \qquad \text{Eq.(10.)}$$

In Eq. 10, the activity coefficient, f_i, is an ion-specific correction factor describing how interactions among charged ions influence each other. Since the activity coefficient is a non-linear function of ionic strength, the activity is a non–linear function of the concentration, too.

The activity decreases with increasing ionic strength up to 0.1 mol/kg and is always lower than the concentration, for the reason that the ions are charged and oppositely charged ions interact with each other to reduce the available charge. Thus the value of the activity coefficient is less than 1 (Fig. 2). Clearly, while increasing ion concentration, the higher the valence state, the stronger is the decrease in activity. In the ideal case of an infinitely dilute solution, where the interactions amongst the ions are close to zero, the activity coefficient is 1 and the activity equals the concentration.

Only mean activity coefficients can be experimentally determined for salts, not activity coefficients for single ions. The MacInnes Convention is one method for obtaining single ion activity coefficients and states that because of the similar size and mobility of the potassium and chloride ions:

$$f_i(K^+) = f_i(Cl^-) = f_\pm(KCl) \qquad \text{Eq.(11.)}$$

1.1.2.5 Ionic strength

The calculation of the ionic strength, the summation of the ionic forces, is one-half the sum of the product of the moles of the species involved, m_i, and their charge numbers z_i.

$$I = 0.5 \cdot \sum m_i \cdot z_i^2 \qquad \text{Eq.(12.)}$$

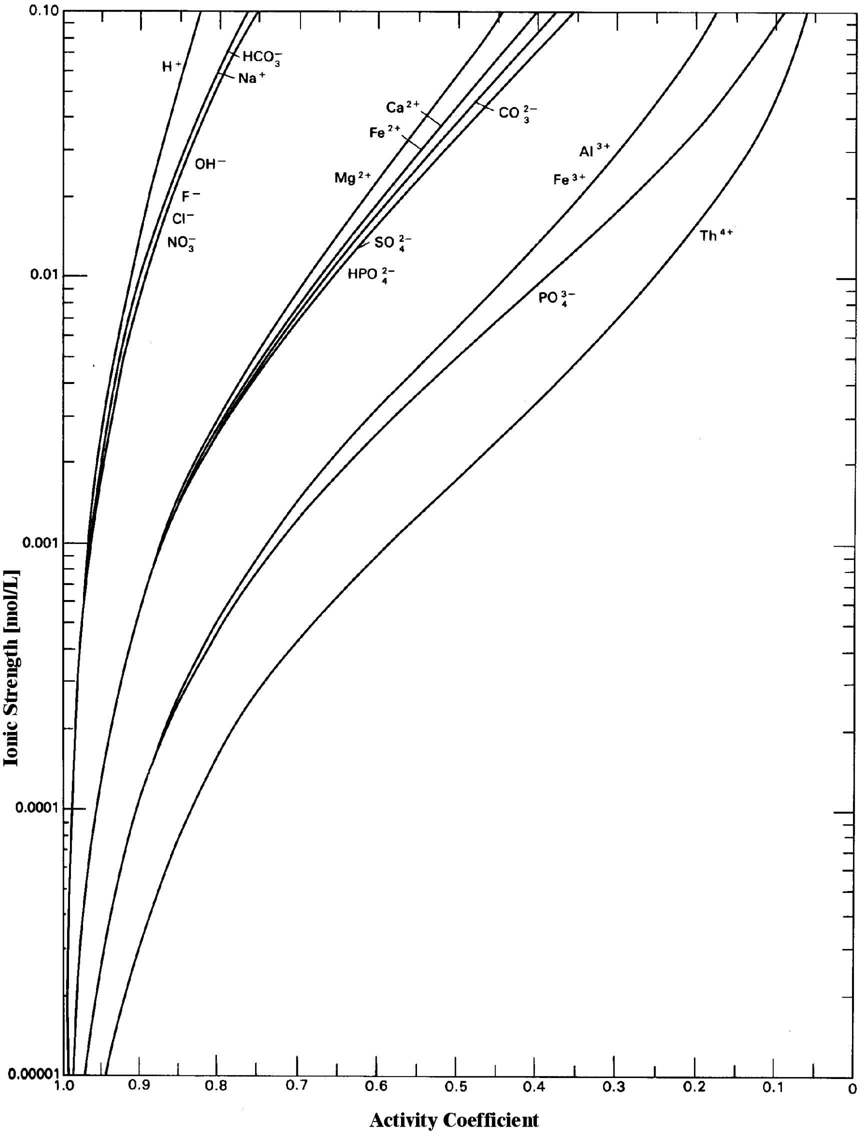


Fig. 2 Relation between ionic strength and activity coefficient in a range up to 0.1 mol/L (after Hem 1985)

1.1.2.6 Calculation of activity coefficient

1.1.2.6.1. Theory of ion dissociation

Given the ionic strength of the solution from the chemical analysis, the activity coefficient can be computed using several approximation equations. All of them are inferred from the DEBYE-HÜCKEL equation and differ in the range of the ionic strength they can be applied for.

DEBYE-HÜCKEL equation (Debye & Hückel 1923)

$$\log(f_i) = -A \cdot z_i^2 \cdot \sqrt{I} \qquad I < 0.005\ \text{mol/kg} \qquad \text{Eq.(13.)}$$

extended DEBYE-HÜCKEL equation

$$\log(f_i) = \frac{-A \cdot z_i^2 \cdot \sqrt{I}}{1 + B \cdot a_i \cdot \sqrt{I}} \qquad I < 0.1\ \text{mol/kg} \qquad \text{Eq.(14.)}$$

GÜNTELBERG equation (Güntelberg 1926)

$$\log(f_i) = -0.5 z_i^2 \frac{\sqrt{I}}{1 + 1.4\sqrt{I}} \qquad I < 0.1\ \text{mol/kg} \qquad \text{Eq.(15.)}$$

DAVIES equation (Davies 1962, 1938)

$$\log(f_i) = -A \cdot z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 \cdot I\right) \qquad I < 0.5\ \text{mol/kg} \qquad \text{Eq.(16.)}$$

“WATEQ” DEBYE-HÜCKEL equation (Truesdell & Jones 1974)

$$\log(f_i) = \frac{-A \cdot z_i^2 \cdot \sqrt{I}}{1 + B \cdot a_i \cdot \sqrt{I}} + b_i \cdot I \qquad I < 1\ \text{mol/kg} \qquad \text{Eq.(17.)}$$

with f = activity coefficient
z = valence
I = ionic strength
a_i, b_i = ion- specific parameters (depend on the ion radius) (selected values see Table 4, complete overview in van Gaans (1989) and Kharaka et al. (1988))
A,B temperature dependent parameters, calculated from the following empirical equations (Eq. 18 to Eq. 21)

$$A = \frac{1.82483 \cdot 10^6 \cdot \sqrt{d}}{(\varepsilon \cdot T_K)^{3/2}} \qquad \text{Eq.(18.)}$$

$$B = \frac{50.2916 \cdot \sqrt{d}}{(\varepsilon \cdot T_K)^{1/2}} \qquad \text{Eq.(19.)}$$

$$d = 1 - \frac{(T_c - 3.9863)^2 \cdot (T_c + 288.9414)}{508929.2 \cdot (T_c + 68.12963)} + 0.011445 \cdot e^{-374.3/T_c} \qquad \text{Eq.(20.)}$$

$$\varepsilon = 2727.586 + 0.6224107 \cdot T_K - 466.9151 \cdot \ln(T_K) - \frac{52000.87}{T_K} \qquad \text{Eq.(21.)}$$

with d = density (after Gildseth et al. 1972 for 0-100°)
ε = dielectric constant (after Nordstrom et al. 1990 for 0-100°C)
T_C = temperature in ° Celsius
T_K = temperature in Kelvin

For temperatures of about 25°C and water with a density of d: A = 0.51, B = 0.33. In some textbooks B is charted as $0.33*10^8$. For the use of the latter, a_i must be in cm, otherwise in Å ($=10^{-8}$ cm).

Table 4 Ion-specific parameters a_i and b_i (after Parkhurst et al. 1980 and (*) Truesdell a. Jones 1974)

Ion	a_i [Å]	b_i [Å]
H^+	4.78	0.24
Li^+	4.76	0.20
Na^+ (*)	4.0	0.075
Na^+	4.32	0.06
K^+ (*)	3.5	0.015
K^+	3.71	0.01
Cs^+	1.81	0.01
Mg^{2+} (*)	5.5	0.20
Mg^{2+}	5,46	0.22
Ca^{2+} (*)	5.0	0.165
Ca^{2+}	4.86	0.15
Sr^{2+}	5.48	0.11
Ba^{2+}	4.55	0.09
Al^{3+}	6.65	0.19

Ion	a_i [Å]	b_i [Å]
Mn^{2+}	7.04	0.22
Fe^{2+}	5.08	0.16
Co^{2+}	6.17	0.22
Ni^{2+}	5.51	0.22
Zn^{2+}	4.87	0.24
Cd^{2+}	5.80	0.10
Pb^{2+}	4.80	0.01
OH^-	10.65	0.21
F^-	3.46	0.08
Cl^-	3.71	0.01
ClO_4^-	5.30	0.08
HCO_3^-, CO_3^{2-} (*)	5.40	0
SO_4^{2-} (*)	5.0	-0.04
SO_4^{2-}	5.31	-0.07

The valid range for the theory of dissociation does not exceed 1 mol/kg, some authors believe the upper limit should be at 0.7 mol/kg (sea water). Fig. 3 shows, that already at an ionic strength of > 0.3 mol/kg (H^+), the activity coefficient does not further decrease but increases, and eventually attains values of more than 1.

The second term in the DAVIES and extended DEBYE-HÜCKEL equations forces the activity coefficient to increase at high ionic strength. This is owed to the fact, that ion interactions are not only based on Coulomb forces any more, ion sizes change with the ionic strength, and ions with the same charge interact.

Moreover, with the increase in the ionic strength a larger fraction of water molecules is bound to ion hydration sleeves, whereby a strong reduction of the concentration of free water molecules occurs and therefore the activity or the activity coefficient, related to 1kg of free water molecules, increases correspondingly.

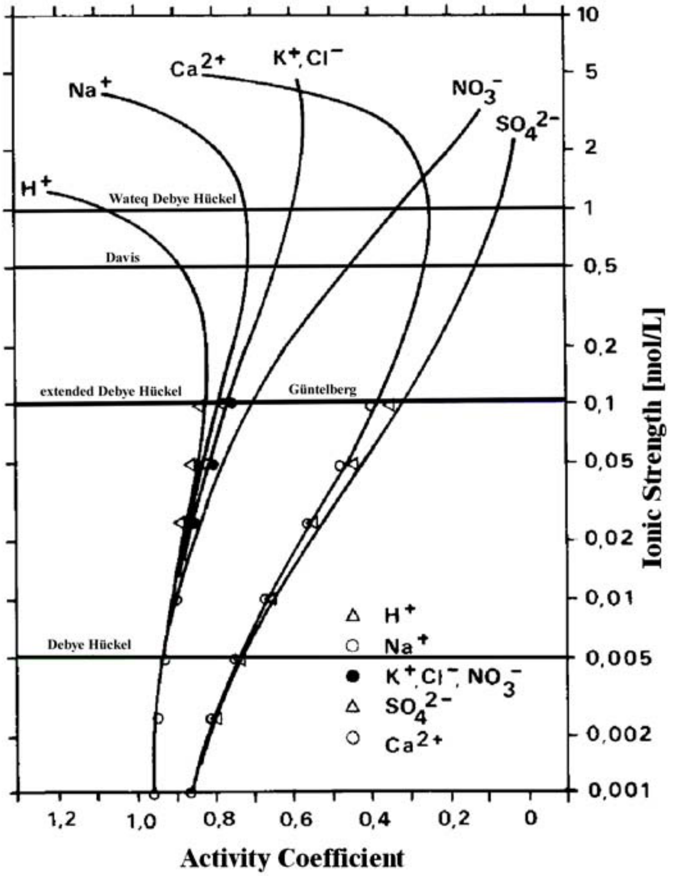


Fig. 3 Relation of ionic strength and activity coefficient in higher concentrated solutions, (up to I = 10mol/kg), valid range for the different theories of dissociation are indicated as lines (modified after Garrels and Christ 1965)

1.1.2.6.2. Theory of ion interaction

For higher ionic strength, e.g. highly saline waters; the PITZER equation can be used (Pitzer 1973). This semi-empirical model is based also on the DEBYE-HÜCKEL equation, but additionally integrates "virial" equations (vires = Latin for forces), that describe ion interactions (intermolecular forces). Compared with the ion dissociation theory the calculation is much more complicated and requires a higher number of parameters that are often lacking for more complex solution species. Furthermore, a set of equilibrium constants (albeit minimal) for complexation reactions is still required.

In the following only a simple example of the PITZER equation is briefly described. For the complete calculations and the necessary data of detailed parameters and equations the reader is referred to the original literature (Pitzer 1973, Pitzer 1981, Whitfield 1975, Whitfield 1979, Silvester and Pitzer 1978, Harvie and Weare 1980, Gueddari et al. 1983, Pitzer 1991).

The calculation of the activity coefficient is separately done for positively (index i) and negatively (index j) charged species applying Eq. 22. In this example the calculation of the activity coefficients for cations is shown, which can be analogously done for anions just exchanging the corresponding indices.

$$\ln f_M = z_M{}^2 \cdot F + S1 + S2 + S3 + |z_M| \cdot S4 \qquad \text{Eq.(22.)}$$

with M = cation
z_M = valence state of cation M
F, S1-S4 = sums, calculated using Eqs. 23-30

$$S1 = \sum_{j=1}^{a} m_j (2 \cdot B_{Mj} + z \cdot C_{Mj}) \qquad \text{Eq.(23.)}$$

$$S2 = \sum_{i=1}^{c} m_i (2 \cdot \phi_{Mj} + \sum_{j=1}^{a} m_j \cdot P_{Mij}) \qquad \text{Eq.(24.)}$$

$$S3 = \sum_{j=1}^{a\text{-}1} \sum_{k=j+1}^{a} m_j{}^2 \cdot P_{Mjk} \qquad \text{Eq.(25.)}$$

$$S4 = \sum_{i=1}^{c} \sum_{j=1}^{a} m_i \cdot m_j \cdot c_{ij} \qquad \text{Eq.(26.)}$$

with B, C, Φ, P = species- specific parameters, which must be known for all combinations of the species
m = molarities [mol/L]
k = index
c = number of cations
a = number of anions

$$F = -\frac{2.303 \cdot A}{3.0} \left(\frac{\sqrt{I}}{1 + 1.2 \cdot \sqrt{I}} + \frac{2}{1.2} \cdot \ln(1 + 1.2 \cdot \sqrt{I}) \right) + S5 + S6 + S7 \qquad \text{Eq.(27.)}$$

$$S5 = \sum_{i=1}^{c} \sum_{j=1}^{a} m_i \cdot m_j \cdot B'_{ij} \qquad \text{Eq.(28.)}$$

$$S6 = \sum_{i=1}^{c-1} \sum_{k=i+1}^{c} m_i^2 \cdot \phi'_{ik} \qquad \text{Eq.(29.)}$$

$$S7 = \sum_{j=1}^{a-1} \sum_{l=j+1}^{a} m_j^2 \cdot \phi'_{jl} \qquad \text{Eq.(30.)}$$

with A = DEBYE-HÜCKEL constant (Eq. 18)
B′, Φ′ = Virial coefficients, modified with regard to the ionic strength
k, l = indices

If the ionic strength exceeds 6 mol/L, the PITZER equation is no longer applicable though.

1.1.2.7 Theories of ion dissociation and ion interaction

Fig. 4 to Fig. 8 show the severe divergence for activity coefficients such as given here for calcium, chloride, sulfate, sodium and water ions, calculated with different equations. The activity coefficients were calculated applying Eq. 13 to Eq. 17 for the corresponding ion dissociation theories, whereas the values for the PITZER equations were gained using the program PHRQPITZ. The limit of validity of each theory is clearly shown.

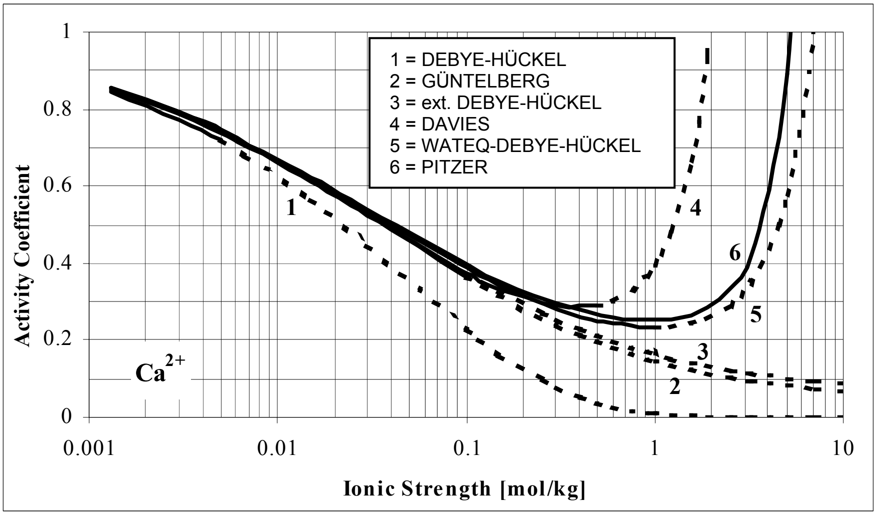


Fig. 4 Comparison of the activity coefficient of Ca^{2+} in relation to the ionic strength as calculated using a $CaCl_2$ solution (a_{Ca} = 4.86, b_{Ca} = 0.15 Table 4) and different theories of ion dissociation and the PITZER equation, dashed lines signify calculated values outside the validity range of the corresponding ion dissociation equation.

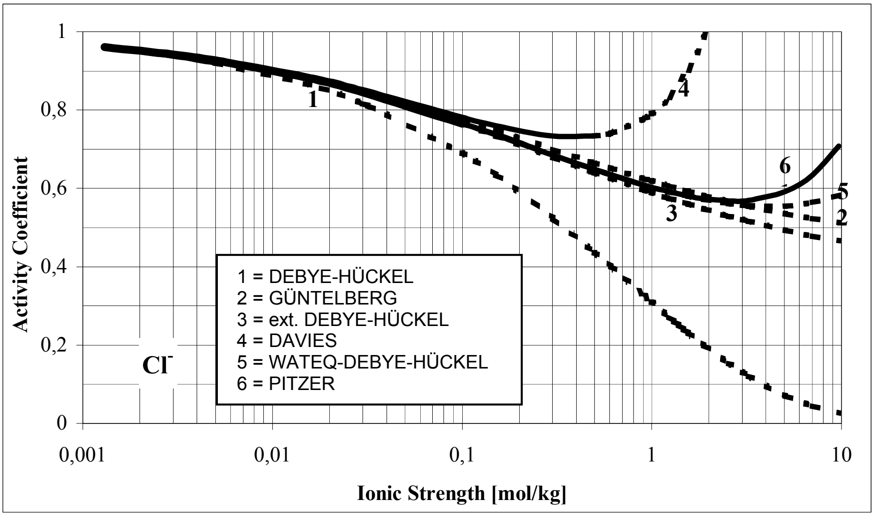


Fig. 5 Comparison of the activity coefficient of Cl^- in relation to the ionic strength as calculated using a $CaCl_2$ solution ($a_{Cl} = 3.71$, $b_{Cl} = 0.01$ Table 4) and different theories of ion dissociation and the PITZER equation, dashed lines signify calculated values outside the validity range of the corresponding ion dissociation equation.

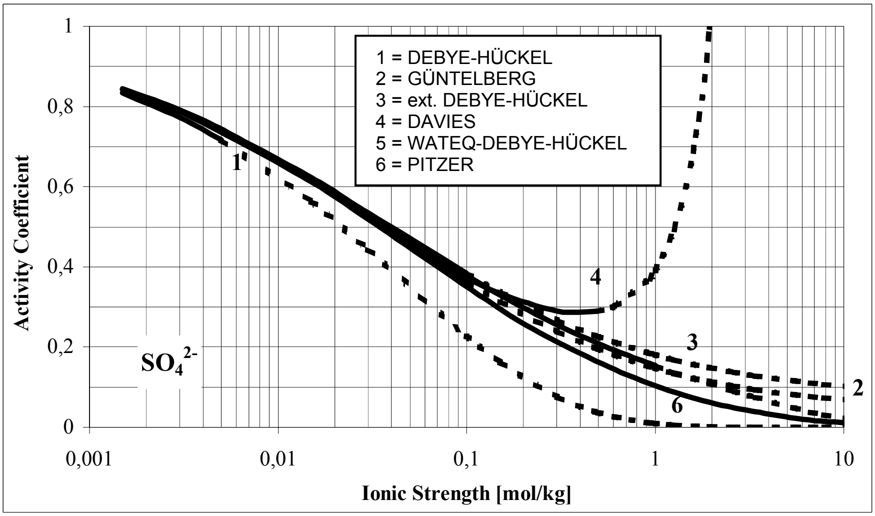


Fig. 6 Comparison of the activity coefficient of SO_4^{2-} in relation to the ionic strength as calculated using a $Na_2(SO_4)$ solution ($a_{SO4\text{-}2}= 5.31$, $b_{SO4\text{-}2}= -0.07$ Table 4) and different theories of ion dissociation and the PITZER equation, dashed lines signify calculated values outside the validity range of the corresponding ion dissociation equation.

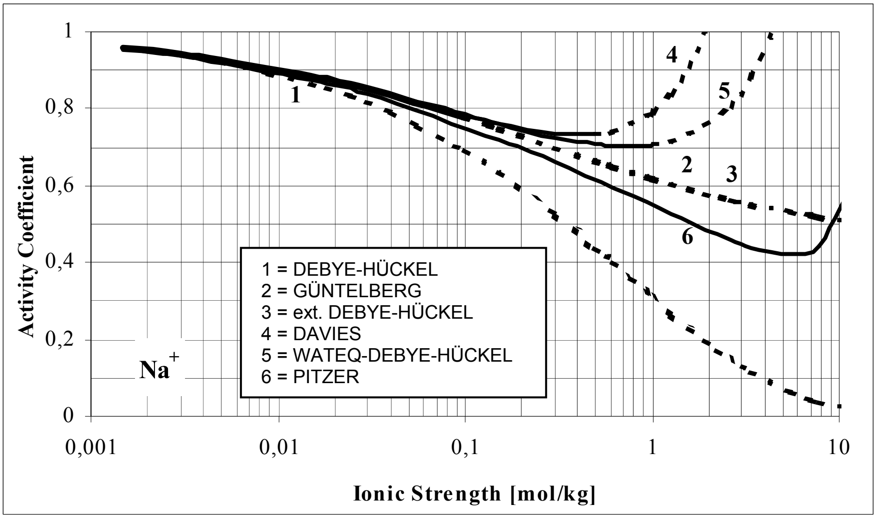


Fig. 7 Comparison of the activity coefficient of Na^+ in relation to the ionic strength as calculated using a $Na_2(SO_4)$ solution (a_{Na} = 4.32, b_{Na} = 0.06 Table 4) and different theories of ion dissociation and the PITZER equation, dashed lines signify calculated values outside the validity range of the corresponding ion dissociation equation.

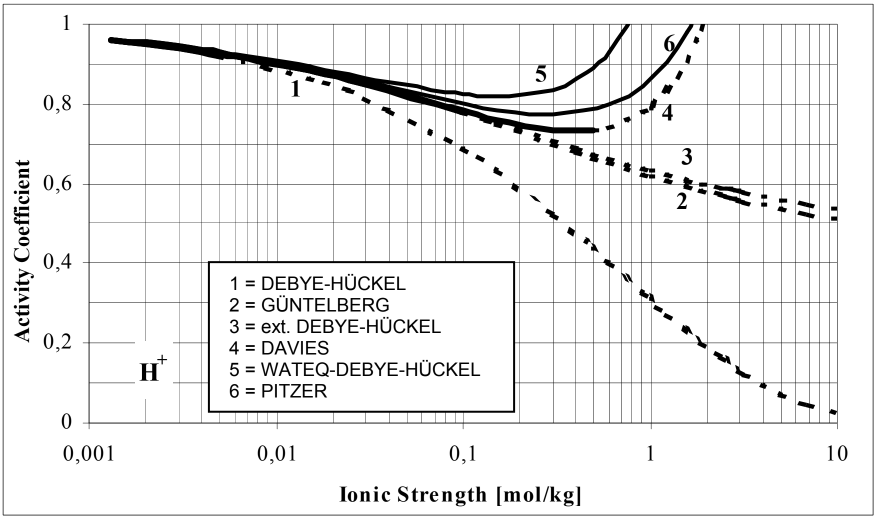


Fig. 8 Comparison of the activity coefficient of H^+ in relation to the ionic strength as calculated from the changing pH of a $CaCl_2$ solution (a_H = 4.78, b_H = 0.24 Table 4) using different theories of ion dissociation and the PITZER equation, dashed lines signify calculated values outside the validity range of the corresponding ion dissociation equation.

In particular, the strongly diverging graph of the simple DEBYE-HÜCKEL equation from the PITZER curve in the range exceeding 0.005 mol/kg (validity limit) is conspicuous. In contrast, the conformity of WATEQ-DEBYE-HÜCKEL and PITZER concerning the divalent calcium and sulfate ions is surprisingly good. Also for chloride the WATEQ-DEBYE-HÜCKEL and PITZER equation show a good agreement as far as 3 mol/kg. On contrary the activity coefficients for sodium and hydrogen ions clearly show strong discrepancies. There the validity range of 1 mol/kg for the WATEQ-DEBYE-HÜCKEL equation must be restricted, since significant differences already occur at ionic strength low as 0.1 mol/kg (one order of magnitude below the cited limit) in comparison to the PITZER equation. These examples demonstrate the flaws of the ion dissociation theory, which are especially grave for the mono-valent ions.

1.1.3 Interactions at the liquid-gaseous phase boundary

1.1.3.1 Henry-Law

Using the linear Henry's law the amount of gas dissolved in water can be calculated for a known temperature and partial pressure.

$$m_i = K_{Hi} \cdot p_i \qquad \text{Eq.(31.)}$$

m_i = molality of the gas [mol/kg]
K_{Hi} = Henry-constant of the gas i
p_i = partial pressure of the gas i[kPa]

Table 5 shows the Henry constants and the inferred amount of gas dissolved in water for different gases of the atmosphere. The partial pressures of N_2 and O_2 in the atmosphere at 25°C and 10^5Pa (1 bar), for example, are 78 kPa and 21 kPa respectively. These pressures correspond to concentrations of 14.00 mg/L for N_2 and 8.43 mg/L for O_2.

Table 5 Composition of the terrestrial atmosphere, Henry constants and calculated concentrations for equilibrium in water at 25°C, partial pressures of the atmosphere and ionic strength of 0 (after Alloway and Ayres 1996, Sigg and Stumm 1994, Umweltbundesamt 1988/89).

Gas	volume %	Henry constant K_H (25°C) in mol/ kg·kPa	Concentration in equilibrium	
N_2	78.1	$6.40 \cdot 10^{-6}$	0.50 mmol/L	14.0 mg/L
O_2	20.9	$1.26 \cdot 10^{-5}$	0.26 mmol/L	8.43 mg/L
Ar	0.943	$1.37 \cdot 10^{-5}$	12.9 mmol/L	0.515 mg/L
CO_2	0.028 ... 0.037	$3.39 \cdot 10^{-4}$	consecutive reactions	consecutive reactions
Ne	0.0018	$4.49 \cdot 10^{-6}$	8 nmol/L	0.16 mg/L
He	$0.51 \cdot 10^{-3}$	$3.76 \cdot 10^{-6}$	19 nmol/L	76 ng/L
CH_4	$1.7 \cdot 10^{-6}$	$1.29 \cdot 10^{-5}$	2.19 nmol/L	35 ng/L
N_2O	$0.304 \cdot 10^{-6}$	$2.57 \cdot 10^{-4}$	0.078 nmol/L	3.4 ng/L

Gas	volume %	Henry constant K_H (25°C) in mol/ kg·kPa	Concentration in equilibrium	
NO	---	$1.9 \cdot 10^{-5}$	consecutive reactions	consecutive reactions
NO_2	$10 .... 22 \cdot 10^{-9}$	$1.0 \cdot 10^{-4}$	consecutive reactions	consecutive reactions
NH_3	$0.2\text{-}2 \cdot 10^{-9}$	0.57	consecutive reactions	consecutive reactions
SO_2	$10 \cdot 10^{-9} ... 19 \cdot 10^{-9}$	0.0125	consecutive reactions	consecutive reactions
O_3	$10 \cdot 10^{-9} ... 100 \cdot 10^{-9}$	$9.4 \cdot 10^{-5}$	0.094 ... 0.94 nmol/L	4.5 ... 45 ng/L

With decreasing temperature the gas solubility increases, such that at 0°C as compared to 25°C 1.6 times the amount of N_2 and 1.7 times the amount of O_2 can be dissolved (Table 6). Because of the linear dependency (Eq. 31) this also results in an increase of the Henry constants.

Table 6 Solubility of gases in water in mg/L under atmospheric pressure (Rösler and Lange 1975).

Temperature	0°C	5°C	10°C	15°C	20°C	25°C
N_2	22.88	20.25	18.09	16.37	15.10	14.00
O_2	14.46	12.68	11.24	10.10	9.18	8.43

Thus Henry's law is only directly applicable for gases, which subsequently do not react any further, as for example nitrogen, oxygen, or argon. For gases that react with water, the application of the Henry's law equation only works if ensuing reactions are taken into account. Although carbon dioxide just dissociates to an extent of 1% into HCO_3^- and CO_3^{2}, which is in turn dependent on the pH value, the subsequent complexation reactions result in a strongly increased solubility of CO_2 in water. Additionally, if protons are used up by the dissolution of a mineral phase (e.g. calcite), these consequent reactions cause increased solution of CO_2, which thus becomes far higher than that calculated by Henry's law.

1.1.4 Interactions at the liquid-solid phase boundary

1.1.4.1 Dissolution and precipitation

Dissolution and precipitation can be described with the help of the mass-action law as reversible and heterogeneous reactions. In general, the solubility of a mineral is defined as the mass of a mineral, which can be dissolved within a standard volume of the solvent.

1.1.4.1.1. Solubility product

The dissolution of a mineral AB into the components A and B occurs according to the mass-action law as follows:

$$AB \leftrightarrow A + B \qquad \text{Eq.(32.)}$$

$$K_{sp} = \frac{\{A\} \cdot \{B\}}{\{AB\}} \qquad \text{Eq.(33.)}$$

Because for a solid phase AB the activity is assumed to be constant at 1, the equilibrium constant of the mass-action law results in a solubility product constant (K_{sp}) or ion-activity product (IAP) as below:

$$K_{sp} = \mathrm{IAP} = \{A\} \cdot \{B\} \qquad \text{Eq.(34.)}$$

Analytically determined analyses for A and B must be transformed into activities of the ions and that means complexing species must be accounted for.

The solubility product depends on the mineral, the solvent, the pressure or the partial pressure of certain gases, the temperature, pH, $E_{H,}$ and on the ions previously dissolved in the water and to what extent these have formed complexes amongst themselves. While partial pressure, pH, E_H, and complex stability are considered in the mass-action law, temperature and pressure have to be taken into account by additional factors.

Dependency of K_{SP} on the temperature

In contrast to the partial pressure, temperature rise does not generally contribute to the increase of the solubility. According to the principle of the smallest constraint (Le Chatelier), only endothermic dissolutions, i.e. reactions, which need additional heat, are favored (e.g. dissolution of silicates, aluminosilicates, oxides, etc.). Yet the dissolution of carbonates and sulfates is an exothermic reaction. Therefore the solubility of carbonates and sulfates is less favorable with increasing temperature.

Dependency of K_{SP} on the pressure

Up to a pressure prevailing at 500 m water depth (5 MPa) the pressure change has almost no influence on the solubility product. There is, however, a strong dependency on the partial pressure of particular gases.

Dependency of K_{SP} on the partial pressure

The increased rate of dissolution and precipitation in the upper layer of the soil is caused by the higher partial pressure of carbon dioxide in the soil (in the growth season about 10 to 100 times higher than in the atmosphere because of the biological and microbiological activity). Average carbon dioxide partial pressure under humid climate conditions in summer is at 3 to 5 kPa (3-5 vol%), whereas it amounts to up to 30 vol% in tropical climates and to up to 60 vol% in heaps or organically contaminated areas. Since the increased partial pressure of CO_2 is accompanied by a higher proton activity, those minerals are preferably dissolved for which the solubility depends on the pH value.

Dependency of K_{SP} on the pH value

Just a few ions like Na^+, K^+, NO_3^- or Cl^+ are soluble to the same extent across the whole range of pH values of normal groundwater. Mainly the dissolution of metals is strongly pH dependent. While precipitating as hydroxides, oxides, and salt under basic conditions, they dissolve and are mobile as free cations under acid conditions. Aluminum is soluble under acid as well as under basic conditions. It precipitates as hydroxide or clay mineral in the pH range of 5 to 8.

Dependency of K_{SP} on the E_H value

For those elements that occur in different oxidation states, the solubility not only depends on the pH but on the redox chemistry too. For example, the solubility of uranium as U^{4+} is almost insoluble at moderate pH values, but U^{6+} is readily soluble. Iron behaves completely different: at pH > 3, the oxidized form, Fe^{3+}, is only soluble to a very small extent; however, Fe^{2+} is readily soluble.

Dependency of K_{SP} on complex stability

In general, the formation of complexes increases the solubility, while the dissociation of complexes decreases it.

The extent to which elements are soluble and thus more mobile is indicated in Table 7. There, the relative enrichment of the elements compared to river water is depicted in a periodic system. Substances, which are readily soluble and thus highly mobile are enriched in seawater, whereas less mobile and less soluble substances are depleted.

1.1.4.1.2. Saturation index

The logarithm of the quotient of the ion activity product (IAP) and solubility product constant (K_{SP}) is called the saturation index (SI). The IAP is calculated from activities that are calculated from analytically determined concentrations by considering the ionic strength, the temperature, and complex formation. The solubility product is derived in a similar manner as the IAP but using equilibrium solubility data corrected to the appropriate water temperature.

$$SI = \log \frac{IAP}{K_{SP}} \qquad \text{Eq.(35.)}$$

The saturation index SI indicates, if a solution is in equilibrium with a solid phase or if under-saturated and super-saturated in relation to a solid phase respectively. A value of 1 signifies a ten-fold supersaturation, a value of -2 a hundred-fold undersaturation in relation to a certain mineral phase. In practice, equilibrium can be assumed for a range of -0.2 to 0.2. If the determined SI value is below -0.2 the solution is understood to be undersaturated in relation to the corresponding mineral, if SI exceeds +0.2 the water is assumed to be supersaturated with respect to this mineral.

Table 7 Periodic system depicting the relative enrichment (ratio > 1) of the elements in sea water as compared to river water; elements enriched in sea water (mobile elements) are shaded (after Faure 1991, Merkel and Sperling 1996, 1998)

H ---																	He
Li 56.7	Be 0.02											B 450	C ---	N ---	O ---	F 1300	Ne
Na 1714	Mg 315											Al 0.016	Si 0.43	P 3.6	S 243	Cl 2500	Ar
K 173	Ca 27.5	Sc 0.17	Ti 0.32	V 1.3	Cr 0.2	Mn 0.04	Fe 0.0015	Co 0.02	Ni 1.7	Cu 0.04	Zn 0.02	Ga 0.2	Ge 1	As 0.85	Se 2.2	Br 3350	Kr
Rb 120	Sr 109	Y 0.18	Zr ---	Nb ---	Mo 18.3	Tc ---	Ru ---	Rh ---	Pd ---	Ag 0.009	Cd 8.0	In ---	Sn 0.013	Sb 2.1	Te ---	I 8.0	Xe
Cs 14.5	Ba 0.7	Lu 0.22	Hf ---	Ta ---	W 3.3	Re ---	Os ---	Ir ---	Pt ---	Au 2.5	Hg 0.14	Tl ---	Pb 0.002	Bi ---	Po ---	At ---	Rn
Fr ---	Ra ---																
“---“ no data or no consistent data in the literature																	
La 0.094	Ce 0.044	Pr 0.14	Nd 0.11	Pm ---	Sm 0.10	Eu 0.10	Gd 0.11	Tb 0.14	Dy 0.15	Ho 0.20	Er 0.22	Tm 0.21	Yb 0.25				
Ac ---	Th 0.0006	Pa ---	U 2.7	Np ---	Pu ---	Am ---	Cm ---	Bk ---	Cf ---	Es ---	Fm ---	Md ---	No ---				

1.1.4.1.3. Limiting mineral phases

Some elements in aquatic systems exist only at low concentrations (µg/L range) in spite of readily soluble minerals. This phenomenon is not always caused by a generally small distribution of the concerned element in the earth crust mineral as for instance with uranium. Possible limiting factors are the formation of new minerals, co-precipitation, incongruent solutions, and the formation of solid-solution minerals (i.e. mixed minerals).

Formation of new minerals

For example Ca^{2+}, in the presence of SO_4^{2-} or CO_3^{2} can be precipitated as gypsum or calcite, respectively. A limiting mineral phase for Ba^{2+} in the presence of sulfate is $BaSO_4$, or barite. If, for instance, a sulfate-containing groundwater is mixed with a $BaCl_2$-containing groundwater, barite becomes the limiting phase and is precipitated until the saturation index for barite attains the value of zero.

Co-precipitation

For elements like radium, arsenic, beryllium, thallium, molybdenum and many others, not only the low solubility of the related minerals but also the co-precipitation or adsorption with other minerals, plays an important role. For instance radium is co-precipitated with iron hydroxides and barium sulfate.

The mobility of radium is determined by redox-sensitive iron, which readily forms iron oxyhydroxides under oxidizing conditions and thus limits the concentrations of iron and radium because radium is effectively sorbed on iron oxyhydroxide. Redox-sensitive elements are elements that change their oxidation state by electron transfer depending on the relative oxidizing or reducing conditions of the aquatic environment (chapter 1.1.5.2.4 and 0). Thus radium behaves like a redox-sensitive element, even though it only occurs in the divalent form.

Incongruent solutions

Solution processes, in which one mineral is dissolving, while another mineral is inevitably precipitating, are called incongruent. Thus, if dolomite is added to water in equilibrium with calcite (SI = 0) then dolomite dissolves until equilibrium for dolomite is established. That leads consequently to an increase for the concentrations of Ca, Mg, and C in water, which in turn inevitably causes supersaturation with respect to calcite and thus precipitation of calcite.

Solid solutions

The examination of naturally occurring minerals shows, that pure mineral phases are rare. In particular they frequently contain trace elements as well as common elements. Classic examples of solid-solution minerals are dolomite or the calcite/rhodocrosite, calcite/strontianite, and calcite/otavite systems.

For these carbonates, the calculation of the saturation index gets more difficult. If, for instance, one considers the calcite/strontianite system, the solubility of both mineral phases is estimated by:

$$K_{\mathrm{calcite}} = \frac{\{Ca^{2+}\} \cdot \{CO_3{}^{2-}\}}{\{CaCO_3\}_s} \qquad \text{Eq.(36.)}$$

and

$$K_{\mathrm{strontianite}} = \frac{\{Sr^{2+}\} \cdot \{CO_3{}^{2-}\}}{\{SrCO_3\}_s} \qquad \text{Eq.(37.)}$$

Assuming a solid-solution mineral made up from a mixture of these two minerals, the conversion of the equations results in:

$$\frac{\{Sr^{2+}\}}{\{Ca^{2+}\}} = \frac{K_{\mathrm{strontianite}} \cdot \{SrCO_3\}_s}{K_{\mathrm{calcite}} \cdot \{CaCO_3\}_s} \qquad \text{Eq.(38.)}$$

That means that a certain activity ratio of Sr and Ca in aqueous solution is associated with a certain activity ratio in the minerals. If, analogously to the non-ideal behavior of the activity coefficient of the aquatic species, a specific correction factor f_{calcite} and $f_{\mathrm{strontianite}}$ for the activity is introduced, the following equation arises:

$$\frac{K_{\mathrm{strontianite}} \cdot f_{\mathrm{strontianite}}}{K_{\mathrm{calcite}} \cdot f_{\mathrm{calcite}}} = \frac{\{Sr\} \cdot X_{\mathrm{calcite}}}{\{Ca\} \cdot X_{\mathrm{strontianite}}} \qquad \text{Eq.(39.)}$$

where X is the molar proportion in the solid-solution mineral. In the simplest case, the ratio of both activity coefficients can be combined in order to obtain a distribution coefficient. The latter can be experimentally determined by semi-empirical approximation in the laboratory.

Using the solubility product constants for calcite and strontianite and assuming a calcium activity of 1.6 mmol/L, a distribution coefficient of 0.8 for strontium and 0.98 for calcite, and a ratio of 50:1 (=0.02) in the solid-solution mineral, the following equation gives the activity of strontium:

$$\{Sr\} = \frac{K_{\mathrm{strontianite}} \cdot f_{\mathrm{strontianite}} \cdot X_{\mathrm{strontianite}} \cdot \{Ca\}}{K_{\mathrm{calcite}} \cdot f_{\mathrm{calcite}} \cdot X_{\mathrm{calcite}}} = \frac{10^{-9.271} \cdot 0.8 \cdot 0.02 \cdot 1.6 \cdot 10^{-3}}{10^{-8.48} \cdot 0.98} = 4.2 \cdot 10^{-6}\,\mathrm{mol/l} \qquad \text{Eq.(40.)}$$

If strontianite is assumed to be the limiting phase, significantly more strontium (activity approx. $2.4 \cdot 10^{-4}$ mol/L) could be dissolved compared to that of the solid-solution mineral phase.

This example shows a tendency with solid-solution minerals. There is a supersaturation or an equilibrium regarding the solid-solution minerals but an undersaturation with respect to the pure mineral phases, i.e. the solid-solution mineral is formed but not one of the pure mineral phases. The prominence of this phenomenon depends upon the values of the activity coefficient of the solid-solution component.

For the calculation of solid-solution mineral behavior, two conceptual models may be used: the end-member model (arbitrary mixing of two or more phases) and the site-mixing model (substituting elements can replace certain elements only at certain sites within the crystal structure).

For some elements, limiting phases (pure minerals and solid-solution minerals) are irrelevant. Thus, there are no limiting mineral phases for Na or B under conditions prevailing in groundwater. Sorption on organic matter (humic and fulvic acids), on clay minerals or iron oxyhydroxides as well as cation exchange may be limiting factors instead of mineral formation. This issue will be addressed in the following.

1.1.4.2 Sorption

The term sorption combines matrix sorption and surface sorption. Matrix sorption can be described as the relatively unspecific exchange of constituents contained in water into the porous matrix of a rock (“absorption”). Surface sorption is understood to be the accretion of atoms or molecules of solutes, gases or vapor at a phase boundary (“adsorption”). In the following only surface sorption will be addressed more thoroughly.

Surface sorption may occur by physical binding forces (van de Waals forces, physisorption), by chemical bonding (Coulomb forces) or by hydrogen bonding (chemisorption). A complete saturation of all free bonds at the defined surface sites is possible involving specific lattice sites and/or functional groups (surface complexation, chapter 1.1.4.2.3). While physisorption is reversible in most cases, remobilization of constituents bound by chemisorption is difficult. Ion exchange is based on electrostatic interactions between differently charged molecules.

1.1.4.2.1. Hydrophobic /hydrophilic substances

Rocks may be hydrophobic or hydrophilic and this property is closely related to the extent of sorption. In contrast to hydrophilic materials, hydrophobic substances have no free valences or electrostatic charge available at their surfaces. Hence, neither hydrated water molecules nor dissolved species can be bound to the surface and in the extreme case, could largely prevent the wetting of the surface with aqueous solution.

1.1.4.2.2. Ion exchange

The ability of solid substances to exchange cations or anions with cation or anions in aqueous solution is called ion-exchange capacity. In natural systems anions are exchanged very rarely, in contrast to cations, which exchange more readily forming a succession of decreasing intensity: $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Be^{2+}$ and $Cs^{+} > K^{+} > Na^{+} > Li^{+}$. Generally, multivalent ions (Ca^{2+}) are more strongly bound than monovalent ions (Na^{+}), yet the selectivity decreases with increasing ionic strength (Stumm and Morgan, 1996). Large ions like Ra^{2+} or Cs^{+} as well as small ions like Li^{+} or Be^{2+} are merely exchanged to a lower extent. The H^{+}, having a high charge density and small diameter, is an exception and is preferentially absorbed.

Moreover, the strength of the binding depends on the respective sorbent, as Table 8 shows for some metals. The comparison of the relative binding strength is based on the pH, at which 50% of the metals are absorbed ($pH_{50\%}$). The lower this pH value, the stronger this distinct metal is bound to the sorbent, as for instance with Fe-oxides: Pb ($pH_{50\%} = 3.1$) > Cu ($pH_{50\%} = 4.4$) > Zn ($pH_{50\%} = 5.4$) > Ni ($pH_{50\%} = 5.6$) > Cd ($pH_{50\%} = 5.8$) > Co ($pH_{50\%} = 6.0$) > Mn ($pH_{50\%} = 7.8$) (Scheffer and Schachtschabel 1982).

Table 8 Relative binding strength of metals on different sorbents (after Bunzl et al. 1976)

Substance	Relative binding strength
Clay minerals, zeolites	Cu>Pb>Ni>Zn>Hg>Cd
Fe, Mn-oxides and –hydroxides	Pb>Cr=Cu>Zn>Ni>Cd>Co>Mn
Organic matters (in general)	Pb>Cu>Ni>Co>Cd>Zn=Fe>Mn
Humic- and Fulvic acids	Pb>Cu=Zn=Fe
Peat	Cu>Pb>Zn>Cd
degraded peat	Cu>Cd>Zn>Pb>Mn

Corresponding to the respective sorbent, ion exchange capacity additionally depends on the pH value (Table 9).

Table 9 Cation exchange capacity at pH 7 and their dependency (after Langmuir 1997)

Substance	CEC (meq/100g)	pH dependency
Clay minerals		
Kaolinite	3-15	high
Illite and Chlorite	10-40	low
Smectite Montmorrilonite	80-150	rare or non existent
Vermiculite	100-150	negligible
Zeolites	100-400	negligible
Mn (IV) and Fe (III) Oxyhydroxides	100-740	high
Humic matter	100-500	high
synthetic cation exchangers	290-1020	low

Fig. 9 shows the pH-dependent sorption of metal cations; Fig. 10 the same for selected anions on iron hydroxide.

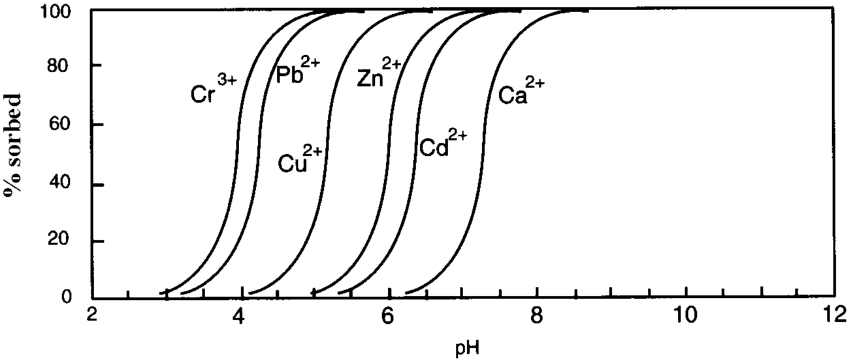


Fig. 9 pH-dependent sorption of metal cations on iron hydroxide (after Drever 1997)

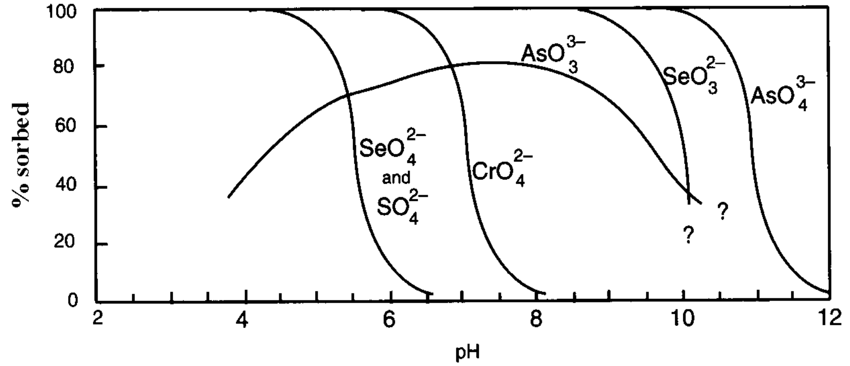


Fig. 10 pH-dependent sorption of anions on iron hydroxide (after Drever 1997)

Description of the ion exchange using the mass-action law

Assuming a complete reversibility of sorption, the ion exchange can be described through the mass-action law. The advantage of this approach is that virtually any number of species can interact at the surface of a mineral.

$$A^+ + B^+R^- \leftrightarrow A^+R^- + B^+$$

$$K_B^A = \frac{\{A^+R^-\}\cdot\{B^+\}}{\{A^+\}\cdot\{B^+R^-\}} = \frac{\{A^+R^-\}/\{A^+\}}{\{B^+R^-\}/\{B^+\}} \qquad \text{Eq.(41.)}$$

with A^+, B^+ monovalent ions
R= exchanger

K_x is the selectivity coefficient and is considered here as an equilibrium constant, even though, in contrast to complexation constants or dissociation constants, it depends not only on pressure, temperature and ionic strength, but also on the respective solid phase with its specific properties of the inner and outer surfaces. Although to a lesser extent, it also depends on they way the reaction is written.

Thus, the exchange of sodium for calcium can be written as follows:

$$\mathrm{Na}^{+} + \frac{1}{2}\mathrm{CaX}_2 \leftrightarrow \mathrm{NaX} \cdot \frac{1}{2}\mathrm{Ca}^{2+}$$

$$K_{\mathrm{Ca}}^{\mathrm{Na}} = \frac{\{\mathrm{NaX}\} \{\mathrm{Ca}^{2+}\}^{0.5}}{\{\mathrm{CaX}_2\} \cdot \{\mathrm{Na}^{+}\}} \qquad \text{Eq.(42.)}$$

This expression is called the Gaines-Thomas convention (Gaines and Thomas 1953). If using the molar concentration instead, it is identical to the Vanselow convention (Vanselow 1932). Gapon (1933) proposed the following form:

$$\mathrm{Na}^{+} + \mathrm{Ca}\frac{1}{2}\mathrm{X} \leftrightarrow \mathrm{NaX} \cdot \frac{1}{2}\mathrm{Ca}^{2+}$$

$$K_{\mathrm{Ca}}^{\mathrm{Na}} = \frac{\{\mathrm{NaX}\} \cdot \{\mathrm{Ca}^{2+}\}^{0.5}}{\{\mathrm{Ca}_{\frac{1}{2}}\mathrm{X}\} \cdot \{\mathrm{Na}^{+}\}} \qquad \text{Eq.(43.)}$$

Important ion exchanger

Important ion exchangers and sorbents are, as can be seen from the Table 8, clay minerals and zeolites (aluminous silicates), metal oxides (mainly iron and manganese oxides), and organic matter.

- Clay minerals consist of 1 to n sheets of Si-O tetrahedrons and of 1 to n layers of aluminum hydroxide octahedral sheets (gibbsite). Al very often replaces Si in the tetrahedral sheet as well as Mg does for Al in the octahedral sheet.
- As ion exchanger, zeolites play an important role in volcanic rocks and marine sediments.
- At the end of the weathering process, often iron and manganese oxides form. Manganese oxides usually form an octahedral arrangement resembling gibbsite. Hematite (Fe_2O_3) and goethite (FeOOH) also show a similar octahedral structure.
- Following Schnitzer (1986) 70 to 80% of organic matter is to be ascribed to humic substances. These are condensed polymers composed of aromatic and aliphatic components, which form through the decomposition of living cells of plants and animals by microorganisms. Humic substances are hydrophilic, of dark color and show molecular masses of some hundred to many thousands. They show widely differing functional groups being able to interact with metal ions. Humic substances (refractional organic acids) can be subdivided into humic and fulvic acids. Humic acids are soluble under alkaline conditions and precipitate under acid conditions. Fulvic acids are soluble under basic and acidic conditions.

Ion exchange or sorption can also occur on colloids, since colloids possess an electric surface charge, at which ions can be exchanged or sorptively bound. The proportion of colloids not caught in small pores preferentially utilizes larger pores, thus sometimes travelling faster than some of the water in groundwater (size-exclusion effect). That is why the colloid-bound contaminant transport is of such special importance.

Furthermore, there are synthetic ion exchangers, which are important for water desalination. They are composed of organic macromolecules. Their porous network, made up from hydrocarbon chains, may bind negatively charged groups (cation exchanger) or positively charged groups (anion exchanger). Cation exchangers are based mostly on sulfo-acidic groups with an organic leftover, anion exchangers are based on substituted ammonium groups with an organic remnant.

Surface charges

The cation-exchange capacity of clay minerals is in a range of 3 to 150 meq/100g (Table 9). These extremely high exchange capacities rely on two physical reasons:

- extremely large surface
- an electric charge of the surfaces

These electric charges can be subdivided into:

- permanent charges
- variable charges

Permanent surface charges can be related to the substitution of metals into the crystal lattice (isomorphism). Since the substitution usually occurs by metals with a low charge, an overall deficit in positive charge results for the crystal. To balance this, a negative potential forms at the surface causing positively charged metals to sorb. The surface charges of clay minerals can be predominantly related to isomorphism, therefore they are permanent to a great portion. However, this is not true for all clay minerals; for kaolinite it is less than 50% (Bohn et al., 1979).

Besides the permanent charge, there are variable surface charges, which depend on the pH of the water. They arise from protonation and deprotonation of functional groups at the surface. Under acid conditions, protons are sorbed on the functional groups that cause an overall positive charge on the surface. Thus the mineral or parts of it behave as an anion exchanger. With high pH, the oxygen atoms of the functional groups stays deprotonized and the mineral, or parts of it, shows an overall negative charge; therefore cations can be sorbed.

For every mineral there is a pH value at which the positive charge caused by protonization equals the negative charge caused by deprotonization, so that the overall charge is zero. This pH is called the pH_{PZC} (Point of Zero Charge). If only deprotonization and protonization have an influence on the surface charge this value is called ZPNPC (zero point of net proton charge) or IEP (iso-electric point). This point is around pH 2.0 for quartz, around pH 3.5 for kaolinite, for goethite, magnetite, and hematite approximately between pH 6 and 7, and for corundum around pH 9.1 (Drever 1997). Fig. 11 shows the pH-dependent sorption behavior of iron hydroxide surfaces. The overall potential of the pH-dependent surface charge does not depend on the ionic strength of water.

Natural systems are a mixture of minerals with constant and variable surface charge. Fig. 12 shows the general behavior in relation to anion and cation sorption. At values exceeding pH 3 the anion exchange capacity decreases considerably. Up to pH 5 the cation exchange capacity is constant, rising extremely at higher values.

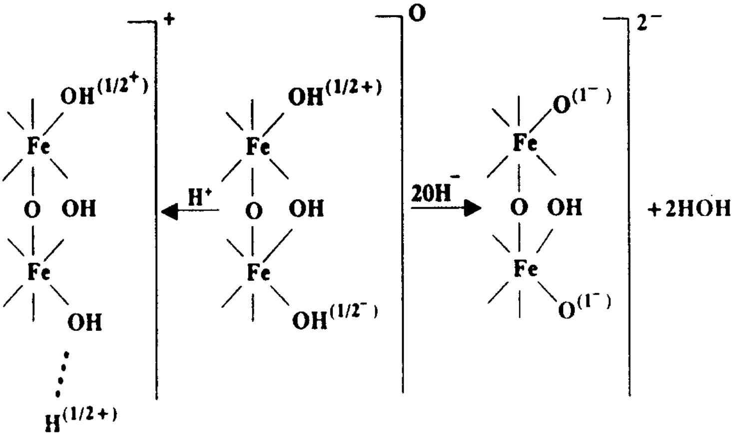


Fig. 11 Schematic depiction of the pH-dependent sorption behaviors of iron hydroxide surfaces at accretion of the H+ and OH- ions (after Sparks 1986).

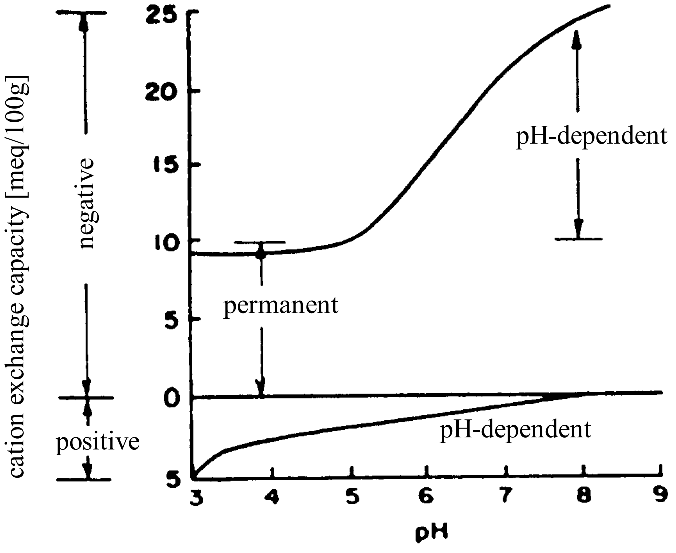


Fig. 12 Cation and Anion exchange behavior of minerals as a function of the pH (after Bohn et al. 1979); "negative" and "positive" relates to the charge of the surfaces, so that "negatives" are cation exchanger and "positives" anion exchanger.

1.1.4.2.3. Mathematical description of the sorption

There is a range of equations used describing the experimental data for the interactions of a substance as liquid and solid phases. They extend from simple empirical equations (sorption isotherms) to complicated mechanistic models based on surface complexation for the determination of electric potentials, e.g. constant-capacitance, diffuse-double layer and triple-layer model.

Empiric models- sorption isotherms

Sorption therms are the depiction of sorptional interactions using simple empirical equations. Initially, the measurements were done at constant temperature, that is why the term isotherm was introduced.

Linear regression isotherm (Henry isotherm)

The most simple form of a sorption isotherm is the linear regression equation.

$$C^{*} = K_{d} \cdot C \qquad \text{Eq.(44.)}$$

with C* = mass of substance, sorbed at a mineral (mg/kg)
K_d = distribution coefficient
C = concentration of the substance in water (mg/L)

Linear sorption terms have the advantage of simplicity and they provide the possibility to convert them into a retardation factor Rf, so that the general transport equation can be easily expanded by applying the correction term:

$$Rf = 1 + \frac{Bd}{q} \cdot \frac{C^{*}}{C} = 1 + \frac{Bd}{q} \cdot K_{d} \qquad \text{Eq.(45.)}$$

with Bd = bulk density
q = water content

A serious disadvantage is that the relation is linear, so that there is no upper limit to the sorption.

Freundlich isotherms

Using the Freundlich isotherm, an exponential relation between sorbed and dissolved molecules is used.

$$C^{*} = K_{d} \cdot C^{n} \qquad \text{Eq.(46.)}$$

$$Rf = 1 + \frac{Bd}{q} \cdot n \cdot K_{d} \cdot C^{n-1} \qquad \text{Eq.(47.)}$$

A further empirical constant n is introduced, which is usually less than 1. The Freundlich isotherm is based on a model of a multi-lamellar coating of the solid surface assuming *a priori* that all sites with the largest binding energy (of electrostatic forces) are occupied (steep section of the curve) and with increasing grade, sites with lower binding energy (flattening of the curve) are occupied.

Using the Freundlich isotherm the shortfall of limitlessness is removed, moreover, as with the linear model, a transformation into a retardation factor Rf is possible.

Langmuir isotherm

The Langmuir isotherm was developed to describe sorbents with a limited number of sorption sites on their surface

$$C^* = \frac{a \cdot b \cdot C}{1 + a \cdot C} \qquad \text{Eq.(48.)}$$

with a = sorption constant
b = maximum sorbable mass of the substance (mg/kg)

$$Rf = 1 + \frac{Bd}{q} \cdot \left[\frac{a \cdot b}{(1 + a \cdot C)^2} \right] \qquad \text{Eq.(49.)}$$

From the scientific point of view, however, all approaches in the sense of the K_d concept (Henry, Freundlich or Langmuir isotherm) are unsatisfactory, since the complex processes on surfaces cannot be described by empirical fitting parameters. Boundary conditions like pH value, redox potential, ionic strength, competition reactions for binding sites are not considered. Thus results from laboratory and field experiments are not transferable to real systems. They are only advisable to provide a suitable prognosis model, if no changes concerning boundary conditions are to be expected and if no parameters for deterministic or mechanistic approach can be determined.

Mechanistic models for surface complexation

Surface complexation is a theory to describe the phenomenon of sorption. At the surface of iron, aluminum, silica, and manganese hydroxides as well as humic substances, there are cations that are not completely surrounded by oxygen ions in contrast to the cations of the inner parts of the crystal lattice. Because of their valence electrons they may bind water molecules. These water molecules distribute after the accretion such that for every sorbed oxygen ion, one hydrogen ion remains. The second hydrogen ion is bound to the oxygen ions in the lattice that is between the lattice cations (Fig. 13). Thus there is a layer of functional groups always containing O, S, or N on the surface of the mineral (double layer).

After Stumm and Morgan (1996) the reaction can be described as follows:

$$\{GH\} + Me^{z+} \leftrightarrow \{GMe^{z-1}\} + H^+ \qquad \text{Eq.(50.)}$$

Here, GH is a functional group as $(R\text{-}COOH)_n$ or $(=AlOH)_n$. The capability of functional groups to form complexes strongly depends on the acid-base behavior and, hence, the change of pH in an aquatic system.

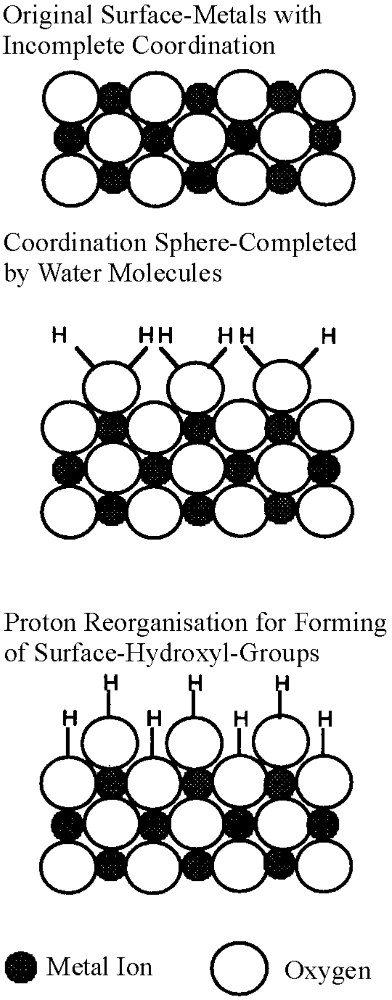


Fig. 13 The process of surface complexation (after Drever 1997)

Similar to solution complexation, surface complexation can be distinguished between inner-spherical complexes (e.g. phosphate, fluoride, copper), where the ion is directly bound to the surface, and outer-spherical (e.g. sodium, chloride) complexes where the ion is covered by a hydration sleeve with the attraction working only electrostatically. The inner-sphere complex is much stronger and not dependent on electrostatic attraction, i.e. a cation can also be sorbed on a positively charged surface (Drever 1997).

On this basis, three models will be discussed, which enable a calculation of the electrical potential, namely the constant-capacitance, the diffuse-double-layer, and the triple-layer model.

Diffuse Double-Layer Model (DDLM)

This model is based on the Gouy-Chapman theory (diffuse double-layer theory). The theory states that in the area of the boundary layer between solid and aqueous phase, independently of the surface charge, increased concentrations of cations and anions within a diffuse layer exists because of electrostatic forces. In contrast to the constant-capacitance model, the electrical potential does not change up to a certain distance from the phase boundaries and is not immediately declining in a linear manner (Fig. 14 a). Diffusion counteracts these forces, leading to dilution with increasing distance from the boundary. This relation can be described physically by the Poisson-Boltzmann equation.

Constant-Capacitance Model (CCM)

The constant-capacitance model assumes that the double layer on the solid-liquid phase boundary can be regarded as a parallel-plate capacitor (Fig. 14 b).

Tripel-Layer Model (TLM)

While CCM and DDLM assume that all ions are at one plane, the triple layer includes different planes, in which the surface complexes are bound. In the original version of Davis et al. (1978) the protons and hydroxide ions are bound at the layer (o-plane) close to the phase boundary, whereas inner-sphere complexes are bound in a β-plane somewhat dislodged. Both planes are assumed as constant-capacity layers. The range outside the β-plane containing the outer-sphere complexes is modeled as a diffuse layer (Fig. 14 c).

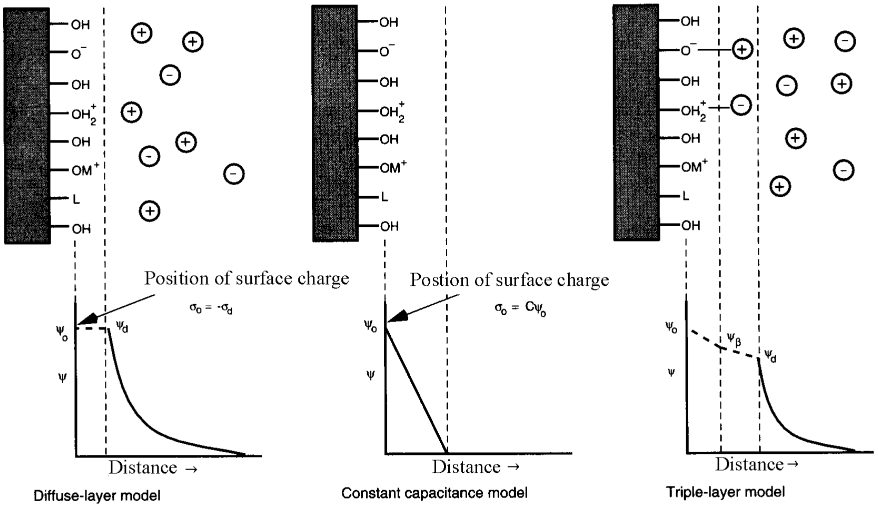


Fig. 14 Idealized distribution of the electrical potential in the vicinity of hydrated oxide surfaces after the (a) diffuse-layer model; (b) the constant-capacitance model; (c) triple-layer model (after Drever 1997).

1.1.5 Interactions in the liquid phase

1.1.5.1 Complexation

Complexation has a significant influence on dissolution and precipitation of minerals as already described in chapter 1.1.4.1.3. In contrast to the dissolution of minerals, complexation is a homogeneous reaction. It can be described by the mass-action law. The complexation constant, K, gives information about the complex stability. Large complex constants indicate a strong tendency for complexation, or high complex stability.

Positively charged, zero charged, and negatively charged complexes can be distinguished. Contaminants for instance have an especially high mobility if they occur as zero charged complexes, since they undergo almost no exchange processes, whereas (positively or negatively) charged complexes show interactions with other ions and solid surfaces.

A complex can be defined as a coordination compound of a positively charged part with a negatively charged part, the ligand. The positively charged part is usually a metal ion or hydrogen, but may also be another positively charged complex. Ligands are molecules, which have at least one free pair of electrons (bases). This ligand can either be free anions like F^-, Cl^-, Br^-, I^- or negatively charged complexes as OH^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}, NO_3^-, and PO_4^{3}.

From the periodic table of elements the following elements can be possible ligands:

Group	4	5	6	7
	C	N	O	F
		P	S	Cl
		As	Se	Br
			Te	I

Beside these inorganic ligands there are also organic ligands like humic or fulvic acids, which occur naturally in almost all waters, but also NTA and EDTA, which enter the hydrosphere as phosphate substitutes in detergents (Bernhardt et al. 1984) and can mobilize metals.

The complex binding can be electrostatic, covalent, or a combination of both. Electrostatically bound complexes, where the metal atom and the ligand are separated by one or more hydrogen molecules, are called outer-sphere complexes. They are less stable and are formed when hard cations come into contact with hard ligands (Table 10).

The Pearson concept of “hard” and “soft” acids and bases considers the number of electrons in the outer shell. Elements with a saturated outer shell and low tendency for polarization (noble gas configuration) are called “hard” acids, while elements with only partially filled outer shell, low electronegativity, and high tendency for polarization are “soft” acids.

Inner-sphere complexes, with covalent bounds between a metal atom and a ligand, form from soft metal atoms and soft ligands or soft metal atoms and hard ligands or hard metal atoms and soft ligands and are much more stable.

Table 10 Classification of metal ions into A and B- type and after the Pearson concept into hard and soft acids with preferred ligands (after Stumm and Morgan 1996)

Metal cations type A („hard spheres“)	Transition metal cations	Metal cations type B („soft spheres“)
H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Al^{3+}, Sc^{3+}, La^{3+}, Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}	V^{2+}, Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ti^{3+}, V^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}	Cu^+, Ag^+, Au^+, Tl^+, Ga^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Sn^{2+}, Tl^{3+}, Au^{3+}, In^{3+}, Bi^{3+}
according to Pearson concept		
hard acids	Transition range	soft acids
all metal cations type A plus Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, UO^{2+}, VO^{2+}	all divalent transition metal cations plus Zn^{2+}, Pb^{2+}, Bi^{3+}	all metal cations type B except for Zn^{2+}, Pb^{2+}, Bi^{3+}
preference for ligand atom		
N >> P, O >> S, F >> Cl		P >> N, S >> O, Cl >> F

Chelates are complexes with ligands that form more than one bond with the positively charged metal ion (multidentate ligands). Such complexes show an especially high stability. Complexes with more than one metal atom are called multi- or polynucleus complexes.

By means of complexation, a metal can occur in normally unknown or rare oxidation states. For instance, Co^{3+}, being a strong oxidizing agent, is normally not stable in aqueous solutions, but it is stable as $Co(NH_3)_6^{3+}$. Furthermore, complexation can prevent disproportionation, as in the case of Cu^+ e.g., which converts into Cu^{2+} and Cu(s) in an aqueous solution, although it is stable as $Cu(NH_3)_2^+$.

General statements about the stability of different complexes are problematic. Inferences from the ionic strength or more general subdivisions into good and poor chelating agents based on the periodic table of elements lead to contradictory statements. They do not appear practical, because the tendency of elements to form complexes critically depends on the corresponding ligand, as Table 11 shows for some examples. And last, but not least, the concentration of the ligand in the solution (main or trace element) is of crucial importance.

Table 11 Complexation constants for hydroxide, carbonate, and sulfate complexes (data from WATEQ4F and (*) CHEMVAL data base); Me = metal cations, n = oxidation state of the cations (n = 1, 2, 3)

Element	Hydroxo complex $Me^n + H_2O = MeOH^{n-1} + H^+$	Carbonate complex $Me^n + CO_3^{2-} = MeCO_3^{n-2}$	Sulfate complex $Me^n + SO_4^{2-} = MeSO_4^{n-2}$
Na^+	-13.9 (*)	1.27	0.7
K^+	-14.5 (*)	no data available	0.85
Ca^{2+}	-12.78	3.224	2.3
Mg^{2+}	-11.44	2.98	2.37
Mn^{2+}	-10.59	4.9	2.25
Ni^{2+}	-9.86	6.87	2.29
Fe^{2+}	-9.5	4.38	2.25

Element	Hydroxo complex $Me^n + H_2O = MeOH^{n-1} + H^+$	Carbonate complex $Me^n + CO_3^{2-} = MeCO_3^{n-2}$	Sulfate complex $Me^n + SO_4^{2-} = MeSO_4^{n-2}$
Zn^{2+}	-8.96	5.3	2.37
Cu^{2+}	-8.0	6.73	2.31
Fe^{3+}	-2.19	no data available	4.04

1.1.5.2 Redox processes

Together with acid-base reactions, where a proton transfer occurs (pH-dependent dissolution/ precipitation, sorption, complexation) redox reactions play an important role for all interaction processes in aqueous systems. Redox reactions consist of two partial reactions, oxidation and reduction, and can be characterized by oxygen or electron transfer. Many redox reactions in natural aqueous systems can actually not be described by thermodynamic equilibrium equations, since they have slow kinetics. If a redox reaction is considered as a transfer of electrons, the following general reaction can be derived:

$$\{\text{oxidized species}\} + n \cdot \{e^-\} = \{\text{reduced species}\} \qquad \text{Eq.(51.)}$$

with n = number of electrons, e^-.

1.1.5.2.1. Measurement of the redox potential

Inserting an inert but highly conductive metal electrode into an aqueous solution allows electrons to transfer both from the electrode to the solution and vice versa. A potential difference (voltage) builds up, which can be determined in a current-less measurement. Per definition, this potential is measured relative to the standard hydrogen electrode with $P(H_2)$ = 100 kPa, pH = 0, temperature = 20°C and a potential of

$$E^o\left(\frac{H^+}{H_2}\right) = 0\,\text{mV} \qquad \text{Eq.(52.)}$$

In the aqueous solution, the potential is measured as an integral over all existing redox species (mixed potential).

Since the use of the standard hydrogen electrode in the field would be very tedious, other reference electrodes are used. Those reference electrodes have a defined Eigenpotential, E_B, which is added to the determined value E_M, to obtain the solution potential, or E_H, with reference to the standard hydrogen electrode. Mostly Ag/AgCl or mercury chloride (Hg_2Cl_2)/ platinum electrodes are used as reference electrodes. The advantage of Ag/AgCl electrodes is the fast response rate, whereas the mercurial chloride/platinum-electrode yields a slower responding rate but a higher precision. In practice, the measurement of the redox potential is, independent of the reference electrode, highly problematic, since natural waters are likely not to be in thermodynamical redox equilibrium and redox species are present in concentrations too low to give an electrode response (Nordstrom and

Munoz 1994). Furthermore the electrode is highly susceptible to contamination effects. While contaminations of a platinum electrode can be disposed of managed, thermodynamic disequilibrium and low concentrations can not. Therefore redox measurements should be aborted after 1 hour if no steady value is reached. The statement derived from the measurement in that case is, that the water is redox species are not in thermodynamical redox equilibrium with the platinum electrode.

1.1.5.2.2. Calculation of the redox potential

The equilibrium redox potential can be calculated from the following Nernst equation:

$$E_h = E^o + \frac{R \cdot T}{n \cdot F} \ln \frac{\{ox\}}{\{red\}} \qquad \text{Eq.(53.)}$$

E^o = standard redox potential of a system where the activities of the oxidized species equal the activities of the reduced species
R = ideal gas constant (8.315 J/K mol)
T = absolute temperature (K)
n = number of transferred electrons (e^-)
F = Faraday constant (96484 C/mol = J/V mol)
{ox} = activity of the oxidized species
{red} = activity of the reduced species

Eq. 53 shows the calculation of single redox potentials, unlike the measured redox potential, which may be a mixed potential of several redox reactions not in equilibrium.

It is important for the determination of the redox potential to provide the redox reaction equation. A reversion of the equation causes a change in the sign.

Table 12 shows some redox sensitive elements in the periodic system of the elements, Table 13 depicts standard potentials for some important redox pairs in aqueous systems.

The equation for the calculation of redox potentials (Eq. 53) derives from the equation of the Gibbs free energy (compare also Eq. 6).

$$G = G^0 - R \cdot T \cdot \ln \frac{\{red\}}{\{ox\}} \qquad \text{Eq.(54.)}$$

$$E_H = -\frac{G}{n \cdot F} \qquad \text{Eq.(55.)}$$

$$-\frac{G}{n \cdot F} = -\frac{G^o}{n \cdot F} - \frac{R \cdot T}{n \cdot F} \cdot \ln \frac{\{red\}}{\{ox\}} \qquad \text{Eq.(56.)}$$

Table 12 Redox sensitive elements in the PSE (bold = most common oxidation states in natural aqueous systems) (after Emsley 1992, Merkel and Sperling 1996, 1998)

H **+1** **0** -1																	**He**
Li **+1** 0	**Be** **+2** 0											**B** **+3** 0	C **+4** +2 0 -2 **-4**	N **+5** +4 **+3** +2 +1 **0** -1 -2 **-3**	**O** **0** -1 **-2**	**F** **-1** 0	**Ne**
Na **+1** 0	**Mg** **+2** +1 0											**Al** **+3** 0	**Si** **+4** +2 0 **-4**	**P** **+5** **+3** 0 -2 **-3**	**S** **+6** +5 **+4** +3 +2 0 **-2**	**Cl** +7 +5 +3 +1 0 **-1**	**Ar**
K **+1** 0	**Ca** **+2** 0 -2	**Sc** **+3** 0	**Ti** **+4** +3 +2 0	**V** +5 +4 **+3** **+2** 0	**Cr** +6 +5 +4 **+3** **+2** +1 0	**Mn** **+7** **+6** **+5** **+4** **+3** **+2** **+1** **0**	**Fe** +6 +4 **+3** **+2** 0	**Co** +6 +5 +4 **+3** **+2** +1 0 -1	**Ni** +6 +4 **+2** 0	**Cu** **+3** **+2** **+1** **0**	**Zn** **+2** 0	**Ga** **+3** **+2** **0**	**Ge** **+4** **+2** 0	**As** **+5** **+3** 0 **-3**	**Se** **+6** +4 0 **-2**	**Br** +7 +5 +1 0 **-1**	**Kr**
Rb **+1** 0	**Sr** **+2** 0 -2	**Y** **+3** 0	**Zr** **+4** 0	**Nb** +5 **+3** 0	**Mo** +6 +5 +4 **+3** +2 0	**Tc** +7 +6 +5 +4 0	**Ru** +8 +7 +6 +4 **+3** **+2** 0	**Rh** **+3** 0	**Pd** +4 **+2** 0	**Ag** +3 **+2** **+1** 0	**Cd** **+2** 0	**In** **+3** **+1** 0	**Sn** **+4** **+2** 0 -4	**Sb** **+5** +4 **+3** 0 **-3**	**Te** **+6** +4 0 -1 **-2**	**I** +7 +5 +1 0 **-1**	**Xe**
Cs **+1** 0	**Ba** +4 **+2** 0 -2	**Lu** **+3** 0	**Hf** **+4** 0	**Ta** **+5** 0	**W** **+6** **+5** **+4** **0**	**Re** +7 +6 +4 +3 0 **-1**	**Os** **+8** **+6** **+3** **+2** **0**	**Ir** +4 **+3** 0	**Pt** **+6** **+4** **+2** **0**	**Au** **+3** **+1** 0	**Hg** **+2** **+1** 0	**Tl** **+3** **+1** 0	**Pb** **+4** **+2** 0 -2	**Bi** **+5** **+3** 0 -3	**Po** +6 +4 **+2** 0 -2	**At** +5 +1 0 **-1**	**Rn**
Fr **+1**	**Ra** **+2**																

Lanthanides and actinides

La **+3** 0	**Ce** **+4** **+3** 0	**Pr** **+4** **+3** 0	**Nd** **+4** **+3** **+2** 0	**Pm** **+3** 0	**Sm** **+3** **+2** 0	**Eu** **+3** **+2** 0	**Gd** **+3** 0	**Tb** **+4** **+3** 0	**Dy** **+4** **+3** **+2** 0	**Ho** **+3** 0	**Er** **+3** 0	**Tm** **+3** **+2** 0	**Yb** **+3** **+2** 0
Ac **+3** 0	**Th** **+4** 0 -3 -4	**Pa** +5 **+4** 0	**U** **+6** +5 **+4** +3 +2 0	**Np** +7 +6 +5 **+4** **+3** 0	**Pu** +7 +6 +5 **+4** **+3** 0	**Am** +6 +5 **+4** **+3** 0	**Cm** **+4** **+3** 0	**Bk** **+4** **+3** 0	**Cf** **+3** **+2** 0	**Es** **+3** **+2** 0	**Fm** **+3** **+2** 0	**Md** **+3** **+2** 0	**No** **+3** **+2** 0

Table 13 Standard potentials and E_H in volts for some important redox couples in aqeous systems at 25°C (modified after Langmuir 1997)

Reaction	**E° Volt**	**E_H Volt / pH 7.0**	**assumptions**
$4H^+ + O_{2(g)} + 4e^- = 2\ H_20$	1.23	0.816	P_{02}=0.2 bar
$NO_3^- + 6\ H^+ + 5e^- = 0.5\ N_{2(g)} + 3\ H_2O$	1.24	0.713	10^{-3} mol N, P_{N2}=0.8 bar
$MnO_2 + 4\ H^+ + 2\ e^- = Mn^{2+} + 2\ H_2O$	1.23	0.544	$10^{-4.72}$ mol Mn
$NO_3^- + 2\ H^+ + 2e^- = NO_2^- + H_2O$	0.845	0.431	$NO_3^-=NO_2^-$
$NO_2^- + 8\ H^+ + 6\ e^- = NH_4^+ + 2\ H_20$	0.892	0.340	$NO_3^-=NH_4^+$
$Fe(OH)_3 + 3\ H^+ + e^- = Fe^{2+} + 3\ H_2O$	0.975	0.014	$10^{-4.75}$ mol Fe
$Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+ + 14\ e^- = FeS_2 + 8\ H_2O$	0.362	-0.156	10^{-475} mol Fe, 10^{-3} mol S
$SO_4^{2-} + 10\ H^+ + 8e^- = H_2S_{(aq)} + 4\ H_2O$	0.301	-0.217	$SO_4^{2-}=H_2S$
$HCO_3^- + 9\ H^+ + 8\ e^- = CH_{4(aq)} + 3\ H_2O$	0.206	-0.260	$HCO_3^-=CH_4$
$H^+ + e^- = 0.5\ H_{2(g)}$	0.0	-0.414	P_{H2}=1.0 bar
$HCO_3^- + 5\ H^+ + 4\ e^- = CH_2O$ (DOM) + $2\ H_2O$	0.036	-0.482	$HCO_3^-=CH_2O$

$$E_H = E^o - \frac{R \cdot T}{n \cdot F} \cdot \ln \frac{\{red\}}{\{ox\}} \qquad \text{Eq.(57.)}$$

Eq. 53 is obtained from Eq. 57 by inversion of numerator and denominator within the argument of the logarithm. That leads to the minus sign in front of the logarithm.

For standard conditions of 25°C and putting in the gas constant and the Faraday constant, a simplified form ensues:

$$E_H = E^o - \frac{0.0591}{n} \cdot \log \frac{\{red\}}{\{ox\}} \qquad \text{Eq.(58.)}$$

Dealing with pH-dependent redox reactions, as e.g. the oxidation of Cl^- to Cl_2 by permanganite at pH 3, the number of protons used and formed must be considered.

$$E_H = E^o - 2.303 \cdot \frac{m \cdot R \cdot T}{n \cdot F} \cdot pH - 2.30 \cdot \frac{R \cdot T}{n \cdot F} \cdot \log \frac{\{red\}}{\{ox\}} \qquad \text{Eq.(59.)}$$

The factor 2.303 results from the conversion of the natural logarithm to the common logarithm. Since redox potentials cannot be used directly in thermodynamic programs (unit: volt!), the pE value was introduced for mathematical convenience. Analogous to the pH value the pE value is the negative common logarithm of the electron activity. Thus, it is calculated using a hypothetic activity, respectively concentration of electrons, which is actually not present in water. For the calculation of the pE value Eq. 51 is used and the following equation is obtained for the equilibrium constant K:

$$\log K = \log \frac{\{red\}}{\{ox\}\{e^-\}^n} = \log \frac{\{red\}}{\{ox\}} + \log \frac{1}{\{e^-\}^n} = \log \frac{\{red\}}{\{ox\}} - n \cdot \log\{\bar{e}\} \qquad \text{Eq.(60.)}$$

$$-n \cdot \log\{e^-\} = \log K - \log \frac{\{red\}}{\{ox\}} \qquad \text{Eq.(61.)}$$

$$-\log\{e^-\} = \frac{1}{n} \log K - \frac{1}{n} \log \frac{\{red\}}{\{ox\}} \qquad \text{Eq.(62.)}$$

$$pE = \frac{1}{n} \log K - \frac{1}{n} \log \frac{\{red\}}{\{ox\}} \qquad \text{Eq.(63.)}$$

The conversion from pE to the measured redox potential E_H follows from:

$$pE = -\log\{e^-\} = \frac{F}{2.303 \cdot R \cdot T} \cdot E_H \qquad \text{Eq.(64.)}$$

F, R, and T=25°C put in again, the following simplified form results [E_H in V]:

$$pE \approx 16.9 \cdot E_H \qquad \text{Eq.(65.)}$$

For the system H_2/H^+ the following is applicable:

$$E_H = E^o\left(\frac{H^+}{H_2}\right) + \frac{R \cdot T}{n \cdot F} \cdot \ln \frac{\{H^+\}^2}{\{H_2\}} \qquad \text{Eq.(66.)}$$

$$E_H = 0 + \frac{R \cdot T}{n \cdot F} \cdot \ln\{H^+\}^2 - \frac{R \cdot T}{n \cdot F} \cdot \ln\{H_2\} \qquad \text{Eq.(67.)}$$

$$E_H = 0 + \frac{2.303 \cdot R \cdot T}{2 \cdot F} \cdot 2 \cdot \log\{H^+\} - \frac{2.303 \cdot R \cdot T}{2 \cdot F} \cdot \log\{H_2\} \qquad \text{Eq.(68.)}$$

$$E_H = 0 - \frac{2.303 \cdot R \cdot T}{F} \cdot pH - \frac{2.303 \cdot R \cdot T}{2 \cdot F} \cdot \log\{H_2\} \qquad \text{Eq.(69.)}$$

Putting in the values for R and F, as well as T =25°C and $P(H_2) = 1 \cdot 10^5$ Pa, it follows:

$$E_H = -0.0591 \cdot pH \qquad \text{Eq.(70.)}$$

An increase or decrease of one pH unit causes a decrease or increase, respectively, of the Nernst voltage by 59.1 mV.

1.1.5.2.3. Presentation in predominance diagrams

The presentation of the predominant species for each redox system is called stability (or better) predominance diagram (also called E_H-pH or pE-pH diagrams). Predominance diagrams are extremely dependent on which elements in which concentrations and at which ionic strength are considered. Usually only the species dissolved in water are depicted (Fig. 15 left). However, if the concentration or activity falls below certain limits, which can be defined by the diagram designer, often the (predominant) precipitating mineral phase is outlined (Fig. 15 right). The lines limiting the single predominance ranges show the pE/pH conditions, under which the activities of two neighboring species equal each other.

How such a E_H-pH diagram can be determined analytically is explained below using the example of the Fe-O_2-H_2O diagram shown in Fig. 15 left. In each E_H-pH diagram the occurrence of the aqueous species is limited by the stability field of water. Above this field H_2O converts to elementary oxygen, below this field to elementary hydrogen (also see Fig. 16).

According to Eq. 71 every oxygen concentration is (analytically) assigned to a certain hydrogen content. This means that oxygen saturated (i.e. completely oxidized) water with the partial pressure of $P(O_2) = 1 \cdot 10^5$ Pa is in equilibrium with hydrogen with a partial pressure of $P(H_2) = 10^{-42.6} \cdot 10^5$ Pa. The other way round hydrogen saturated (completely reduced) water is in equilibrium with oxygen of a partial pressure $P(O_2) = 10^{-85.2} \cdot 10^5$ Pa.

$$\begin{array}{lcl} 4\,e^- + 4\,H_2O & = & 2\,H_2(g) + 4\,OH^- \\ 4\,OH^- & = & O_2(g) \;\; + 2\,H_2O + \; 4\,e^- \\ \hline 2\,H_2O & = & 2\,H_2(g) + O_2(g) \end{array}$$

$$K = \frac{\{pH_2\}^2 \cdot \{pO_2\}}{\{H_2O\}^2} = 10^{-85.2} \qquad \text{Eq.(71.)}$$

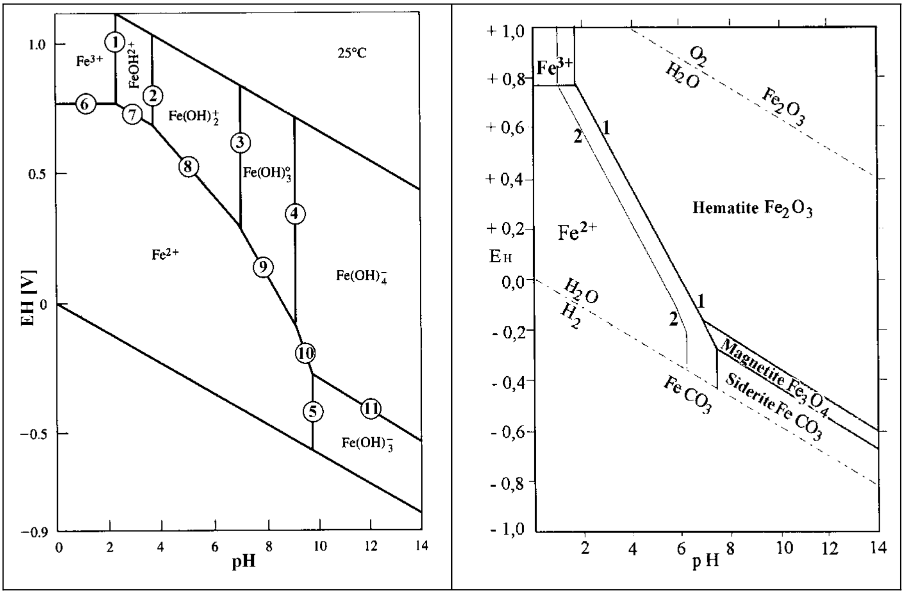


Fig. 15 Left: E_H-pH diagram for the system $Fe\text{-}O_2\text{-}H_2O$ (at 25°C, the numbers 1-11 correspond to the reaction equations described in the text for the calculation of the stability fields, modified after Langmuir 1997) Right: E_H-pH diagram for the system $Fe\text{-}O_2\text{-}H_2O\text{-}CO_2$ (at 25°C, $P(CO_2) = 10^{-2}$ atm), for fields where the total activity is $< 10^{-6}$ (1) resp. $< 10^{-4}$ (2) mol/ L the predominant, precipitating mineral phase is outlined (modified after Garrels and Christ 1965).

The diagram's vertical boundaries (Fig. 15, number 1-5) are reactions that describe a dissolution in water (hydrolysis) independent of the E_H value. The boundaries of the respective predominance fields are calculated via the equilibrium constants for the conversion of the species at each side of the boundary line into each other.

No.	Reaction couples	Reaction equation	-log K = pH
1	$Fe^{3+}/ FeOH^{2+}$	$Fe^{3+} + H_2O = FeOH^{2+} + H^+$	2.19
2	$FeOH^{2+}/ Fe(OH)_2{}^+$	$FeOH^{2+} + H_2O = Fe(OH)_2{}^+ + H^+$	3.48
3	$Fe(OH)_2{}^+/ Fe(OH)_3{}^0$	$Fe(OH)_2{}^+ + H_2O = Fe(OH)_3{}^0 + H_2O$	6.89
4	$Fe(OH)_3{}^0/ Fe(OH)_4{}^-$	$Fe(OH)_3{}^0 + H_2O = Fe(OH)_4{}^- + H^+$	9.04
5	$Fe^{2+}/ Fe(OH)_3{}^-$	$Fe^{2+} + 3H_2O = Fe(OH)_3{}^- +3H^+$	9.08

In contrast, the conversion of Fe^{3+} into Fe^{2+} (Fig. 15, number 6), is a pure redox reaction, independent of the pH-value (horizontal boundary). It is calculated after Eq. 58:

$$E_H = E^o - \frac{0.0591}{n} \cdot \log \frac{\{red\}}{\{ox\}}$$

For the calculation of the boundary line the activity of both species is equal, i.e. {red} = {ox}. Thus the argument of the logarithm is 1 and the logarithm is 0, i.e. $E_H = E_0$.

No.	Reaction couples	Reaction equation	E_0 (V)	$E_H = E_0$
6	Fe^{3+} / Fe^{2+}	$Fe^{3+} + e^- = Fe^{2+}$	0.770	0.770

The boundaries running diagonally display species transformations, which depend on pH and E_H. After Eq. 59

$$E_H = E^o - 2.303 \cdot \frac{m \cdot R \cdot T}{n \cdot F} \cdot pH - 2.303 \cdot \frac{R \cdot T}{n \cdot F} \cdot \log \frac{\{red\}}{\{ox\}}$$

the calculation of the boundary line ({ox}={red}) follows:

$$E_H = E^o - \frac{0.0591 \cdot m}{n} \cdot pH$$

with m= number of protons used or formed in the reaction

No	Reaction couples	Equation of reaction	E_0 (V)	Equation for boundary line
7	$FeOH^{2+}/ Fe^{2+}$	$FeOH^{2+} + H^+ + e^- = Fe^{2+} + H_2O$	0.899	0.899-0.0591 pH
8	$Fe(OH)_2^{+}/ Fe^{2+}$	$Fe(OH)_2^+ + 2H^+ + e^- = Fe^{2+} + 2H_2O$	1.105	1.105-0.118 pH
9	$Fe(OH)_3^{0}/ Fe^{2+}$	$Fe(OH)_3^0 + 3H^+ + e^- = Fe^{2+} + 3H_2O$	1.513	1.513-0.177 pH
10	$Fe(OH)_4^{-}/ Fe^{2+}$	$Fe(OH)_4^- + 4H^+ + e^- = Fe^{2+} + 4H_2O$	2.048	2.048-0.236 pH
11	$Fe(OH)_4^{-}/$ $Fe(OH)_3^0$	$Fe(OH)_4^- + H^+ + e^- = Fe(OH)_3^0 + H_2O$	0.308	0.308-0.0591 pH

How E_H-pH-diagrams change if besides O_2, H_2O and CO_2 other species, as e.g. hydrogen carbonate or sulfate, are also considered can be modeled numerically in chapter 3.1.3.1and 3.1.3.2. E_H-pH diagrams can also be used to characterize natural waters at a first approximation (Fig. 16). However, the problems concerning the precision and uncertainties of E_H measurements must be taken into account (chapter 1.1.5.2.1).

Partial pressure or fugacity diagrams provide another possibility of presentation. Analogous to the activity for the concentration the fugacity is an effective pressure, which describes the tendency of a gas for volatilization from a phase (Latin fugere = flee). Under low-pressure conditions, the fugacity equals the partial pressure. In fugacity diagrams the species distribution species is displayed as dependent on the partial pressure of e.g. O_2, CO_2 or S_2 (Fig. 17). Furthermore there is the possibility to show the species distribution in 3-D models (Fig. 18). Such illustrations easily get confusing though.

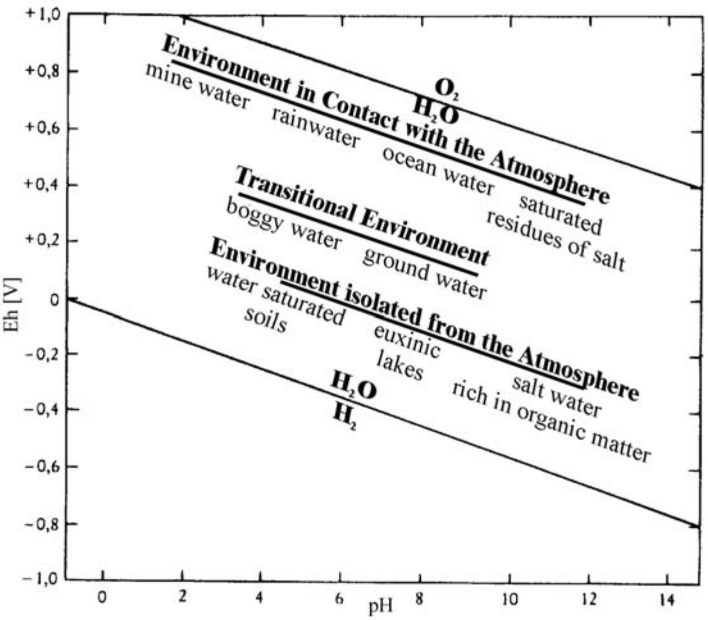


Fig. 16 Classification of natural waters under various E_H/pH conditions (modified after Wedepohl 1978)

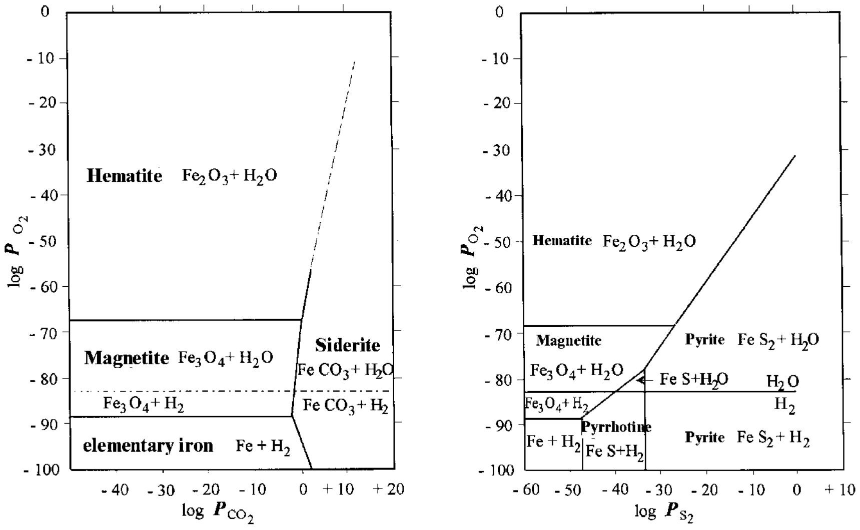


Fig. 17 Left: Fugacity diagram of some iron compounds as a function of $P(O_2)$ and $P(CO_2)$ at 25°C (modified after Garrels u. Christ 1965), Right: Fugacity diagram of some iron and sulfide compounds as a function of $P(O_2)$ and $P(S_2)$ at 25°C (modified after Garrels u. Christ 1965)

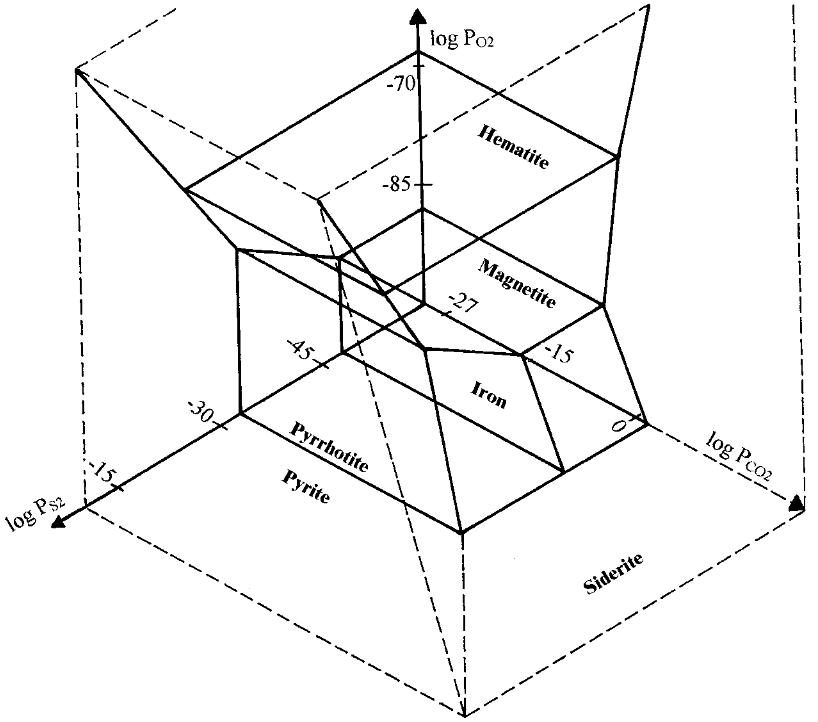


Fig. 18 3-D illustration of a fugacity diagram of some iron compounds as a function of $P(O_2)$, $P(CO_2)$ and $P(S_2)$ at 25°C and a total pressure of 1 atm or higher (modified after Garrels and Christ 1965)

1.1.5.2.4. Redox buffer

Analogous to acid-base-buffers, there are also buffers in the redox system, which can support strong variations of the pE value. Yet the redox equilibrium in ground water can be easily disturbed (Käss 1984). In Fig. 19 some redox buffers are depicted in a pE/pH diagram together with a rough division of ground waters into four ranges. Field 1 characterizes near-surface water with a short residence time, free oxygen, and no degradation processes. Most ground waters lie in the range of field 2 without free oxygen, but also without significant reduction of sulfate. Ground waters with long residence times, a high proportion of organic substances and high concentrations of sulfite plot into the range of field 3. Field 4 contains young mud and peat waters, where a fast degradation of organic material occurs under anaerobic conditions.

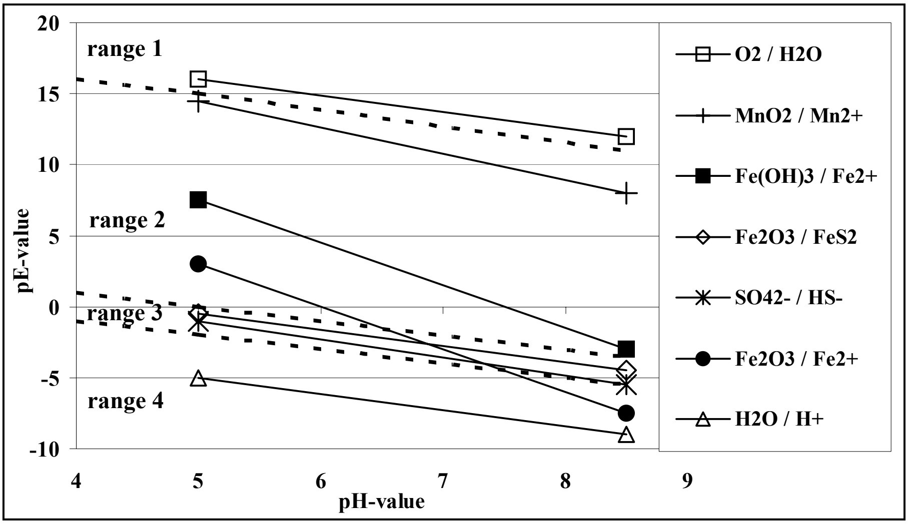
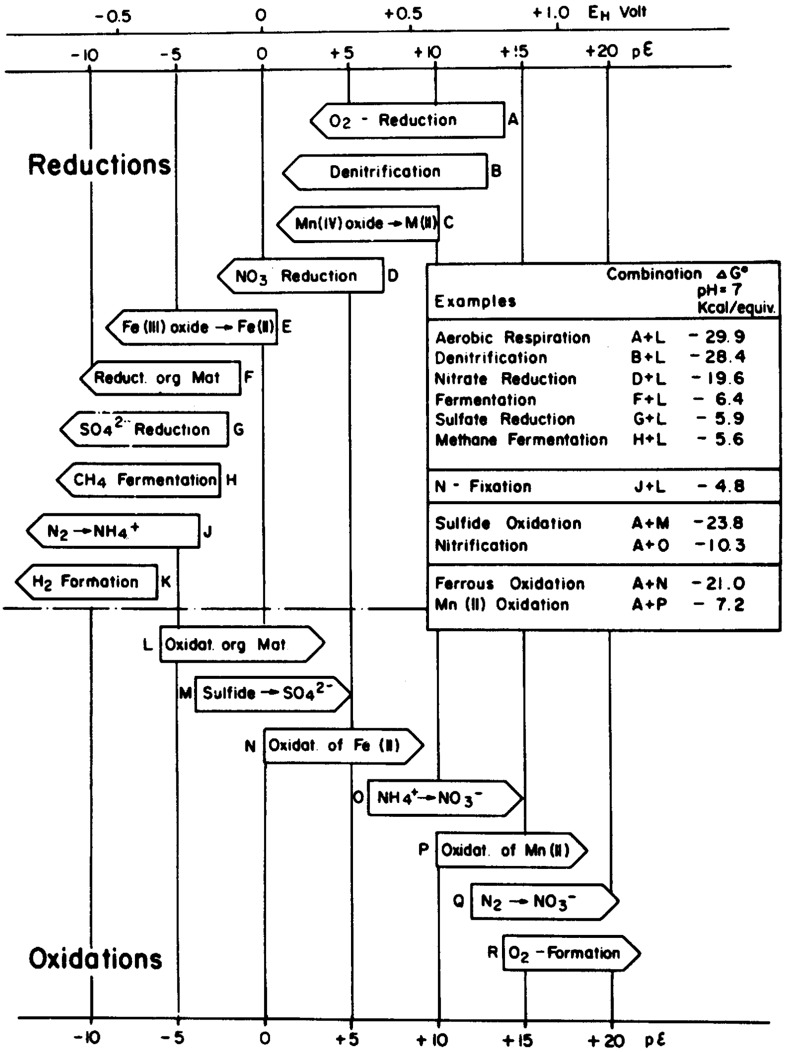


Fig. 19 Redox buffer and subdivision of natural ground waters into 4 redox ranges within the stability field of water; black dashed lines indicate the boundaries of the four redox ranges (after Drever 1997)

1.1.5.2.5. Significance of redox reactions

Oxidation and reduction processes play a major role both in the saturated zone as well as in the unsaturated zone. Within the unsaturated zone there is generally sufficient oxygen from the gas phase to guarantee high redox potentials (500 to 800 mV) in the water. Despite of that, reducing or partly reducing conditions might occur in small pore spaces (micro-milieus). In aquifers close to the surface oxidizing conditions usually prevail too. Thus low redox potentials in such aquifers can indicate anthropogenic contamination.

With increasing depth, even under natural geogenic conditions, oxygen contents and consequently the redox potential in groundwater decreases. Microorganism, which use the oxygen for their metabolism are the reason for that. If the oxygen, dissolved in water, is used up, they can gain oxygen, respectively energy form the reduction of NO_3^- to N_2 (via NO_2^- and $N_2O(g)$), Fe^{3+} to Fe^{2+} or SO_4^{2-} to $H_2S(aq)$. The occurrence of organically bound carbon in the groundwater or in the aquifer is required for those reductions. Fig. 20 shows some microbially catalysed redox in dependence of pE/E_H conditions.



Examples	Combination	ΔG° pH = 7 Kcal/equiv.
Aerobic Respiration	A+L	- 29.9
Denitrification	B+L	- 28.4
Nitrate Reduction	D+L	- 19.6
Fermentation	F+L	- 6.4
Sulfate Reduction	G+L	- 5.9
Methane Fermentation	H+L	- 5.6
N - Fixation	J+L	- 4.8
Sulfide Oxidation	A+M	-23.8
Nitrification	A+O	-10.3
Ferrous Oxidation	A+N	-21.0
Mn (II) Oxidation	A+P	- 7.2

Fig. 20 Microbially catalyzed redox reactions in dependence on pE/E$_H$ value (after Stumm and Morgan 1996)

Fig. 21 schematically shows the most significant hydrogeochemical processes in aqueous systems, and at the water-solid interface.

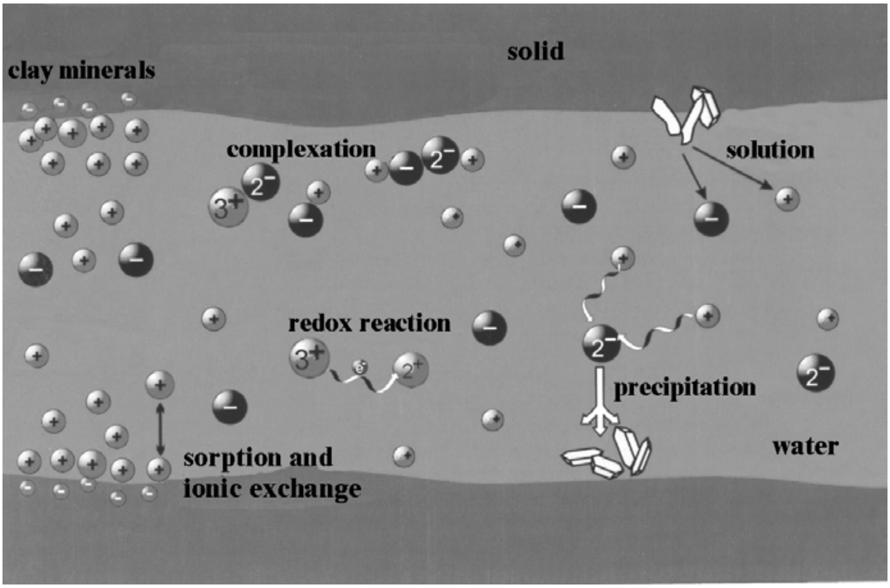


Fig. 21 Synopsis of the interaction processes in aqueous systems

1.2 Kinetics

For the reactions considered in the previous chapter the adjustment of the thermodynamic equilibrium, as the most stable time-independent form of a closed system, was always assumed. To what extent or in which time this equilibrium is reached can not be described by thermodynamic laws. Thus, slow reversible, irreversible or heterogeneous reactions actually require the consideration of kinetics, i.e. of the rate at which a reaction occurs or the equilibrium adjusts.

1.2.1 Kinetics of various chemical processes

1.2.1.1 Half-life

Fig. 22 shows the residence times t_R of waters in the hydrosphere and the half-life $t_{1/2}$ of various reactions. If $t_{1/2} \ll t_R$ then it can be assumed that the system is roughly in equilibrium and thermodynamic models can be used. If, on the other hand, $t_R \ll t_{1/2}$ kinetic models must be applied.

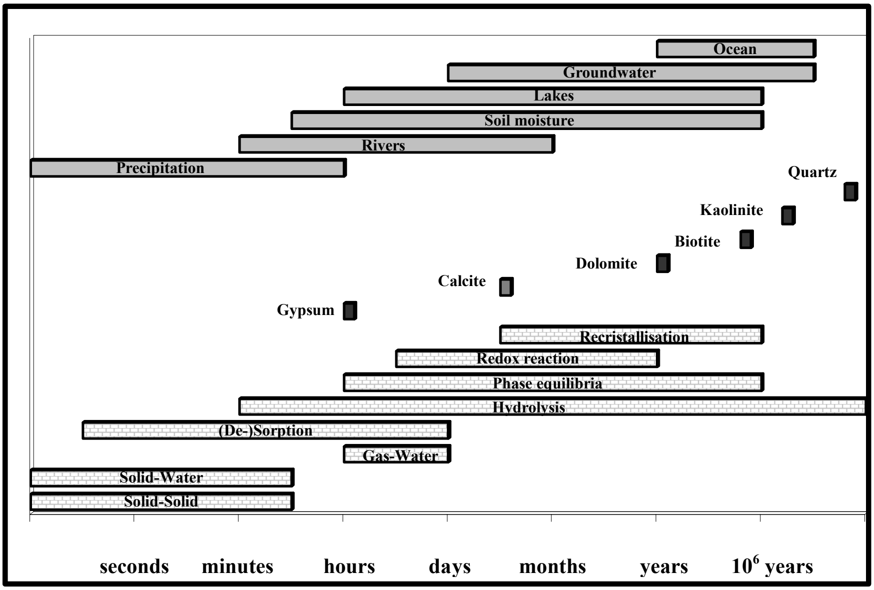


Fig. 22 Schematic comparison between the residence times t_R of waters in the hydrosphere (ocean to rainfall), the dissolution of various minerals in unsaturated solutions at pH 5 (quartz to gypsum) and the half-life $t_{1/2}$ of chemical processes (recristallization to solid-solid reactions) (data after Langmuir 1997, Drever 1997)

Acid-base reactions and complexation processes predominantly with low stability constants (solid-solid, solid-water-interface in Fig. 22) occur within micro- to milliseconds. Unspecific sorption with the formation of a disordered surface film is also a fast reaction, while the kinetics of specific sorption and mineral crystallization generally are considerably slower. For ion exchange the reaction rate depends on the type of binding and exchange. Those processes are the fastest where the exchange only occurs at the edges of mineral grains, as e.g. with kaolinite. Incorporation of ions in mineral sheets is much slower, e.g. into montmorillonite or vermiculite, or the intrusion into basal sheets, as for illite. Dissolution and precipitation processes (the range of phase equilibrium in Fig. 22) sometimes take only hours, but could also need several thousands of years. Redox reactions have long half-lifes in the range of years, especially when catalysts are lacking.

1.2.1.2 Kinetics of mineral dissolution

For interactions between solid and liquid phases, two cases have to be distinguished: weathering of rock-forming minerals and the weathering of trace minerals.

For the weathering of rock-forming minerals, the solution kinetics is determined by the solubility product and transport in the vicinity of the solid-water-interface. If the dissolution rate of a mineral is higher than the diffusive transport from the solid-water interface, saturation of the boundary layer and an exponential decrease with increasing distance from the boundary layer results. In the following text this kind of solution is referred to as solubility-product controlled. If the dissolution rate of the mineral is lower than diffusive transport, no saturation is attained. This process is called diffusion-controlled solution (Fig. 23 right).

In the experiment solubility-product controlled and diffusion-controlled solution can be distinguished by the fact that for diffusion controlled solution an increase in mixing leads to an increase in the reaction rate. Since this assumption is necessarily true the other way round, it is easier to calculate if the reaction proceeds faster or slower than the molecular diffusion. If it is faster, the reaction is controlled by the solubility product; if it is slower, it is diffusion controlled.

For the weathering of trace minerals from the solid matrix, the dissolution occurs selectively on spots where the mineral is exposed to the surface. These mineral surfaces are usually not smooth, but show dislocations (screw, jump, step dislocations) and point defects (vacant sites, interstitial sites) (Fig. 23 left). Dissolved ions are immediately transported from the surface into solution, so that no gradient can develop. Since the total concentrations of trace minerals in the solution are low, no equilibrium can be reached. In the following the dissolution of trace minerals is called surface-controlled.

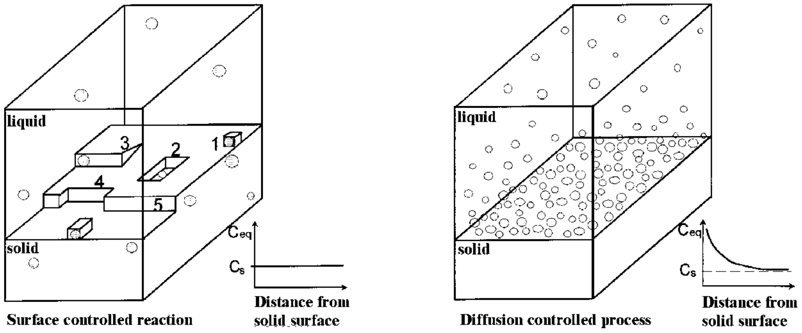


Fig. 23 Comparison between surface-controlled reactions (left; 1= interstitial sites, 2= vacant sites, 3= screw dislocation, 4= jump dislocation, 5=step dislocation) and diffusion-controlled processes (right)

1.2.2 Calculation of the reaction rate

The reaction rate can be determined by inverse geochemical modeling as increase of the products or decrease of the reactants along a flow path over time. In most cases the forward reaction (A + B → C) and the simultaneously proceeding reverse reaction (C → A + B) have different reaction rates. The total kinetics is the sum of both.

$$v^{+} = k^{+} \prod_{i} (X_i)^{n_i} \qquad \text{Eq. (72.)}$$

$$v^{-} = k^{-} \prod_{i} (X_i)^{n_i} \qquad \text{Eq. (73.)}$$

$$K_{eq} = \frac{k^{+}}{k^{-}} = \prod_{i} (X_i)_{eq}^{n_i} \qquad \text{Eq. (74.)}$$

with:
v^+ = rate of the forward reaction
k^+ = rate constant of the forward reaction
v^- = rate of the reverse reaction
k^- = rate constant of the reverse reaction
X = reactant or product
n = stoichiometric coefficient
K_{eq} = equilibrium constant

Table 14 Calculation of reaction rate, time law and half-life of a reaction in dependence of its order

	chemical reactions	reaction rate time law	half life time
0.order reaction		$v = -K_k$ $(A) = -K_k \cdot t + (A_0)$	$t_{1/2} = \frac{(A_0)}{2 \cdot K_k}$ dependent on concentration
1.order reaction	$A \rightarrow B$ $A \rightarrow B + C$	$\frac{d(A)}{dt} = -K_k \cdot (A)$ $(A) = (A_0) \cdot e^{-K_k \cdot t}$	$t_{1/2} = \frac{1}{K_k} \cdot \ln 2$ independent on concentration
2.order reaction	$A + A \rightarrow C + D$ $A + B \rightarrow C + D$	$\frac{d(A)}{dt} = -K_k \cdot (A) \cdot (B)$ $\frac{d(A)}{dt} = -K_k \cdot (A)^2$ $\frac{1}{(A)} = -K_k \cdot t + \frac{1}{A_0}$	$t_{1/2} = \frac{1}{(A_0) \cdot K_k}$ dependent on concentration
3.order reaction	$A + B + C \rightarrow D$	$\frac{d(A)}{dt} = -K_k \cdot (A) \cdot (B) \cdot (C)$	

Table 14 shows the calculation of the reaction rate, the time law, and the half-life depending on the reaction´s order. The order results from the sum of the exponents of the concentrations. The number does not necessarily have to be an integer. The half-life states in which time half of the reactants is converted into the products. Reaction rate constants k are 10^{12} to 10^{-11} L/s for first order reactions and 10^{10} to 10^{-11} L/(mol*s) for second order reactions.

1.2.2.1 Subsequent reactions

Frequently chemical processes do not occur in one reaction but as a series of reactions.

$$A + B \xrightarrow{k_1} C \qquad A + B \xleftarrow{-k_1} C$$

$$C \xrightarrow{k_2} D \qquad C \xleftarrow{-k_2} D \qquad \text{Eq. (75.)}$$

The equilibrium constant K_{12} is derived from the principle of the microscopic reversibility, i.e. at equilibrium every single and every reversible reaction occurs at the same rate.

$$K_{12} = \frac{\{D\}}{\{A\} \cdot \{B\}} = \frac{k_1 \cdot k_2}{(\text{-}k_1) \cdot (-k_2)} \qquad \text{Eq. (76.)}$$

For subsequent reactions the total reaction rate depends on the reaction with the lowest reaction rate.

1.2.2.2 Parallel reactions

For reactions that run independently of each other (parallel reactions) and result in the same product, the reaction with the fastest reaction rate determines the kinetics of the whole process.

$$A + B \xleftrightarrow{k_1} C + D \qquad \text{Eq. (77.)}$$

$$A \xleftrightarrow{k_2} C + E \qquad \text{Eq. (78.)}$$

$$A + F + G \xleftrightarrow{k_3} C + H \qquad \text{Eq. (79.)}$$

With $k_1 > k_2 > k_3$ the reaction of Eq. 77 dominates first. Another reaction can become predominant, when the boundary conditions change in the course of the reaction, as e.g. the pH value during calcite dissolution.

1.2.3 Controlling factors on the reaction rate

The reaction rate mainly depends on the concentration of reactants and products. According to the collision theory, frequent collisions and rapid conversions occur at high concentrations. Yet not all collisions cause conversions, a certain position of the molecules to each other as well as a certain threshold energy are required. Besides the concentration, pH, light, temperature, organics, presence of catalysts, and surface-active trace substances can have a significant influence on reaction rates.

The empirical Arrhenius equation describes the dependency of the reaction rate on the temperature

$$\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \qquad \text{Eq. (80.)}$$

with k= velocity constant
A = empiric constant
R = general gas constant (8.315 J/K mol)
T = temperature
E_a = activation energy

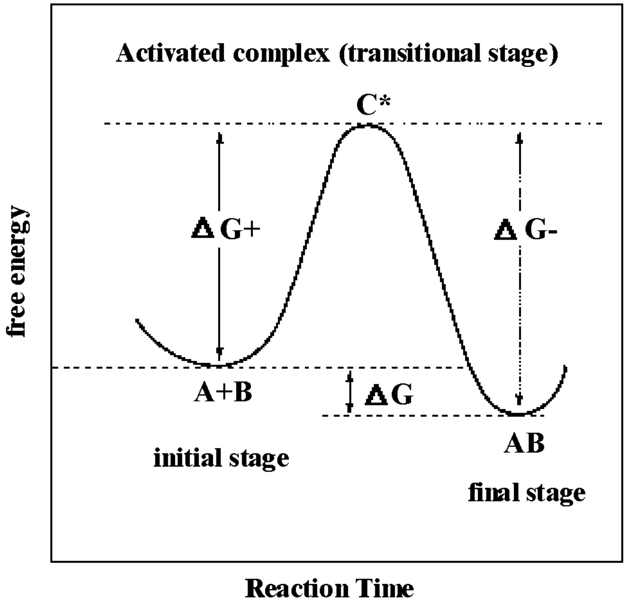


Fig. 24 Scheme of the free energies ΔG and formation of an activated complex C^* as a transitional state of the reaction A+B = AB (after Langmuir 1997)

The activation energy is the energy required for initiating a reaction. According to the theory of the transitional state an instable activated complex forms, which has a fairly high potential energy from the kinetic energy of the reactants and decays within a short period of time. Its energy is converted into the binding energy respectively the kinetic energy of the product (Fig. 24).

Table 15 shows typical values for the activation energy of some chemical processes.

Table 15 Activation energy of some chemical processes (after Langmuir 1997)

Reaction or process	range of typical E_a-values [kcal/mol]
Physical adsorption	2-6
Diffusion in solution	<5
Reactions in cells and organisms	5-20
Mineral solution and precipitation	8-36
Mineral solution via surface controlled reaction	10-20
Ion exchange	>20
Isotope exchange in solution	18 to 48
Solid phase diffusion in minerals at low temperatures	20 to 120

1.2.4 Empiric approaches for kinetically controlled reactions

A kinetically controlled reaction can be described by the equation:

$$\frac{m_i}{d_t} = c_{ik} \cdot k_k \qquad \text{Eq. (81.)}$$

with m_i/dt = converted mass (mol) per time (s)
c_{ik} = concentration of the species i
k_k = reaction rate (mol/kg/s)

The general kinetic reaction rate of minerals is:

$$R_K = r_K \cdot \left(\frac{A_0}{V}\right) \cdot \left(\frac{m_k}{m_{0k}}\right)^n \qquad \text{Eq. (82.)}$$

with r_k = specific reaction rate (mol/m^2/s)
A_0 = initial surface of the mineral (m^2)
V = mass of solution (kg water)
m_{0k} = initial mineral mass (mol)
m_k = mass of the mineral (mol) at a time t

$(m_k/m_{0k})^n$ is a factor, which takes into account the change in A_0 /V during the dissolution. For a steady dissolution from surfaces and cubes n is 2/3. Frequently not all parameters are available, so that simple approaches are useful like:

$$R_K = k_K \cdot (1 - SR)^{\sigma} \qquad \text{Eq. (83.)}$$

In Eq. 83 k_K is an empiric constant and SR is the saturation rate (ion activity product / solubility product). Frequently the exponent σ equals 1. The advantage of this simple equation is that it is valid both for supersaturation and undersaturation. With saturation R_K becomes zero. R_K can also be expressed by the saturation index [log (SR)] (Appelo et al. 1984):

$$R_K = k_K \cdot \sigma \cdot SI \qquad \text{Eq. (84.)}$$

Another example is the Monod equation, which contains a concentration dependent term:

$$R_k = r_{max}\left(\frac{C}{k_m + C}\right) \qquad \text{Eq. (85.)}$$

with r_{max} = maximum reaction rate
k_m = concentration, at which the rate is 50% of the maximum rate

The Monod rate is widely used for the simulation of the degradation of organic matter (van Cappellen & Wang 1996). It can be derived from the general equation for first order kinetics:

$$\frac{ds_C}{dt} = -k_1 s_C \qquad \text{Eq. (86.)}$$

with: s_C = organic carbon content [mol/kg soil]
k_l = decay constant for first order kinetic reactions [1/s]

If for instance the degradation of organic carbon in an aquifer is considered, a first order degradation parameters ($k_l = 0.025$ / a for 0.3 mM O_2 and $k_l = 5\cdot10^{-4}$ / a for 3 µM O_2) can be described by the coefficients $r_{max} = 1.57\cdot10^{-9}$ / s and $K_m = 294$ µM in the Monod equation, oxygen being the limiting substance. A similar estimation can be done for nitrate as limiting substance: $k_l = 5\cdot10^{-4}$ / a for 3 mM NO_3 and $k_l = 1\cdot10^{-4}$ / a for 3 µM NO_3, which results in $r_{max} = 1.67\cdot10^{-11}$ / s and K_m = 155 µM. The corresponding Monod equation is as follows:

$$R_C = 6 \cdot s_C \cdot \left(\frac{s_C}{s_{C_0}} \right) \left\{ \frac{1.57 \cdot 10^{-9} m_{O_2}}{2.94 \cdot 10^{-4} + m_{O_2}} + \frac{1.67 \cdot 10^{-11} m_{NO_3^-}}{1.55 \cdot 10^{-4} + m_{NO_3^-}} \right\} \qquad \text{Eq. (87.)}$$

whereas the factor 6 arises, if the concentration s_C is converted from mol/kg soil to mol/ kg pore water. Plummer et al. (1978) found the following rates for the carbonate dissolution and precipitation:

$$r_{Calcite} = K_1 \cdot \{H^+\} + K_2\{CO_2\} + K_3\{H_2O\} - K_4\{Ca^{2+}\}\{HCO_3^-\} \qquad \text{Eq. (88.)}$$

The constants K_1, K_2 and K_3 depend on the temperature and describe the forward reaction:

$$k_1 = 10^{(0.198 - 444.0 / T_K)} \qquad \text{Eq. (89.)}$$

$$k_2 = 10^{(2.84 - 2177.0 / T_K)} \qquad \text{Eq. (90.)}$$

if temperature ≤ 25°C

$$k_3 = 10^{(-5.86 - 317.0 / T_K)} \qquad \text{Eq. (91.)}$$

if temperature > 25°C

$$k_3 = 10^{(-1.1 - 1737.0 / T_K)} \qquad \text{Eq. (92.)}$$

K_4 describes the reverse reaction and can be replaced by the term

$$1 - \left(\frac{IAP}{K_{calcit}} \right)^{\frac{2}{3}} \qquad \text{Eq. (93.)}$$

where IAP is the ion activity product and $K_{calcite}$ is the calcite solubility product.

1.3 Reactive mass transport

1.3.1 Introduction

In the previous part of the book chemical interactions were described without any consideration of transport processes in aqueous systems. Models for reactive mass transport combine these chemical interactions with convective and dispersive transport, so that they can model the spatial distribution coupled to the chemical behavior. Requirement for every transport model is a flow model as accurate as possible.

1.3.2 Flow models

Flow models show potential or velocity fields resulting from the groundwater flow, unsaturated flow, or in the soil. These potential fields adequately describe the flow process together with further boundary conditions, such as pore volume, dispersivity, etc., in order to calculate the transport behavior (Table 16).

Table 16 Description of homogenous, laminar transport processes of a mass C in the saturated and unsaturated zone (without dispersion and diffusion)

	saturated zone	unsaturated zone / soil
effective head	hydraulic head (gravitational and pressure head)	matrix head (gravitational and capillary head)
Model equation	DARCY $\frac{\partial c}{\partial t} = K \frac{\partial h}{\partial l} \cdot \frac{c}{\partial z}$	RICHARDS $\frac{\partial c}{\partial t} = \left(K(P_k) \frac{\partial P_m}{\partial z} \right) \cdot \frac{c}{\partial z}$
Permeability K	Constant	function of matrix head P_m

1.3.3 Transport models

1.3.3.1 Definition

The description of transport is closely connected to the terms convection, diffusion dispersion, and retardation as well as decomposition. First, it is assumed that there are no interactions between the species dissolved in water and the solid phase, through which the water is flowing. Moreover, it is assumed that water is the only fluid phase. The multiphase flow water-air, water-organic phase (e.g. oil or DNAPL) or water-gas is not considered here.

Convection (also known as advection) is the vector, which results from the DARCY or the RICHARDS equations. It describes the flow velocity or the flow distance for a certain time t. In general convection has the major influence on mass transport. Magnitude and direction of the convective transport are controlled by:

the disposition of the flow field
the distribution of the hydraulic permeabilities within the flow field
the disposition of the water table or the potentiometric surface
the occurrence of sources or sinks

Concentration gradients are leveled out by diffusion by means of molecular motion. The vector of diffusion is generally much smaller than the vector of convection in groundwater. With increasing flow velocity diffusion can be neglected. In sediments, in which the k_f value is very low, and consequently the convective proportion is very small or even converging towards zero (e.g. for clay), the diffusion could become the controlling factor of mass transport.

The third term in mass transport is dispersion. The dispersion describes the mass flow, which results from velocity variations due to the geometry and the structure of the rock system. From this definition it follows that the smaller the vector of convection the smaller the effect of dispersion. The other way round, an increasing effect of dispersion occurs with higher flow velocity. Consequently the mathematical description of the species distribution is an overlap of convection, diffusion, and dispersion.

All phenomena that cause species not to spread with the velocity of the water in soil or in groundwater are called retardation. Retardation is possible without any mass decrease. Frequently, though, retardation is combined with degradation. This "degradation" of the concentration of a species can occur by means of radioactive decay of a radionuclide or biological degradation of an organic substance. Also sorption and cation exchange can be included in this definition of "degradation", because the considered element is entirely or partially removed from the aqueous phase.

Fig. 25 shows a simplified illustration of the described phenomena for the one-dimensional case.

1.3.3.2 Idealized transport conditions

Within the groundwater transport including simple chemical reactions can be described by the following equation in a one-dimensional form:

$$\frac{\partial C_i}{\partial t} = D_l \frac{\partial^2 C_i}{\partial z^2} + D_t \frac{\partial^2 C_i}{\partial z^2} + D \frac{\partial^2 C_i}{\partial z^2} - v \frac{C_i}{\partial z} + C_{SS} \qquad \text{Eq. (94.)}$$

dispersion diffusion advection sources/sinks

with C_i = concentration for the species i dissolved in water [mol/L]
t = time [s]
D_l = longitudinal dispersion coefficient [m^2/s]
D_t = transversal dispersion coefficient [m^2/s]
D = diffusion coefficient [m^2/s]
z = spatial coordinate [m]

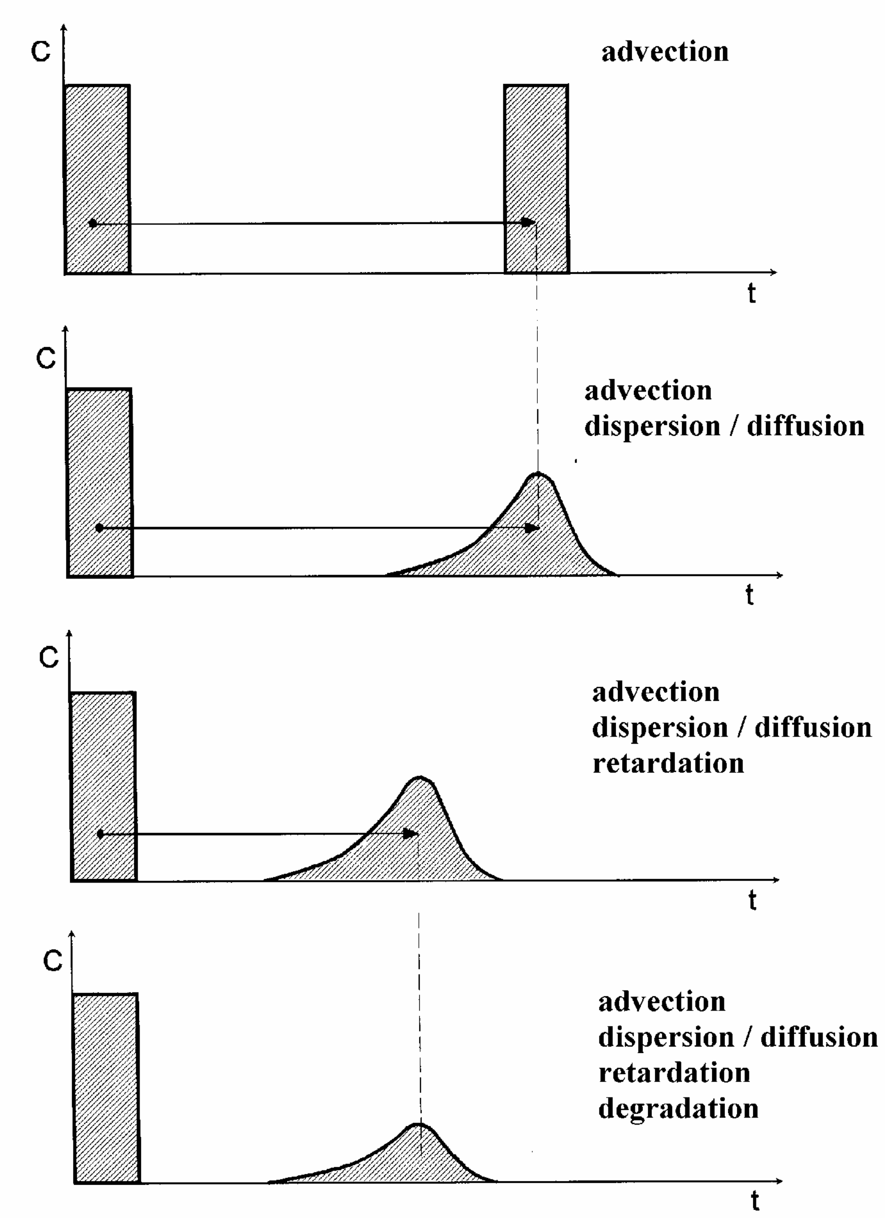


Fig. 25 Convection, dispersion / diffusion, retardation and degradation of a species (single peak input) versus time along a flow path

v = flow velocity [m/s]
C_{SS} = concentration of the species (source or sink)

Assuming some simplifications, analytical solutions for the transport equation may be inferred from arguments by analogy with the basic equations of heat conduction and diffusion (e.g. Lau et al. (1959), Sauty (1980), Kinzelbach (1983), and Kinzelbach (1987)).

1.3.3.3 Real transport conditions

Convection, diffusion, and dispersion can only describe part of the processes occurring during transport. Only the transport of species that do not react at all with the solid, liquid or gaseous phase (ideal tracers) can be described adequately by the simplified transport equation (Eq. 94). Tritium as well as chloride and bromide can be called ideal tracers in that sense. Their transport can be modeled by the general transport equation as long as no double-porosity aquifers are modeled. Almost all other species in water somehow react with other species or a solid phase. These reactions can be subdivided into the following groups, some of which have already been considered in the previous part of the book.

- Reactions between the aqueous and the gaseous phase (chapter 1.1.3)
- Dissolution and precipitation processes (chapter 1.1.4.1)
- Sorption and desorption of species in water on the solid phase (chapter 1.1.4.2)
- Anion and cation exchange (chapter 1.1.4.2.2)
- Formation of colloids
- Sorption on colloids
- Homogeneous reactions within the aqueous phase (chapter 1.1.5)

All chemical reactions comprise at least two species. For models of transport processes in groundwater or in the unsaturated zone reactions are frequently simplified by a basic sorption or desorption concept. Hereby, only one species is considered and its increase or decrease is calculated using a K_s or K_d value. The K_d value allows a transformation into a retardation factor that is introduced as a correction term into the general mass transport equation (chapter 1.1.4.2.3).

As already explained in chapter 1.1.4.2.3, the K_d concept must be rejected in most cases, because of its oversimplification and its low suitability for application to natural systems. For example, in degradation only the degrading substance is considered. This concept might be applicable for radioactive decay, yet if the decomposition of organic matter is considered, it is crucial to consider decomposition products (metabolites) that form and play an important role in transport themselves.

For the saturated and the unsaturated zone, the general mass transport equation can be extended as follows, describing exchange processes with the sediment as well as interactions with the gas phase, and within the aqueous phase.

$$\frac{1}{\partial t}\partial\left(C_i + \left(S_i \frac{d}{n}\right) + \frac{G_i}{n}\right) = D_l \frac{\partial^2 C_i}{\partial z^2} + D\frac{\partial^2 C_i}{\partial z^2} - v\frac{C_i}{\partial z} \qquad \text{Eq. (95.)}$$

with v = pore velocity [m/s]
C_i = concentration of the species i [mol/L]
S_i =concentration of the species i on/ in the solid phase [mol/g]
n = porosity
d = density [g/L]
G_i = concentration of the species i in the gas phase [mol/L]
D_l = longitudinal dispersion coefficient [m^2/s]
D = diffusion coefficient [m^2/s]
z = spatial coordinate [m]
t = time [s]

1.3.3.3.1. Exchange within double-porosity aquifers

Diffusive exchange between mobile and immobile water can be expressed mathematically as a mixing process between two zones: One zone containing stagnant water is coupled to a “mobile” zone, where water flows. The diffusive exchange can be described by first order kinetics.

$$\frac{\partial M_{im}}{\partial t} = \theta_{im} \cdot R_{im} \frac{\partial c_{im}}{\partial t} = \alpha\,(c_m - c_{im}) \qquad \text{Eq. (96.)}$$

The index “m” stands for mobile and “im” for immobile. M_{im} is the number of moles of a species in the immobile zone and R_{im} the retardation factor of the immobile zone, c_m and c_{im} are the concentrations in mol/kg in the mobile and immobile zone respectively. The symbol α stands for an exchange factor (1/s). The retardation factor R = 1+ (dq/dc) is determined by chemical reactions. The integrated form of Eq. 96 is:

$$\begin{aligned} c_{im} &= \beta \cdot f \cdot c_{m0} + (1 - \beta \cdot f)c_{im0} \\ \text{with} \quad \beta &= \frac{R_m \theta_m}{R_m \theta_m + R_{im} \theta_{im}} \\ f &= 1 - \exp\left(\frac{\alpha t}{\beta \theta_{im} R_{im}}\right) \end{aligned} \qquad \text{Eq. (97.)}$$

with c_{m0} and c_{im0} being the initial concentrations, and θ_m and θ_{im} the saturated porosities of the mobile and immobile zones respectively. R_m is the retardation factor of the mobile zone. From these the mixing factor $mixf_{im}$ can be defined, which is a constant for a time t.

$$mixf_{in} = \beta \cdot f \qquad \text{Eq. (98.)}$$

If this factor is implemented into the Eq.97, the result is:

$$c_{im} = mixf_{im} \cdot c_{m0} + (1 - mixf_{im})c_{im0} \qquad \text{Eq. (99.)}$$

Analogously, it follows for the mobile concentration:

$$c_m = (1 - mixf_m)c_{m0} + mixf_m \cdot C_{im0} \qquad \text{Eq. (100.)}$$

The exchange factor α is, according to van Genuchten (1985), dependent on the geometry of the stagnant zone. For a sphere, the relation is:

$$\alpha = \frac{D_e \theta_{im}}{(af_{s \to 1})^2} \qquad \text{Eq. (101.)}$$

with D_e = diffusion coefficient in the sphere (m^2/s)
a = radius of the sphere (m)
f_{s1} = shape factor (Table 17)

Alternatively, the problem can be solved numerically by applying a finite differences grid on the stagnant zone and determining the diffusive exchange iteratively (Parkhurst and Appelo, 1999; Appelo and Postma, 1994).

Table 17 Shape factors for the first order diffusive exchange between mobile and immobile water (Parkhurst & Appelo, 1999)

Shape of stagnant region	Dimensions (x,y,z) or 2 r,z	First-order equivalent $f_{s \to 1}$	Comments
Sphere	2a	0.21	2a = diameter
Plane sheet	2a, ∞, ∞	0.533	2a = thickness
Rectangular prism	2a, 2a, ∞	0.312	Rectangle
	2a,2a,16a	0.298	
	2a,2a,8a	0.285	
	2a,2a,6a	0.277	
	2a,2a,4a	0.261	
	2a,2a,3a	0.246	
	2a,2a,2a	0.22	Cube
	2a,2a,4a/3	0.187	
	2a,2a,a	0.162	
	2a,2a,2a/3	0.126	
	2a,2a,2a/4	0.103	
	2a,2a,2a/6	0.0748	
	2a,2a,2a/8	0.0586	
Solid cylinder	2a, ∞	0.302	2a = diameter
	2a,16a	0.298	
	2a,8a	0.277	
	2a,6a	0.27	
	2a,4a	0.255	
	2a,3a	0.241	
	2a,2a	0.216	

Shape of stagnant region	Dimensions (x,y,z) or 2 r,z	First-order equivalent $f_{s\rightarrow 1}$	Comments
	2a,4a/3	0.185	
	2a,a	0.161	
	2a,2a/3	0.126	
	2a,2a/4	0.103	
	2a,2a/6	0.0747	
	2a,2a/8	0.0585	
Pipe wall (surrounds the mobile pore)	$2r_i,2r_0$,		2 r_i = pore diameter
	2a,4a	0.657	2 r_0 = outer diameter of pipe
	2a,10a	0.838	wall thickness (r_0 - r_i) = a (Gl. 99)
	2a,20a	0.976	
	2a,40a	1.11	
	2a,100a	1.28	
	2a,200a	1.4	
	2a,400a	1.51	

1.3.3.4 Numerical methods of transport modeling

The numerical methods for solving the transport equation can be subdivided into two groups:

- Solution of the transport equation including the chemical reactions (one equation system for each species to be solved)
- Coupled methods (transport model coupled with hydrogeochemical code)

For coupled models solving the transport equation can be done by means of the finite-difference method (and finite volumes) and of the finite-elements method. Algorithms based on the principle of particle tracking (or random walk), as for instance the method of characteristics (MOC), have the advantage of not being prone to numerical dispersion (see 1.3.3.4.1).

1.3.3.4.1. Finite-difference / finite-element method

For the finite difference method the area is discretized by rectangular cells. The distance of neighboring nodes can differ. The nodes are usually set in the center of gravity of each cell and present the average concentration of the cells. The mass transport is simulated by modeling the chemical reactions for every node in discrete time intervals. Convective, diffusive, and dispersive mass transport is calculated along the four sides of each cell, e.g. by considering the weighted means of the concentrations of neighboring cells. The ratio between convective and dispersive mass flow is called Grid-Peclet number P_e (Eq. 102).

$$P_e = \frac{|v| \cdot L}{D}$$

Eq. (102.)

with D= dispersivity
L= cell length

and $|v| = \sqrt{v_x^2 + v_y^2 + v_z^2}$ Eq. (103.)

Both the spatial discretisation and the choice of the type of differences (e.g. uplift differences, central differences) have a strong influence on the result. This fuzziness caused by the application of different methods is subsumed as "numeric dispersion".

Numeric dispersion can be eliminated largely by a high-resolution discretisation. The Grid-Peclet number helps for the definition of the cell size. Pinder and Gray (1977) recommend the P_e to be ≤ 2. The high resolution discretisation, however, leads to extremely long computing times. Additionally the stability of the numeric finite-differences method is influenced by the discretisation of time. The Courant number (Eq. 104) is a criterion, so that the transport of a particle is calculated within at least one time interval per cell.

$$Co = \left| v \frac{dt}{L} \right| < 1$$ Eq. (104.)

Methods applying reverse differences in time are called implicit. Generally these implicit methods, as e.g. the Crank-Nicholson method, show high numerical stability. On the other side, there are explicit methods, and the methods of iterative solution algorithms. Besides the strong attenuation (numeric dispersion) there is another problem with the finite differences method, and that is the oscillation.

With the finite-elements method the discretisation is more flexible, although, as with the finite-differences method, numeric dispersion and oscillation effects can occur (Fig. 26).

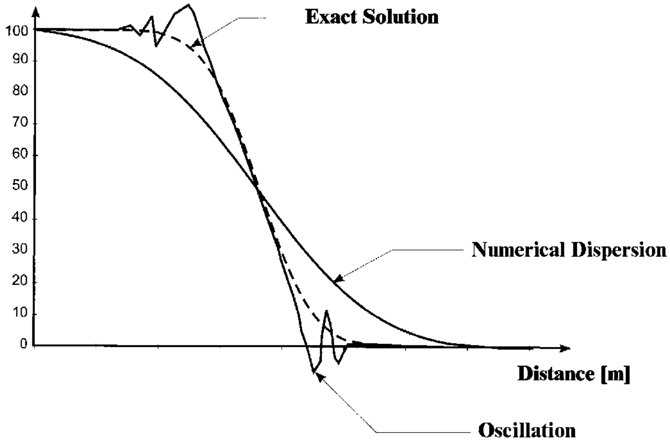


Fig. 26 Numeric dispersion and oscillation effects for the numeric solution of the transport equation (after Kovarik, 2000)

1.3.3.4.2. Coupled methods

In physics, the random walk method has already been in use for decades to understand and model diffusion processes. Prickett et al. (1981) developed a simple model for groundwater transport to calculate the migration of contamination. An essential advantage of the methods of random walk and particle tracking is that they are free of numeric dispersion and oszillations (Abbot 1966).

For the method of characteristics (MOC), the convective term is dealt with separately from the dipersive transport term by establishing a separate coordinate system along the convection vector for solving the dispersion problem. In most modeling programs, the convection is approximated with discrete particles. A certain number of particles with defined concentrations is used and moved along the velocity field (Konikoff and Bredehoeft, 1978).

Particularly sophisticated models deal with reactive mass transport, including both the accurate description of the convective and dispersive transport of species, as well as the modeling of interactions of species in water, with solid and gaseous phases (precipitation, dissolution, ion exchange, sorption).

Coupled reactive transport modeling does the flow modeling separately as first step. After that a modified method of characteristics (MMOC) is carried out based on the calculated flow field. The particles present a complete water analysis or a discrete water volume with certain chemical properties. These particles or water volumes are then moved for every single time step and using a hydrochemical modeling code (e.g. PHREEQC, MINTEQA2), the interactions of the particles with their environment (i.e. rock, gaseous phases), and with each other are calculated. The results of this thermodynamic modeling are subsequently transferred back to the particles before these are "moved" one time step further. Some examples for such models are TREAC, MINTRAN, and PHAST.

An extremely simplified application of the described approach is already implemented in the PHREEQC program. Reactive mass transport can be modeled for the one-dimensional case at constant flow rates considering diffusion and dispersion.

Taking into consideration a high possible number of chemical reactions for the reactive mass transport, like what is done for coupled models, the computing times mainly result from the calculations within the thermodynamic code. The 2d or 3d models easily lead to unreasonably long computing times. Since information on the chemical heterogeneity of an aquifer is frequently lacking, the calculation of a 1d model is generally preferable.

However, there is a severe disadvantage with one-dimensional models: they do not take into account the dilution due to the transversal dispersion. Consequently a mass M, that is not susceptible to any chemical reaction, occurs "blurred" at a point x downstream from x_0 (the location of M input) due to longitudinal dispersion. The dispersion leads to a smaller maximum concentration, however, and the mass integral equals the mass added at x_0. Thus, the impulse of mass remains constant along any simulated one-dimensional distance.

In reality, however, transversal dispersion D_t causes mass exchange in y and z direction leading to dilution. This dilution is a function of D_t and the flow velocity

v. If D_t and v are constant within the flow field, than the resulting dilution can by described by a linear function or a constant factor, respectively. The value for this factor can be determined using a conservative 3d model taking into account the aquifer thickness in particular. If, for instance in a conservative tracer model the contaminant concentration decreases by 50 percent along a certain distance through dispersion, it follows that, using a 1d model of reactive mass transport, half of the water within the column has to be substituted by uncontaminated groundwater.