

ESS 312 Notes on Aqueous Geochemistry



- Why understanding mineral solubility is important ...

TABLE 8.7 Composition of average precipitation and soil moisture in soils on weathered sandy dolomite near State College, Pennsylvania

Species/ parameter	Average precipitation	Soil 1 m deep	Soil 3 m deep	Increase 1 m to 3 m	Net change relative to Cl ⁻ 1 m to 3 m
Ca ²⁺	1.2	3.3	108	33 times	2.9 times
Mg ²⁺	0.4	0.8	7.3	9 times	0.8 times
Na ⁺	0.5	6.9	21	3.0 times	0.3 times
K ⁺	1.0	1.8	5	2.7 times	0.2 times
HCO ₃ ⁻	0.0	1.9	144	76 times	6.6 times
SO ₄ ²⁻	3.6	2.9	17	5.9 times	0.5 times
NO ₃ ⁻	1.4	24	53	2.2 times	0.2 times
Cl ⁻	1.0	4.8	55	11.5 times	—
SiO ₂ (aq)	0.0	45	95	2.1 times	0.2 times
TDS (sum)	9.1	70	500	5.6 times	0.5 times
pH	4.5	5.9	6.5	(H 0.74 times lower)	0.02 times
P _{CO₂} (bar)	0.00032	0.003	0.04	13 times	1.2 times

Note: The sample from 1 m deep was collected May 1, 1974, the sample from 3 m deep on October 12, 1974. Concentrations are in mg/L unless otherwise noted.

Source: Data from Sears (1976).

- Mineral dissolution changes the composition of rainwater passing through soils

TABLE 8.8 Median values of pH and TDS and of major (>1 mg/L) constituents in surface waters and groundwaters

Major Constituents		
Constituent or parameter	Surface-water (mg/L)	Groundwater (mg/L)
HCO ₃ ⁻	58	200
Ca ²⁺	15	50
Cl ⁻	7.8	20
K ⁺	2.3	3
Mg ²⁺	4.1	7
Na ⁺	6.3	30
SO ₄ ²⁻	3.7	30
SiO ₂ (aq)	14	16
pH	—	7.4
TDS	120	350

- Dissolved ion concentrations are typically higher in groundwater than surface waters

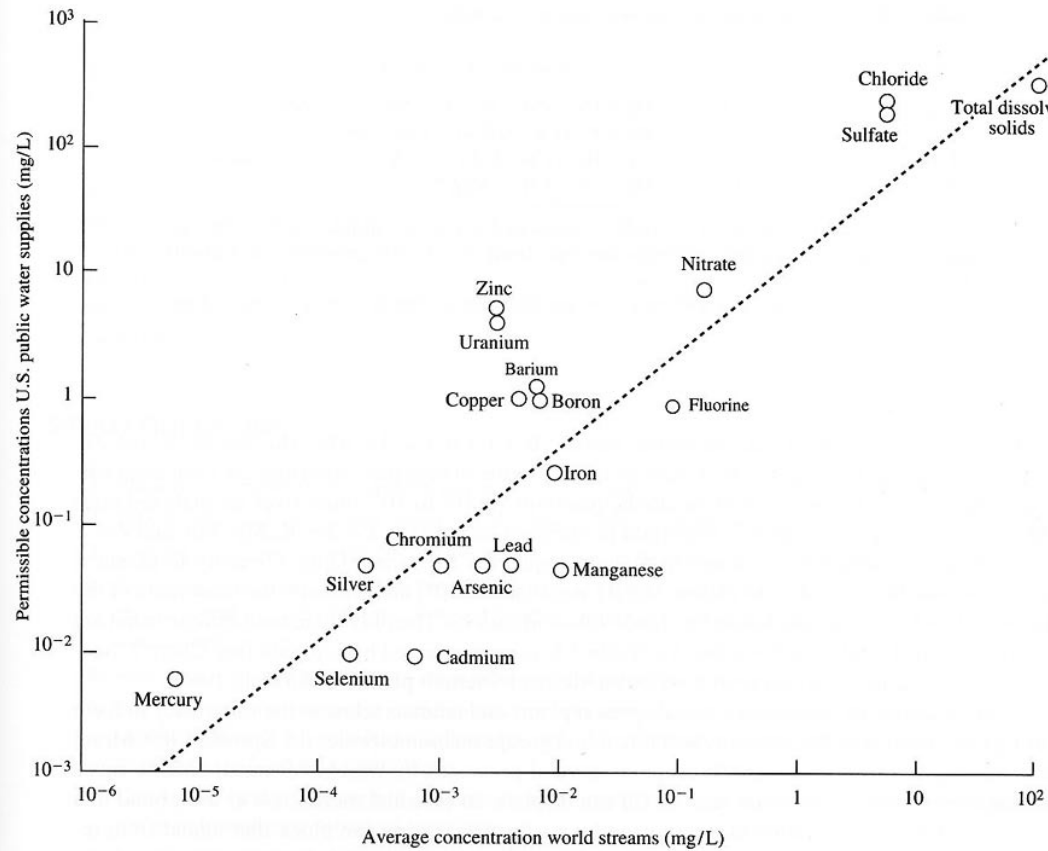


Figure 3.15 Correlation between trace-element concentrations in streams and permissible concentrations in water supplies. From R. M. Garrels et al. 1975. *Chemical cycles and the global environment*.

- Some elements regarded as toxic are essential nutrients at natural levels

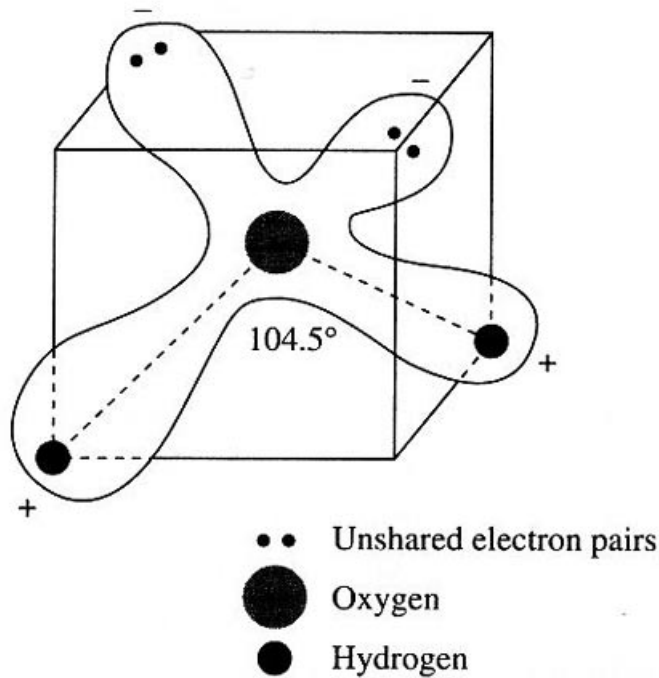


Figure 3.1 Electron cloud of the water molecule showing hydrogen and oxygen nuclei and unshared electrons. The “side of the jack” with hydrogens is positive and the other “side” is negative, giving rise to the dipolar character of water. The H-O-H bond angle is 104.5° . From E. K. Berner and R. A. Berner. *The global water cycle, geochemistry and environment*. Copyright © 1987. Used by permission of Prentice Hall, Inc., Upper Saddle River, NJ.

- Asymmetrical charge distribution around the water molecule enhances dissolution and complexation

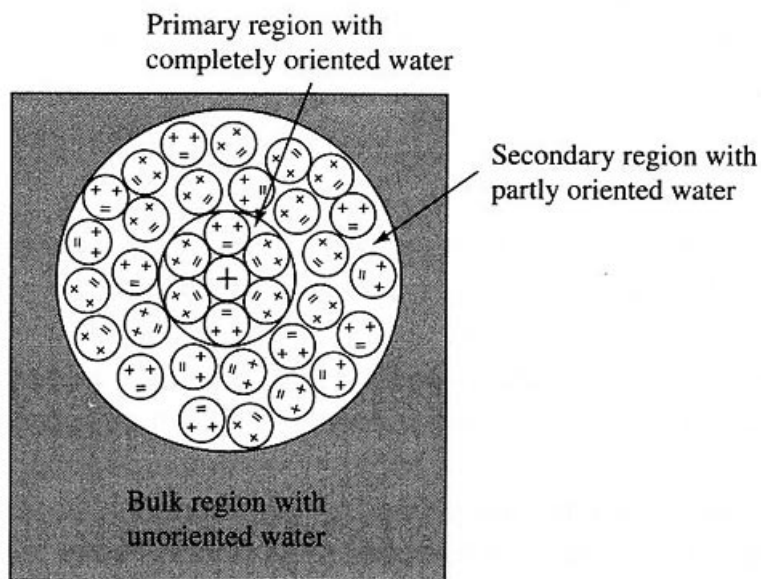


Figure 3.2 A cation aquo complex, showing the primary region with oriented water molecules in contact with the cation, typically in six- or fourfold coordination. The plot is schematic in that the water molecules in the primary region actually occur in a spherical envelope surrounding the cation. A secondary spherical envelope of partially oriented water molecules lies farther away from the cation. Water molecules in the bulk solution beyond this secondary region are unoriented. From J. O. Bockris and A. K. N. Reddy, 1973, *Modern electrochemistry*, vol. 1. © 1973, Plenum Pub. Corp. Used by permission.

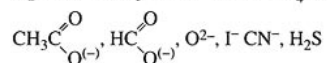
- The simplest complexes are cations associated with oriented water molecules

3.1.2 General Observations on Complexation

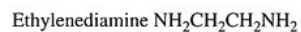
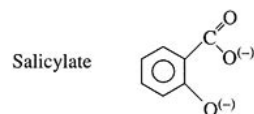
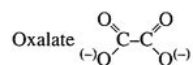
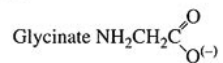
- The stability of complexes usually increases with increasing charge and/or decreasing radius of cations for a given ligand, or of ligands for a given cation. Ion pairs or outer-sphere complexes are weak and electrostatically bonded. Inner-sphere complexes involve important covalent bonding between the cation and ligand, and are generally stronger (have larger K_{assoc} values) than outer-sphere complexes.
 - Cations and ligands that form strong complexes also tend to form minerals with low solubilities (low K_{sp} values).
 - Complexing tends to increase the solubility of minerals that contain the species being complexed. Complexing of a species may also enhance or inhibit its adsorption and will usually affect its toxicity and bioavailability.
 - The more saline a water, the more ions in it (especially multivalent ions) exist as complexes.
 - The more saline a water, the more soluble minerals tend to be in it, both because of complex formation and activity-coefficient effects (see Chap. 4).
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- Rules for complex formation and its effect on mineral solubility, from Langmuir's text (Aqueous Environmental Geochemistry; Prentice Hall)

TABLE 3.2 Some important ligands and the nature of their bonding in complexes

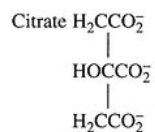
Monodentate



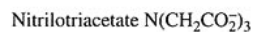
Bidentate



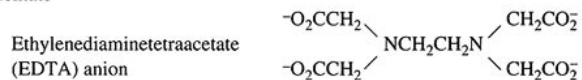
Tridentate



Tetradentate



Hexadentate



Note: Inorganic ligands are chiefly monodentate, whereas organic ligands are most often multidentate in complexes.

Source: Modified after Pagenkopf (1978) and Phillips and Williams (1965).

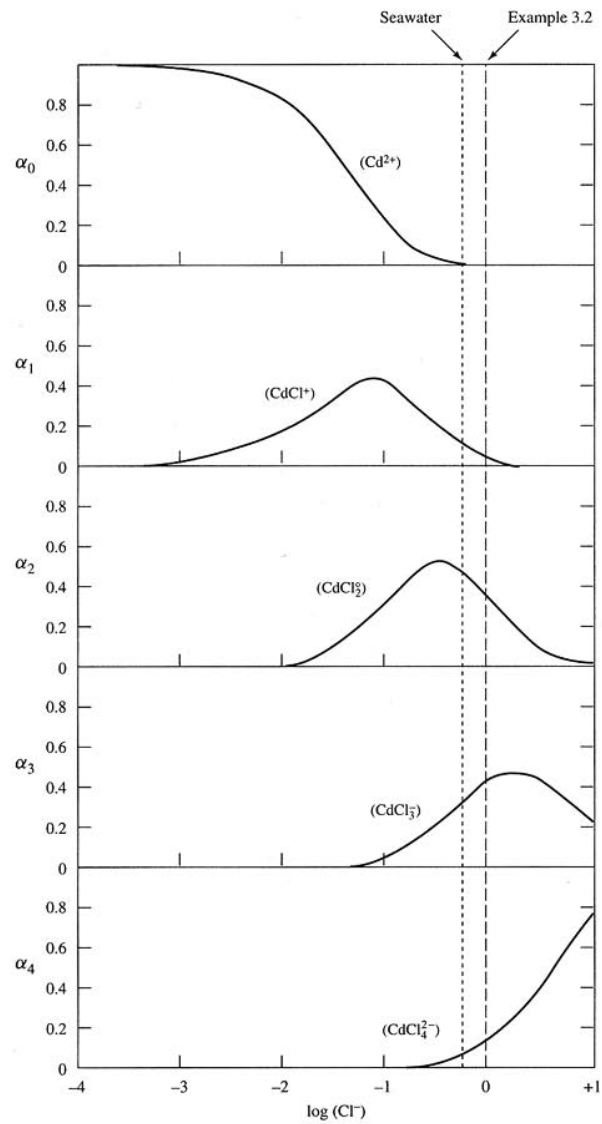


Figure 3.3 Fraction of Cd present as the free ion and as chloride complexes as a function of chloride ion concentration (M) for a total Cd concentration of 0.010 M at 25°C. Also shown are the distribution of species as computed in Example 3.2, and in seawater. Modified after J. N. Butler, 1964. *Ionic equilibrium, a mathematical approach*. Used by permission.

Table 6.5. Major Inorganic Species in Natural Waters

Condition	Element	Major Species	Fresh Water [M ⁿ⁺]/M _T	Seawater [M ⁿ⁺]/M _T
Hydrolyzed, anionic	B(III)	H ₃ BO ₃ , B(OH) ₄ ⁻		
	V(V)	HVO ₄ ²⁻ , H ₂ VO ₄ ⁻		
	Cr(VI)	CrO ₄ ²⁻		
	As(V)	HAsO ₄ ²⁻		
	Se(VI)	SeO ₄ ²⁻		
	Mo(VI)	MoO ₄ ²⁻		
	Si(IV)	Si(OH) ₄		
Predominantly free aquo ions	Li	Li ⁺	1.00	1.0 ^a
	Na	Na ⁺	1.00	0.98 ^a
	Mg	Mg ²⁺ (Mg ²⁺ , Mg SO ₄)	0.94	0.90 ^a
	K	K ⁺	1.00	0.98 ^a
	Ca	Ca ²⁺ (Ca ²⁺ , CaSO ₄)	0.94	0.89 ^a
	Sr	Sr ²⁺	0.94	0.71
	Cs	Cs ⁺	1.00	0.93
	Ba	Ba ²⁺	0.95	0.86

	Be(II)	BeOH ⁺ , Be(OH) ₂ ⁰	1.5 × 10 ⁻³	1.8 × 10 ⁻³
	Al(III)	Al(OH) ₃ (s), Al(OH) ₂ ⁺ , Al(OH) ₄ ⁻	1 × 10 ⁻⁹	6 × 10 ⁻¹⁰
	Ti(IV)	TiO ₂ (s), Ti(OH) ₄ ⁰		
	Mn(IV)	MnO ₂ (s)		
	Fe(III)	Fe(OH) ₃ (s), Fe(OH) ₂ ⁺ , Fe(OH) ₄ ⁻	2 × 10 ⁻¹¹	1 × 10 ⁻¹²
	Co(II)	Co ²⁺ , CoCO ₃ ⁰	0.5	0.58
	Ni(II)	Ni ²⁺ , NiCO ₃ ⁰ (Ni ²⁺ , NiCl)	0.4	0.47
Complexation with OH ⁻ , CO ₃ ²⁻ , HCO ₃ ⁻ , Cl ⁻	Cu(II)	CuCO ₃ ⁰ , Cu(OH) ₂ ⁰	0.01	9.3 × 10 ⁻²
	Zn(II)	Zn ²⁺ , ZnCO ₃ ⁰ (Zn ²⁺ , ZnCl)	0.4	0.45
	Ag(I)	Ag ⁺ , AgCl ⁰ (AgCl ₂ ⁻ , AgCl)	0.6	5.5 × 10 ⁻⁶
	Cd(II)	Cd ²⁺ , CdCO ₃ ⁰ (CdCl ₂)	0.5	2.7 × 10 ⁻²
	La(III) ^b	LaCO ₃ ⁺ , La(CO ₃) ₂ ⁻	8 × 10 ⁻³	0.38
	Hg(II)	Hg(OH) ₂ ⁰ (HgCl ₄ ²⁻)	1 × 10 ⁻¹⁰	6 × 10 ⁻¹⁵
	Tl(I), (III)	Tl ⁺ , Tl(OH) ₃ , Tl(OH) ₄ ⁻	2 × 10 ^{-21c}	3 × 10 ^{-21c}
	Pb(II)	PbCO ₃ ⁰ (PbCl ⁺ , PbCO ₃)	5 × 10 ⁻²	3 × 10 ⁻²
	Bi(III)	Bi(OH) ₃ ⁰	7 × 10 ⁻¹⁶	1.6 × 10 ⁻¹⁵
	Th(IV)	Th(OH) ₄ ⁰		2 × 10 ⁻¹⁶
	U(VI)	UO ₂ (CO ₃) ₂ ²⁻ , UO ₂ (CO ₃) ₃ ⁴⁻	1 × 10 ^{-7d}	1 × 10 ^{-7d}

^aSee Tableau 6.6.

^bLa(III) is representative of the lanthanides.

^cRedox state of Tl(I) under natural conditions is uncertain; ratio is for Tl(III).

^dAs UO₂²⁺.

Note: Freshwater data from Sigg and Xue (1994); most seawater data from Turner et al. (1981). Where major species in seawater deviate from those in fresh waters, the major seawater species are given in parentheses. Fresh water conditions are:

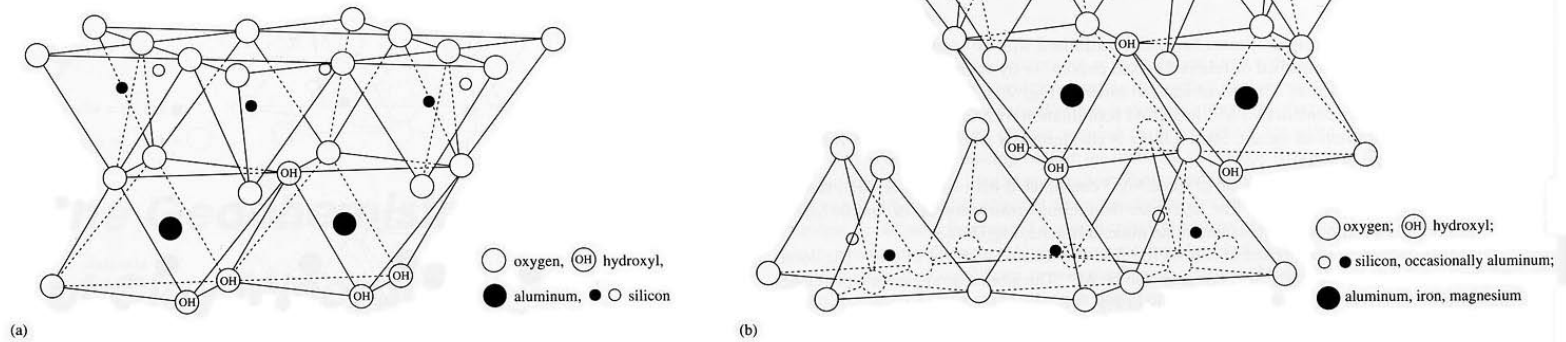
pH = 8
 [SO₄]_T = 3 × 10⁻⁴ M
 [Ca²⁺]_T = 10⁻³ M
 [Na⁺]_T = 2.5 × 10⁻⁴ M
 O₂ at saturation with air, I = 5 × 10⁻³ M

Alk = 2 × 10⁻³ M
 [Cl⁻] = 2.5 × 10⁻⁴ M
 [Mg²⁺]_T = 0.3 × 10⁻³ M

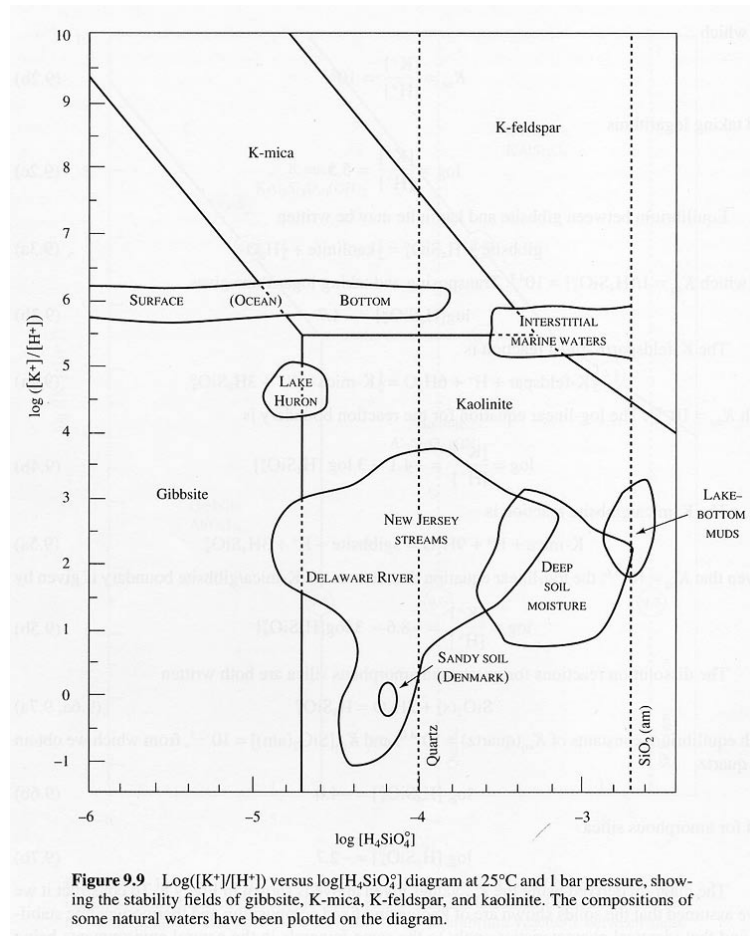
For seawater conditions see Tableau 6.7.

- Important complexes for elements in natural waters, and their approximate concentrations

Figure 9.2 (a) A T:O or two-layer structure, which is composed of a tetrahedral and an octahedral layer bonded through shared oxygen and hydroxyl groups. A T:O structure is common to the kaolinite and serpentine mineral groups. (b) A T:O:T or three-layer structure. A T:O:T structure is found in the micas, and in the smectite, vermiculite, and chlorite group minerals. From *Clay mineralogy* by R. E. Grim. Copyright © 1968 by McGraw-Hill, Inc. Used with permission of The McGraw-Hill Book Companies.



- Al, Mg and Fe^{2+} substitute into the octahedral layers of clay minerals. Al can substitute for Si in the tetrahedral layers, as long as charge is balanced by interlayer cations such as K^+



- Natural waters plotted on the K^+/H^+ vs SiO_2 diagram. Note many are saturated with respect to quartz, but almost none wrt amorphous silica

TABLE A1.2 (continued)

III Carbonate Species					
Reaction	ΔH_r° (kcal/mol)	log K	Reaction	ΔH_r° (kcal/mol)	log K
$\text{CO}_2(\text{g}) = \text{CO}_2(\text{aq})$	-4.776	-1.468	$\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3^\circ$	3.545	3.224
$\text{CO}_2(\text{aq}) + \text{H}_2\text{O} = \text{H}^+ + \text{HCO}_3^-$	2.177	-6.352	$\text{Mg}^{2+} + \text{CO}_3^{2-} = \text{MgCO}_3^\circ$	2.713	2.98
$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$	3.561	-10.329	$\text{Sr}^{2+} + \text{CO}_3^{2-} = \text{SrCO}_3^\circ$	5.22	2.81
$\text{Ca}^{2+} + \text{HCO}_3^- = \text{CaHCO}_3^+$	2.69	1.106	$\text{Ba}^{2+} + \text{CO}_3^{2-} = \text{BaCO}_3^\circ$	3.55	2.71
$\text{Mg}^{2+} + \text{HCO}_3^- = \text{MgHCO}_3^+$	0.79	1.07	$\text{Mn}^{2+} + \text{CO}_3^{2-} = \text{MnCO}_3^\circ$	—	4.90
$\text{Sr}^{2+} + \text{HCO}_3^- = \text{SrHCO}_3^+$	6.05	1.18	$\text{Fe}^{2+} + \text{CO}_3^{2-} = \text{FeCO}_3^\circ$	—	4.38
$\text{Ba}^{2+} + \text{HCO}_3^- = \text{BaHCO}_3^+$	5.56	0.982	$\text{Na}^+ + \text{CO}_3^{2-} = \text{NaCO}_3^-$	8.91	1.27
$\text{Mn}^{2+} + \text{HCO}_3^- = \text{MnHCO}_3^+$	—	1.95	$\text{Na}^+ + \text{HCO}_3^- = \text{NaHCO}_3$	—	-0.25
$\text{Fe}^{2+} + \text{HCO}_3^- = \text{FeHCO}_3^+$	—	2.0	$\text{Ra}^{2+} + \text{CO}_3^{2-} = \text{RaCO}_3^\circ$	1.07	2.5

Mineral	Reaction	ΔH_r° (kcal/mol)	log K
Calcite	$\text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{2-}$	-2.297	-8.480
Aragonite	$\text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{2-}$	-2.589	-8.336
Dolomite (ordered)	$\text{CaMg}(\text{CO}_3)_2 = \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-}$	-9.436	-17.09
Dolomite (disordered)	$\text{CaMg}(\text{CO}_3)_2 = \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-}$	-11.09	-16.54
Strontianite	$\text{SrCO}_3 = \text{Sr}^{2+} + \text{CO}_3^{2-}$	-0.40	-9.271
Siderite (crystalline)	$\text{FeCO}_3 = \text{Fe}^{2+} + \text{CO}_3^{2-}$	-2.48	-10.89
Siderite (precipitated)	$\text{FeCO}_3 = \text{Fe}^{2+} + \text{CO}_3^{2-}$	—	-10.45
Witherite	$\text{BaCO}_3 = \text{Ba}^{2+} + \text{CO}_3^{2-}$	0.703	-8.562
Rhodocrosite (crystalline)	$\text{MnCO}_3 = \text{Mn}^{2+} + \text{CO}_3^{2-}$	-1.43	-11.13
Rhodocrosite (synthetic)	$\text{MnCO}_3 = \text{Mn}^{2+} + \text{CO}_3^{2-}$	—	-10.39

- Useful constants

TABLE A1.2 (continued)

V Sulfate Species					
Reaction	ΔH_r° (kcal/mol)	log K	Reaction	ΔH_r° (kcal/mol)	log K
$H^+ + SO_4^{2-} = HSO_4^-$	3.85	1.988	$Mn^{2+} + SO_4^{2-} = MnSO_4^0$	3.37	2.25
$Li^+ + SO_4^{2-} = LiSO_4^-$	—	0.64	$Fe^{2+} + SO_4^{2-} = FeSO_4^0$	3.23	2.25
$Na^+ + SO_4^{2-} = NaSO_4^-$	1.12	0.70	$Fe^{2+} + HSO_4^- = FeHSO_4^+$	—	1.08
$K^+ + SO_4^{2-} = KSO_4^-$	2.25	0.85	$Fe^{3+} + SO_4^{2-} = FeSO_4^+$	3.91	4.04
$Ca^{2+} + SO_4^{2-} = CaSO_4^0$	1.65	2.30	$Fe^{3+} + 2SO_4^{2-} = Fe(SO_4)_2^-$	4.60	5.38
$Mg^{2+} + SO_4^{2-} = MgSO_4^0$	4.55	2.37	$Fe^{3+} + HSO_4^- = FeHSO_4^{2+}$	—	2.48
$Sr^{2+} + SO_4^{2-} = SrSO_4^0$	2.08	2.29	$Al^{3+} + SO_4^{2-} = AlSO_4^+$	2.15	3.02
$Ba^{2+} + SO_4^{2-} = BaSO_4^0$	—	2.7	$Al^{3+} + 2SO_4^{2-} = Al(SO_4)_2^-$	2.84	4.92
$Ra^{2+} + SO_4^{2-} = RaSO_4^0$	1.3	2.75	$Al^{3+} + HSO_4^- = AlHSO_4^{2+}$	—	0.46

Mineral	Reaction	ΔH_r° (kcal/mol)	log K
Gypsum	$CaSO_4 \cdot 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$	-0.109	-4.58
Anhydrite	$CaSO_4 = Ca^{2+} + SO_4^{2-}$	-1.71	-4.36
Celestite	$SrSO_4 = Sr^{2+} + SO_4^{2-}$	-1.037	-6.63
Barite	$BaSO_4 = Ba^{2+} + SO_4^{2-}$	6.35	-9.97
Radium sulfate	$RaSO_4 = Ra^{2+} + SO_4^{2-}$	9.40	-10.26
Melanterite	$FeSO_4 \cdot 7H_2O = Fe^{2+} + SO_4^{2-} + 7H_2O$	4.91	-2.209
Alunite	$KAl_3(SO_4)_2(OH)_6 + 6H^+ = K^+ + 3Al^{3+} + 2SO_4^{2-} + 6H_2O$	-50.25	-1.4

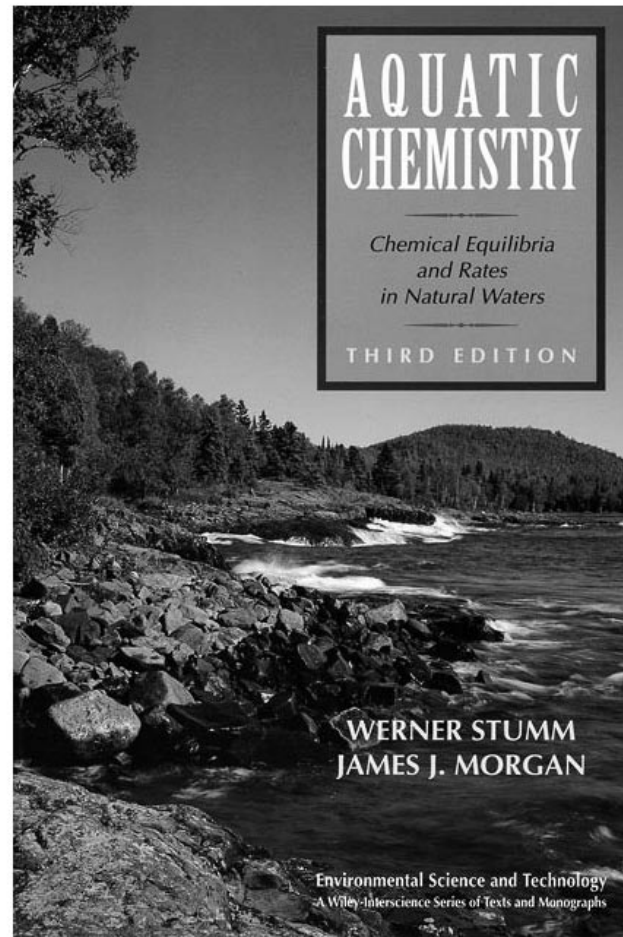
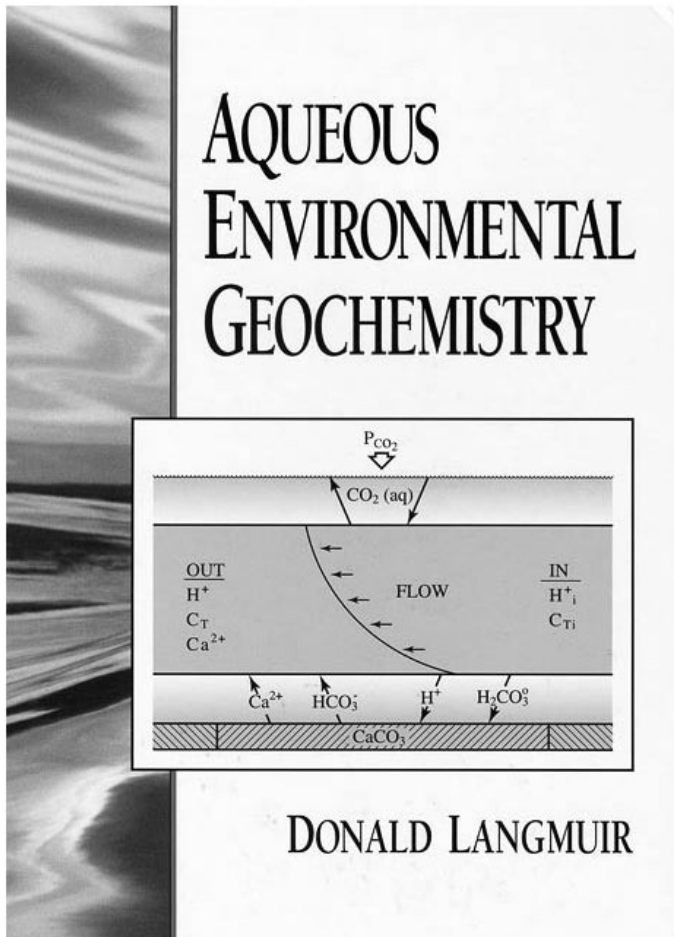
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- Useful constants

TABLE A1.2 (continued)

II Oxide and Hydroxide Species					
Reaction	ΔH_r° (kcal/mol)	log K	Reaction	ΔH_r° (kcal/mol)	log K
$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$	13.362	-14.000	$\text{Fe}^{3+} + \text{H}_2\text{O} = \text{FeOH}^{2+} + \text{H}^+$	10.4	-2.19
$\text{Li}^+ + \text{H}_2\text{O} = \text{LiOH}^\circ + \text{H}^+$	0.0	-13.64	$\text{Fe}^{3+} + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_2^+ + 2\text{H}^+$	17.1	-5.67
$\text{Na}^+ + \text{H}_2\text{O} = \text{NaOH}^\circ + \text{H}^+$	0.0	-14.18	$\text{Fe}^{3+} + 3\text{H}_2\text{O} = \text{Fe}(\text{OH})_3^\circ + 3\text{H}^+$	24.8	-12.56
$\text{K}^+ + \text{H}_2\text{O} = \text{KOH}^\circ + \text{H}^+$	—	-14.46	$\text{Fe}^{3+} + 4\text{H}_2\text{O} = \text{Fe}(\text{OH})_4^- + 4\text{H}^+$	31.9	-21.6
$\text{Ca}^{2+} + \text{H}_2\text{O} = \text{CaOH}^+ + \text{H}^+$	—	-12.78	$2\text{Fe}^{3+} + 2\text{H}_2\text{O} = \text{Fe}_2(\text{OH})_2^{4+} + 2\text{H}^+$	13.5	-2.95
$\text{Mg}^{2+} + \text{H}_2\text{O} = \text{MgOH}^+ + \text{H}^+$	—	-11.44	$3\text{Fe}^{3+} + 4\text{H}_2\text{O} = \text{Fe}_3(\text{OH})_4^{5+} + 4\text{H}^+$	14.3	-6.3
$\text{Sr}^{2+} + \text{H}_2\text{O} = \text{SrOH}^+ + \text{H}^+$	—	-13.29	$\text{Al}^{3+} + \text{H}_2\text{O} = \text{AlOH}^{2+} + \text{H}^+$	11.49	-5.00
$\text{Ba}^{2+} + \text{H}_2\text{O} = \text{BaOH}^+ + \text{H}^+$	—	-13.47	$\text{Al}^{3+} + 2\text{H}_2\text{O} = \text{Al}(\text{OH})_2^+ + 2\text{H}^+$	26.90	-10.1
$\text{Ra}^{2+} + \text{H}_2\text{O} = \text{RaOH}^+ + \text{H}^+$	—	-13.49	$\text{Al}^{3+} + 3\text{H}_2\text{O} = \text{Al}(\text{OH})_3^\circ + 3\text{H}^+$	39.89	-16.9
$\text{Fe}^{2+} + \text{H}_2\text{O} = \text{FeOH}^+ + \text{H}^+$	13.2	-9.5	$\text{Al}^{3+} + 4\text{H}_2\text{O} = \text{Al}(\text{OH})_4^- + 4\text{H}^+$	42.30	-22.7
$\text{Mn}^{2+} + \text{H}_2\text{O} = \text{MnOH}^+ + \text{H}^+$	14.4	-10.59			

- Useful constants



- Two good books if you're looking for more information