Fundamentals of aquatic chemistry

Figure 2 – Relation between Pb rates applied to the soil and Pb concentrations in jack bean shoots, without and with EDTA treatment. NS nonsignificant; *significant at p < 0.05; **significant at p < 0.001.
Major aquatic chemical processes

Interaction among metals and ligands
Metal ions in aquatic systems

The properties of metal-containing species dissolved in water depend on both the metal ion (type, nature, oxidation state) and the availability of the surrounding potential ligands (affinity, coordination type).

Transport, solubilities, (bio)availability, biological effects depend all on:

**SPECIATION** of metal ions is crucial for their environmental chemistry in natural and waste waters:

- in principle, metals should be present as aquo complexes;
- sometimes they may be also dissolved as organometallic derivatives (*i.e.* metal-carbon bond(s) are present);
- once in water they can undergo several complexation reactions depending on the type of ligands available as well as the pH of the environment.
Speciation

Distribution of an element amongst defined chemical species in a system.

(http://goldbook.iupac.org/ST06861.html)

![Citric acid (AH₃) speciation](pubs.rsc.org)
A coordination compound, or metal complex is the product of a Acid-Base Lewis reaction (coordination sphere, coordination numbers (2,4,6)):

\[ [M^{n+}L_m]^{n+} \]

- **M**\(^{n+}\): metal ion
- **L**: ligand
- **m**: number of ligands
- **n**: charge of the complex

**Diagram:**
- Arrows indicate the movement of electrons:
  - **e\(^-\)** acceptor
  - **e\(^-\)** donor

**Equation:**

\[ M^{n+} + mL \rightleftharpoons [ML_m]^{n+} \]
Basics of Coordination Chemistry

Complex = coordination compound

A molecular entity formed by loose association involving two or more component molecular entities (ionic or uncharged), or the corresponding chemical species. The bonding between the components is normally weaker than in a covalent bond. The term has also been used with a variety of shades of meaning in different contexts: it is therefore best avoided when a more explicit alternative is applicable. In inorganic chemistry the term 'coordination entity' is recommended instead of 'complex'.

http://goldbook.iupac.org/C01203.html
Basics of Coordination Chemistry
Coordination/complexation: effects on water chemistry

Complexation may have a number of effects:

- once coordinated to the metal center, ligands change their properties and may undergo subsequent reactions (e.g. redox, decarboxylation, hydrolysis, biodegradation);
- the complex may become soluble (compared to the starting metal-containing species) and, thus, dissolve in water;
- the complex may become insoluble (compared to the starting metal-containing species) and, thus, deposit as a residue;
- complexation strongly influences metals’ absorption, distribution, transport and fate (and, consequently, bioavailability, toxicity, uptake by living organisms).
Environmental toxicology: chemical aspects

Aquatic chemistry (2)

Relevant metal complexes: hemoglobin/Fe

http://www.chemistry.wustl.edu/~edudev/LabTutorials/Hemoglobin/MetalComplexinBlood.html
Relevant metal complexes: chlorophyll

Figure 1. Chemical Structures of Natural Chlorophylls

Chlorophyll a

Chlorophyll b

lpi.oregonstate.edu
Environmental toxicology: chemical aspects
Aquatic chemistry (2)

Monodentate ligands

- Monodentate ligands:
  - \( \text{H} - \text{O} - \text{H} \) (monohydric alcohol)
  - \( \text{C} = \text{O} \) (carbonyl)
  - \( \text{N} - \text{H} \) (ammonia)
  - \( \text{Cl} - \text{H} \) (chlorine)
  - \( \text{C} = \text{N} \) (formamide)
  - \( \text{O} - \text{H} \) (monohydric alcohol)

Environmental Toxicology, Master Sc. in Industrial Biotechnology
Silvia Gross
Bidentate ligands

Oxalate (ox)

\[ \text{Oxalate (ox)} \]

\[ [\text{Cr(ox)}_3]^{3-} \]
Environmental toxicology: chemical aspects
Aquatic chemistry (2)

Bidentate ligands

phenantroline (phen)

etilendiamine (en)
Environmental toxicology: chemical aspects

Aquatic chemistry (2)

**Bidentate ligands**

- acetilacetonate (acac)

- bipyridil (bipy)

---

*Environmental Toxicology, Master Sc. in Industrial Biotechnology*

Silvia Gross
Tetradentate ligands
Tetradsentate ligands
Hexadentate ligands (a very important one)

Etylendiamintetraacetate (EDTA$^{4-}$)
### Ligand nomenclature

<table>
<thead>
<tr>
<th>formula</th>
<th>name</th>
<th>ligand name</th>
<th>formula</th>
<th>name</th>
<th>ligand name</th>
</tr>
</thead>
<tbody>
<tr>
<td>:NH₃</td>
<td>ammonia</td>
<td>ammine</td>
<td>Cl⁻</td>
<td>chloride</td>
<td>chloro</td>
</tr>
<tr>
<td>H₂O</td>
<td>water</td>
<td>aqua</td>
<td>F⁻</td>
<td>fluoride</td>
<td>fluoro</td>
</tr>
<tr>
<td>:C=O:</td>
<td>carbon monoxide</td>
<td>carbonyl</td>
<td>:C=N⁻</td>
<td>cyanide</td>
<td>cyano</td>
</tr>
<tr>
<td>:PH₃</td>
<td>phosphine</td>
<td>phosphine</td>
<td>OH⁻</td>
<td>hydroxide</td>
<td>hydroxo</td>
</tr>
<tr>
<td>:N≡O</td>
<td>nitric oxide</td>
<td>nitrosyl</td>
<td>:NO₂⁻</td>
<td>nitrite</td>
<td>nitro (NO₂⁻)</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>nitrate</td>
<td>nitrato</td>
<td>:NO₂⁻</td>
<td>nitrite</td>
<td>nitrito (ONO⁻)</td>
</tr>
<tr>
<td>NH₂⁻</td>
<td>amide</td>
<td>amido</td>
<td>*SO₄⁻²</td>
<td>sulfate</td>
<td>sulfato</td>
</tr>
<tr>
<td>*C₂O₄⁻²</td>
<td>oxalate</td>
<td>oxalato</td>
<td>SCN⁻</td>
<td>thiocyanate</td>
<td>thiocyanato</td>
</tr>
<tr>
<td>*CO₃⁻²</td>
<td>carbonate</td>
<td>carbonato</td>
<td>*S₂O₃⁻²</td>
<td>thiosulfate</td>
<td>thiosulfato</td>
</tr>
<tr>
<td>*O⁻²</td>
<td>oxide</td>
<td>oxo</td>
<td>C₃H₅N⁺</td>
<td>pyridine</td>
<td>pyridine</td>
</tr>
</tbody>
</table>
Complex formation

- Multistep process, more than one formation constant
- Speciation of metal depends also on complexation (e.g., Fe(CN)$_n^{m-}$)

\[
\begin{align*}
M^+ + L &\rightarrow ML & K_1 \\
ML^+ + L &\rightarrow ML_2 & K_2 \\
ML_2^+ + L &\rightarrow ML_3 & K_3 \\
ML_{n-1}^+ + L &\rightarrow ML_n & K_n
\end{align*}
\]
### Chelating ligands

<table>
<thead>
<tr>
<th>Chelating agent</th>
<th>Full chemical name</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASDA</td>
<td>Aspartic acid-N,N-diacetic acid</td>
<td></td>
</tr>
<tr>
<td>CDTA</td>
<td>1,2-diaminocyclohexane-N,N,N',N'-tetra-acetic acid</td>
<td>1.81</td>
</tr>
<tr>
<td>DTPA</td>
<td>Diethylenetriamine-N,N,N',N'-pentaa-acetic acid</td>
<td>2.08</td>
</tr>
<tr>
<td>EDDHA</td>
<td>Ethylenediamine-N,N',diorthohydroxy-phenylacetic acid</td>
<td>1.46</td>
</tr>
<tr>
<td>EDDHMA</td>
<td>Ethylene diamine-N,N',diorthohydroxy-paramethylenylacetic acid</td>
<td>1.45</td>
</tr>
<tr>
<td>EDDS</td>
<td>Ethylenediamine-N, N'-disuccinic acid</td>
<td>1.91</td>
</tr>
<tr>
<td>GLDA</td>
<td>Glutamic acid-N,N-diacetic acid</td>
<td>2.01</td>
</tr>
<tr>
<td>HBED</td>
<td>N,N'-bis(2-hydroxybenzyl)-ethylenediamine-N,N'-diacetic acid</td>
<td>1.58</td>
</tr>
<tr>
<td>HEDTA</td>
<td>N-Hydroxyethylendiamine, N,N',N'-triacetic acid</td>
<td>2.16</td>
</tr>
<tr>
<td>IDS</td>
<td>Imino-N,N-disuccinic acid</td>
<td>1.91</td>
</tr>
<tr>
<td>MGDA</td>
<td>Methylglycine-N,N-diacetic acid</td>
<td>1.90</td>
</tr>
<tr>
<td>PDTA 1,2</td>
<td>Propylene 1,2-diamine N,N,N',N'tetra-acetic acid</td>
<td>2.06</td>
</tr>
<tr>
<td>TTHA</td>
<td>Triethylenetetraamine-N,N,N',N'',N''',N''''-hexaacetic acid</td>
<td>2.03</td>
</tr>
</tbody>
</table>

Chelation describes a particular way by which ions and molecules bind metal ions.
Chelating ligands

Common potential water pollutants, but also used in water treatment (e.g. remediation of heavy metals)

Can bind most of the metal ions naturally occurring in waters (Mg$^{2+}$, Ca$^{2+}$, Mn$^{2+}$, Fe$^{2+}$, Fe$^{3+}$, Cu$^{2+}$, Zn$^{2+}$) as well as contaminants such as Co$^{2+}$, Ni$^{2+}$, Sr$^{2+}$, Cd$^{2+}$, Ba$^{2+}$ and Pb$^{2+}$.

In general, since a chelating agent may bind a metal ion in more than one coordination site simultaneously, chelating complexes are more stable than monodentate analogues.

Stability tends to increase with the number of chelating sites available from the same ligand.
Environmental toxicology: chemical aspects
Aquatic chemistry (2)

Ligand nomenclature
Synthetic chelating agents

- Synthetic chelating agents are common water pollutants (sewage effluents, industrial wastewater).
- Not only polluting themselves, but also a source of metal chelators.
- The most important synthetic chelating agents are **aminopolycarboxylates**, such as ethylenediaminotetraacetate (EDTA) and nitrilotriacetate (NTA).
- Complexation is very strong, giving rise to complexes so stable that it is almost impossible to find “free” (i.e. unbound) chelating agents in natural waters.
- Aminopolycarboxylates are responsible for solubilizing metal ions, thus allowing their transport in waters.
- Complexation may enhance leaching of heavy metals from plumbing or mine activities.
Hexadentate ligands (a very important one): NTA

Nitrilotriacetic acid
Environmental toxicology: chemical aspects
Aquatic chemistry (2)

NTA

\[ pK_1 = 1.10 \text{ (COOH)}, \quad pK_2 = 1.97 \text{ (COOH)}, \quad pK_3 = 2.43 \text{ (COOH)}, \quad pK_4 = 9.33 \text{ (NH}^+\text{)} \]
Hexadentate ligands (a very important one): EDTA

Etilendiaminatetraacetate (EDTA$^{4-}$)
Environmental toxicology: chemical aspects

Aquatic chemistry (2)

Hexadentate ligands (a very important one): EDTA

\[
\text{HO}_2\text{CCH}_2\quad +\quad \text{CH}_2\text{CO}_2\text{H}
\]

\[
\text{HNCH}_2\text{CH}_2\text{NH}\quad +\quad \text{CH}_2\text{CO}_2\text{H}
\]

\[
\text{HO}_2\text{CCH}_2\quad +\quad \text{CH}_2\text{CO}_2\text{H}
\]

\[
\text{H}_6\text{Y}^{2+}
\]

\[
pK_1 = 0.0 \quad (\text{CO}_2\text{H})
\]

\[
pK_2 = 1.5 \quad (\text{CO}_2\text{H})
\]

\[
pK_3 = 2.0 \quad (\text{CO}_2\text{H})
\]

\[
pK_4 = 2.66 \quad (\text{CO}_2\text{H})
\]

\[
pK_5 = 6.16 \quad (\text{NH}^+)
\]

\[
pK_6 = 10.24 \quad (\text{NH}^+)
\]
Hexadentate ligands (a very important one): EDTA
Environmental toxicology: chemical aspects

Aquatic chemistry (2)

Hexadentate ligands (a very important one): EDTA

<table>
<thead>
<tr>
<th>Ion</th>
<th>( \log K_f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>2.95</td>
</tr>
<tr>
<td>Na⁺</td>
<td>1.86</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.8</td>
</tr>
<tr>
<td>Be²⁺</td>
<td>9.7</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>8.79</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>10.65</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>8.72</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>7.88</td>
</tr>
<tr>
<td>Ra²⁺</td>
<td>7.4</td>
</tr>
<tr>
<td>Sc³⁺</td>
<td>23.1</td>
</tr>
<tr>
<td>Y³⁺</td>
<td>18.08</td>
</tr>
<tr>
<td>La³⁺</td>
<td>15.36</td>
</tr>
<tr>
<td>V⁵⁺</td>
<td>12.7</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>13.6</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>13.89</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>14.30</td>
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<tr>
<td>Co²⁺</td>
<td>16.45</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>18.4</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>18.78</td>
</tr>
<tr>
<td>Ti³⁺</td>
<td>21.3</td>
</tr>
</tbody>
</table>

Table 12-2 Formation constants for metal-EDTA complexes

Use to find \( K_f \)

**via Gross**
Environmental toxicology: chemical aspects
Aquatic chemistry (2)

Synthetic chelating agents and environmental relevance

- Sources: EDTA used to sequester metal ions in textile industry (prevents metal impurities from modifying colors of fabrics), in the pulp and paper industry, and in cosmetics. NTA used as water softening in detergents.

- A major concern about their presence into the aquatic ecosystem is the solubilization of heavy metals from solids.

- Their chelating capability is STRONGLY dependent on the pH of the environment as well as on the type of metal ions.

- EDTA is poorly biodegradable whereas NTA (and its cobalt, iron, zinc, aluminum, copper and nickel complexes) are somewhat degraded by Chlatobacter heintzii bacteria.

- EDTA was shown to increase migration of radioactive nuclides.
Environmental toxicology: chemical aspects

Aquatic chemistry (2)

Chelating agents: phosphates/phosphonates

Phosphorous:
Nutrient, key element for plants and animals
Essential for plant growth
Metabolism
  ADP to ATP, DNA & RNA
Fertilizers and Detergents
Biological productivity &
water quality

Too much = eutrophication
Chelating agents: phosphates/polyphosphates

Orthophosphoric acid

Pyrophosphoric acid

Trimetaphosphoric acid

Tripolyphosphoric acid

Phosphoric anhydride ($P_4O_{10}$)

Tetrapolyphosphoric acid

Linear structure of orthophosphate

Linear structure of polyphosphate

Very strong chelating agents,
Particularly the chain polyphosphates
Ring phosphates much less efficient (steric hindrance)
Chelating agents: phosphates/phosphonates

- Phosphorus occurs naturally in rocks
  - Weathering releases phosphate ions (PO$_4^{-3}$)

- Inorganic
  - Orthophosphates
  - Polyphosphates (Metaphosphates)

- Organic phosphate

Source of water pollution: see eutrophication
Environmental toxicology: chemical aspects
Aquatic chemistry (2)

Chelating agents: phosphorous cycle

The Phosphorus Cycle

- Animal manures and biosolids
- Plant residues
- Crop harvest
- Atmospheric deposition
- Mineral fertilizers
- Runoff and erosion
- Primary minerals (apatite)
- Mineral surfaces (clays, Fe and Al oxides, carbonates)
- Secondary compounds (CaP, FeP, MnP, AlP)
- Plant uptake
- Soil solution phosphorus: $\text{HPO}_4^{2-}$, $\text{H}_2\text{PO}_4^{-1}$
- Weathering
- Adsorption
- Dissolution
- Precipitation
- Leaching (usually minor)
- Immobilization
- Mineralization
Chelating agents: phosphorous from antroposphere

• Commercial synthetic fertilizers
  – Apatite mining
  – Aurora Phosphate Mine
• Polyphosphates are used in boilers
• Water softening, detergent builders, water treatment
• Heavy-duty synthetic detergents
  – Contain polyphosphates
  – 12-13% phosphorus
• Domestic wastewater
  – 2-3x inorganic P due to detergents
Chelating agents: environmental issues

- Waste Water Treatment (sequester Ca$^{2+}$ ions, prevent CaCO$_3$ precipitation)
  - Average person releases 1.5 g/day
  - Prior to the development of detergents:
    - Inorganic 2-3 mg/L
    - Organic 0.5 – 1 mg/L

- EPA (Environmental Protection Agency of U.S.):
  - Sewage effluent should not contain > 1 mg/L
  - Unpolluted waters usually < 0.1 mg/L
Chelating agents: phosphates/phosphonates

Orthophosphates

Readily available to the biological community
Typically found in low concentrations in unpolluted waters

\[
\begin{align*}
H_3PO_4 &\quad (pK_a = 2.17) \\
H_2PO_4^- &\quad (pK_a = 7.31) \\
HPO_4^{2-} &\quad (pK_a = 12.36) \\
PO_4^{3-} &
\end{align*}
\]

Polyphosphates

— Molecularly dehydrated forms of orthophosphates
— Used in detergents and treating boiler waters
— In water, they are transformed to orthophosphates and available for plant uptake
Environmental toxicology: chemical aspects
Aquatic chemistry (2)

Distribution diagram for 0.1 M orthophosphate solution
(pK$_1$ = 2.1; pK$_2$ = 7.2; pK$_3$ = 12.3)
Chelating agents: phosphates

Organic

Phosphate bound or tied up in plant tissue, waste solids, or other organic material
When decomposed through bacterial action, phosphate released and returned to environment
Chelating agents: phosphonates

- inhibition of scale and corrosion
- metal finishing
- cleaning and laundry agents
- paper and textile production
- environmental chemistry less known because difficulty to detect them analytically
- not very biodegradable

NTMP NitriloTris(MethylenePhosphonic) acid
Naturally-occurring chelating agents

Humic substances are degradation-resistant materials (abundant in natural waters and soil) formed upon decomposition of vegetation. Abundant in water and soil. *Most important class of naturally occurring complexing agents.*

Materials extracted with strong base and then acidified:

- **Humins**: the fraction of humic substances insoluble in water at any pH value.
  
  Not extractable plant.

- **Humic acids**: the fraction of humic substances that is not soluble in water under acidic conditions (pH < 2) but is soluble at higher pH values.

- **Fulvic acids**: the fraction of humic substances soluble in water at any pH condition.
Naturally-occurring chelating agents

Source: wikipedia.org
Naturally-occurring chelating agents

Fulvic acid

Model structure of fulvic acid

Source: Internet
Naturally-occurring chelating agents

Acid-base, sorptive, complexing action

The binding of metal ions is one of the most important functions of humic substances

- **Humins**: $10^4$ Da, polyelectrolytes, macromolecules
- **Humic acids**: $10^4$ Da, polyelectrolytes, macromolecules
- **Fulvic acids**: $10^2$ Da effects on soluble species

Range of compounds with common origin and properties

Fe, Al strong bound → iron solubilization and transport

Less Ni(II), Pb(II), Ca(II), Zn(II)

Mg(II) intermediate strength

![Chemical structures](image)
Naturally-occurring chelating agents

- They bind mainly to iron and aluminum, but also to nickel, lead, calcium and zinc (magnesium to a much lesser extent).
- The role of fulvic acids is still under investigation (keep the balance of naturally-occurring metal ions in natural waters?)
Humic substances and trihalomethanes (THM)

- THM carcinogenic substances
- Seem to be formed in the presence of humic substances during disinfection of water by chlorination
- Humic substances produce THM by reaction with chlorine
- Typically: C 45-55%, O 30-45%, H 3-6%, N 1-5%, S 0-1%

Chloroform, Bromodichloromethane, Chlorodibromomethane, Bromoform
Environmental toxicology: chemical aspects
Aquatic chemistry (2)

Humic substances and trihalomethanes (THM)

<table>
<thead>
<tr>
<th>Disinfectant</th>
<th>Significant organohalogen products</th>
<th>Significant inorganic products</th>
<th>Significant non-halogenated products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine/hypochlorous acid</td>
<td>THMs, HAAs, HANs, chloral hydrate, chloropicrin, chlorophenols, N-chloramines, halofuranones, bromohydrins</td>
<td>Chlorate (mostly from hypochlorite use)</td>
<td>Aldehydes, cyanoalkanoic acids, alkanoic acids, benzene, carboxylic acids</td>
</tr>
<tr>
<td>Chlorine dioxide</td>
<td></td>
<td>chlorite, chlorate</td>
<td>unknown</td>
</tr>
<tr>
<td>Chloramine</td>
<td>HANs, cyanogen chloride, organic chloramines, chloramino acids, chloral hydrate, haloketones</td>
<td>nitrate, nitrite, chlorate, hydrazine</td>
<td>aldehydes, ketones</td>
</tr>
<tr>
<td>Ozone</td>
<td>bromoform, MBA, DBA, DBAC, cyanogen bromide</td>
<td>chlorate, iodate, bromate, hydrogen peroxide, hypobromous acid, epoxides, ozonates</td>
<td>aldehydes, ketoacids, ketones, carboxylic acids</td>
</tr>
</tbody>
</table>
Humic substances and trihalomethanes (THM)

Chlorine reacts with humic substances (dissolved organic matter) present in most water supplies, forming a variety of halogenated disinfectant by-products (DBPs) such as THMs, HAAs, HANs, chloral hydrate and chloropicrin, as follows:

\[
\text{HOCl} + \text{Dissolved Organic Carbon} \rightarrow \text{DBPs}
\]

It is generally accepted that the reaction between chlorine and humic substances, a major component of natural organic matter (NOM), is responsible for the production of organochlorine compounds during drinking-water treatment.

Humic and fulvic acids show a high reactivity towards chlorine and constitute 50–90% of the total DOC in river and lake waters.
Bioremediation approach by using humic acid

In situ anaerobic bioremediation of chlorinated solvents such as perchloroethene (PCE) frequently faces the problem of accumulating toxic, lower chlorinated compounds such as dichloroethene (cis-DCE) and vinyl chloride (VC). In the present study, the efficacy of the sequential application of electron donors, supporting reductive dechlorination, and of humic acids, acting as extracellular electron shuttles facilitating the anaerobic oxidation of recalcitrant intermediates, was explored in microcosm studies.

Sequential application of electron donors and humic acids for the anaerobic bioremediation of chlorinated aliphatic hydrocarbons

Environmental toxicology: chemical aspects
Aquatic chemistry (2)

Major aquatic chemical processes
Environmental toxicology: chemical aspects

Aquatic chemistry (2)

Unnautilus fossile, animale marino che forma la sua con-
Solubility of solids and of gases

**Solubilities of gases in water**: Henry law and Clausius-Clapeyron equation (solubility as a function of T)

\[ X(g) \rightarrow X(aq) \]

**Solubilities of solids in water**: solubility product \((K_{ps})\)

\[ X(s) \rightarrow X(aq) \]
Environmental toxicology: chemical aspects

Aquatic chemistry (2)

Solubility product

\[ \text{CaSO}_4(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{SO}_4^{2-}(aq) \]

\[ K_{ps} = [\text{Ca}^{2+}] \times [\text{SO}_4^{2-}] \]

Solubility (s)

\[ K_{ps} = [\text{Ca}^{2+}] \times [\text{SO}_4^{2-}] = s \times s \]

In general:

\[ A_xB_y(s) \rightleftharpoons xA^{y+}(aq) + yB^{x-}(aq) \]

\[ K_{ps} = [A^{y+}]^x \times [B^{x-}]^y \]

\[ [A^{y+}] = x \times s \]

\[ [B^{x-}] = y \times s \]

\[ K_{ps} = (x \times s)^x \times (y \times s)^y \]
## Solubilities of Ionic Compounds in Water

<table>
<thead>
<tr>
<th>Anion</th>
<th>Soluble†</th>
<th>Slightly Soluble</th>
<th>Insoluble</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₃⁻ (nitrate)</td>
<td>All</td>
<td>—</td>
<td>Be(CH₃COO)₂</td>
</tr>
<tr>
<td>CH₃COO⁻ (acetate)</td>
<td>Most</td>
<td>—</td>
<td>MgF₂, CaF₂</td>
</tr>
<tr>
<td>ClO₃⁻ (chlorate)</td>
<td>All</td>
<td>—</td>
<td>AgCl, Hg₂Cl₂</td>
</tr>
<tr>
<td>ClO₄⁻ (perchlorate)</td>
<td>Most</td>
<td>KClO₄</td>
<td>AgBr, Hg₂Br₂</td>
</tr>
<tr>
<td>F⁻ (fluoride)</td>
<td>Group I, AgF, BeF₂</td>
<td>SrF₂, BaF₂, PbF₂</td>
<td>AgI, HgI₂, PbI₂, HgI₂</td>
</tr>
<tr>
<td>Cl⁻ (chloride)</td>
<td>Most</td>
<td>PbCl₂</td>
<td>SrSO₄, BaSO₄, PbSO₄</td>
</tr>
<tr>
<td>Br⁻ (bromide)</td>
<td>Most</td>
<td>PbBr₂, HgBr₂</td>
<td></td>
</tr>
<tr>
<td>I⁻ (iodide)</td>
<td>Most</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>SO₄²⁻ (sulfate)</td>
<td>Most</td>
<td>CaSO₄, Ag₂SO₄, Hg₂SO₄</td>
<td></td>
</tr>
<tr>
<td>S²⁻ (sulfide)</td>
<td>Groups I and II, (NH₄)₂S</td>
<td>—</td>
<td>Most</td>
</tr>
<tr>
<td>CO₃²⁻ (carbonate)</td>
<td>Group I, (NH₄)₂CO₃</td>
<td>—</td>
<td>Most</td>
</tr>
<tr>
<td>SO₃²⁻ (sulfite)</td>
<td>Group I, (NH₄)₂SO₃</td>
<td>—</td>
<td>Most</td>
</tr>
<tr>
<td>PO₄³⁻ (phosphate)</td>
<td>Group I, (NH₄)₃PO₄</td>
<td>—</td>
<td>Most</td>
</tr>
<tr>
<td>OH⁻ (hydroxide)</td>
<td>Group I, Ba(OH)₂</td>
<td>Sr(OH)₂, Ca(OH)₂</td>
<td>Most</td>
</tr>
</tbody>
</table>

†Soluble compounds are defined as those that dissolve to the extent of 10 or more grams per liter; slightly soluble compounds, 0.1 to 10 grams per liter; and insoluble compounds, less than 0.1 gram per liter at room temperature.
# Environmental toxicology: chemical aspects

## Aquatic chemistry (2)

<table>
<thead>
<tr>
<th>Table 16.2</th>
<th>Solubility Product Constants $K_{sp}$ at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Iodates</strong></td>
<td></td>
</tr>
<tr>
<td>AgIO$_3$</td>
<td>$[\text{Ag}^+][\text{IO}_3^-] = 3.1 \times 10^{-8}$</td>
</tr>
<tr>
<td>CuIO$_3$</td>
<td>$[\text{Cu}^+][\text{IO}_3^-] = 1.4 \times 10^{-7}$</td>
</tr>
<tr>
<td>Pb(IO$_3)_2$</td>
<td>$[\text{Pb}^{2+}][\text{IO}_3^-]^2 = 2.6 \times 10^{-13}$</td>
</tr>
<tr>
<td><strong>Carbonates</strong></td>
<td></td>
</tr>
<tr>
<td>Ag$_2$CO$_3$</td>
<td>$[\text{Ag}^+]_2[\text{CO}_3^-] = 6.2 \times 10^{-12}$</td>
</tr>
<tr>
<td>BaCO$_3$</td>
<td>$[\text{Ba}^{2+}][\text{CO}_3^-] = 8.1 \times 10^{-9}$</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>$[\text{Ca}^{2+}][\text{CO}_3^-] = 8.7 \times 10^{-9}$</td>
</tr>
<tr>
<td>PbCO$_3$</td>
<td>$[\text{Pb}^{2+}][\text{CO}_3^-] = 3.3 \times 10^{-14}$</td>
</tr>
<tr>
<td>MgCO$_3$</td>
<td>$[\text{Mg}^{2+}][\text{CO}_3^-] = 4.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>SrCO$_3$</td>
<td>$[\text{Sr}^{2+}][\text{CO}_3^-] = 1.6 \times 10^{-9}$</td>
</tr>
<tr>
<td><strong>Chromates</strong></td>
<td></td>
</tr>
<tr>
<td>Ag$_2$CrO$_4$</td>
<td>$[\text{Ag}^+]_2[\text{CrO}_4^-] = 1.9 \times 10^{-12}$</td>
</tr>
<tr>
<td>BaCrO$_4$</td>
<td>$[\text{Ba}^{2+}][\text{CrO}_4^-] = 2.1 \times 10^{-10}$</td>
</tr>
<tr>
<td>PbCrO$_4$</td>
<td>$[\text{Pb}^{2+}][\text{CrO}_4^-] = 1.8 \times 10^{-14}$</td>
</tr>
<tr>
<td><strong>Oxalates</strong></td>
<td></td>
</tr>
<tr>
<td>CuC$_2$O$_4$</td>
<td>$[\text{Cu}^{2+}][\text{C}_2\text{O}_4^-] = 2.9 \times 10^{-8}$</td>
</tr>
<tr>
<td>FeC$_2$O$_4$</td>
<td>$[\text{Fe}^{2+}][\text{C}_2\text{O}_4^-] = 2.1 \times 10^{-7}$</td>
</tr>
<tr>
<td>MgC$_2$O$_4$</td>
<td>$[\text{Mg}^{2+}][\text{C}_2\text{O}_4^-] = 8.6 \times 10^{-5}$</td>
</tr>
<tr>
<td>PbC$_2$O$_4$</td>
<td>$[\text{Pb}^{2+}][\text{C}_2\text{O}_4^-] = 2.7 \times 10^{-11}$</td>
</tr>
<tr>
<td>SrC$_2$O$_4$</td>
<td>$[\text{Sr}^{2+}][\text{C}_2\text{O}_4^-] = 5.6 \times 10^{-8}$</td>
</tr>
<tr>
<td><strong>Sulfates</strong></td>
<td></td>
</tr>
<tr>
<td>BaSO$_4$</td>
<td>$[\text{Ba}^{2+}][\text{SO}_4^-] = 1.1 \times 10^{-10}$</td>
</tr>
<tr>
<td>CaSO$_4$</td>
<td>$[\text{Ca}^{2+}][\text{SO}_4^-] = 2.4 \times 10^{-5}$</td>
</tr>
<tr>
<td>PbSO$_4$</td>
<td>$[\text{Pb}^{2+}][\text{SO}_4^-] = 1.1 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

| **Fluorides** |                                              |
| BaF$_2$      | $[\text{Ba}^{2+}][\text{F}^-]^2 = 1.7 \times 10^{-6}$ |
| CaF$_2$      | $[\text{Ca}^{2+}][\text{F}^-]^2 = 3.9 \times 10^{-11}$ |
| MgF$_2$      | $[\text{Mg}^{2+}][\text{F}^-]^2 = 6.6 \times 10^{-9}$ |
| PbF$_2$      | $[\text{Pb}^{2+}][\text{F}^-]^2 = 3.6 \times 10^{-8}$ |
| SrF$_2$      | $[\text{Sr}^{2+}][\text{F}^-]^2 = 2.8 \times 10^{-9}$ |

| **Chlorides** |                                              |
| AgCl         | $[\text{Ag}^+][\text{Cl}^-] = 1.6 \times 10^{-10}$ |
| CuCl         | $[\text{Cu}^{2+}][\text{Cl}^-] = 1.0 \times 10^{-6}$ |
| Hg$_2$Cl$_2$ | $[\text{Hg}^{2+}][\text{Cl}^-]^2 = 2 \times 10^{-10}$ |

| **Bromides** |                                              |
| AgBr         | $[\text{Ag}^+][\text{Br}^-] = 7.7 \times 10^{-13}$ |
| CuBr         | $[\text{Cu}^{2+}][\text{Br}^-] = 4.2 \times 10^{-8}$ |
| Hg$_2$Br$_2$ | $[\text{Hg}^{2+}][\text{Br}^-]^2 = 1.3 \times 10^{-21}$ |

| **Iodides** |                                              |
| AgI          | $[\text{Ag}^+][\text{I}^-] = 1.5 \times 10^{-16}$ |
| CuI          | $[\text{Cu}^{2+}][\text{I}^-] = 5.1 \times 10^{-12}$ |
| Pbi$_2$      | $[\text{Pb}^{2+}][\text{I}^-]^2 = 1.4 \times 10^{-8}$ |
| HgI$_2$      | $[\text{Hg}^{2+}][\text{I}^-]^2 = 1.2 \times 10^{-28}$ |

| **Hydroxides** |                                              |
| AgOH         | $[\text{Ag}^+][\text{OH}^-] = 1.5 \times 10^{-8}$ |
| Al(OH)$_3$   | $[\text{Al}^{3+}][\text{OH}^-]^3 = 3.7 \times 10^{-15}$ |
| Fe(OH)$_3$   | $[\text{Fe}^{3+}][\text{OH}^-]^3 = 1.1 \times 10^{-36}$ |
| Fe(OH)$_2$   | $[\text{Fe}^{2+}][\text{OH}^-]^2 = 1.6 \times 10^{-14}$ |
| Mg(OH)$_2$   | $[\text{Mg}^{2+}][\text{OH}^-]^2 = 1.2 \times 10^{-11}$ |
| Mn(OH)$_2$   | $[\text{Mn}^{2+}][\text{OH}^-]^2 = 2 \times 10^{-13}$ |
| Zn(OH)$_2$   | $[\text{Zn}^{2+}][\text{OH}^-]^2 = 4.5 \times 10^{-17}$ |
### Table 16.3: Equilibrium Constants for Metal Sulfide Dissolution at 25°C

<table>
<thead>
<tr>
<th>Metal Sulfide</th>
<th>$K^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuS</td>
<td>$5 \times 10^{-37}$</td>
</tr>
<tr>
<td>PbS</td>
<td>$3 \times 10^{-28}$</td>
</tr>
<tr>
<td>CdS</td>
<td>$7 \times 10^{-28}$</td>
</tr>
<tr>
<td>SnS</td>
<td>$9 \times 10^{-27}$</td>
</tr>
<tr>
<td>ZnS</td>
<td>$2 \times 10^{-25}$</td>
</tr>
<tr>
<td>FeS</td>
<td>$5 \times 10^{-19}$</td>
</tr>
<tr>
<td>MnS</td>
<td>$3 \times 10^{-14}$</td>
</tr>
</tbody>
</table>

$K^+$ is the equilibrium constant for the reaction $\text{MS(s)} + \text{H}_2\text{O(ℓ)} \rightleftharpoons \text{M}^{2+}(aq) + \text{OH}^-(aq) + \text{HS}^-(aq)$. 

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*Silvia Gross*
Environmental toxicology: chemical aspects
Aquatic chemistry (2)

Solubility (g KBr per 100 g water) vs. Temperature (°C)