

Complexation Reactions

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OBJECTIVES

To understand the processes that control the chemical speciation, *i.e.*, the different chemical compounds, of metals in natural waters. How can we determine this speciation at chemical equilibrium and why is it important? Please read Chapter 6 pages: 319 - 375.

INTRODUCTION

Natural and Anthropogenic Processes: Of the 108 known elements in the periodic table 82% have metallic properties. Among these elements, 30 are of key importance and their chemical form or “speciation” needs to be assessed carefully because they are either toxic or present in very toxic compounds (e.g., methyl mercury CH_3Hg^+). A large number of metals are present in rocks or in aqueous solutions as traces (< 100 ppm). Anthropogenic activities contribute each year to an increase in the release of metals (e.g., mining and smelting, electronics, ...), and therefore an acceleration of their natural chemical cycles.

Every year the chemical industry releases about 100,000 different organic molecules. These compounds usually end-up in aquatic systems where already a large number of organic compounds

are already present. Many of these organic compounds present some environmental concerns since they can bind efficiently metals (metal ligation). As a result, numerous chemical species are formed as complexes of metals with ligands. Aquatic systems are therefore complicated systems where competing reactions such precipitation, acid/base equilibria, and multiple complexations are occurring simultaneously.

On the other hand, some metals such as Cu, Zn, Co, Fe, Mn, Ni, Cr, V, Mo, Se, and Sn, that are present at trace levels, are essential elements for living organisms (oligo-elements). They play important role in various biological functions (*ca.* 50% of known proteins have specific sites that necessitate metals for proper activity) at trace levels. With increasing concentrations in the environment they become toxic past a certain threshold. Other metals (*e.g.*, Ag, As, Pb, Hg) have no known biological functions and usually considered toxic.

KEY CONCEPT

In order to understand the fate of metals in the environment, the determination of the chemical speciation of metals is central, and therefore complexation reactions play a key role.

Chemical Principles: All chemical reactions have one common denominator:

The atoms, molecules or ions tend to improve the stability of their electronic configuration

In a broad sense, two types of reactions can achieve this goal:

1. **Redox Processes** that change the oxidation state, *i.e.*, remove or add electrons.
2. **Coordination Reactions**, where the coordinative relationships change. That is, changing the coordinative partner(s)

or the coordination number - that is indicative of the structure and that specifies the number of nearest neighbors atoms). Three types of reactions fulfill this goal: **1) Acid/Base** when the acid is introduced into water the coordinative partner of the proton changes; **2) Precipitation Reactions;** **3) Complexation Reactions.**

Coordination chemistry is therefore a central topic of study for understanding the detail nature of complexation reactions. But it is beyond the scope of this class. Modern chemistry principles relying on molecular orbital theory (MOT) and ligand field theory (LFT) allow to explain many features of complexation reactions. These theories look at how metals and ligands share electrons.

DEFINITIONS

Inner-Sphere Complexes: Metal Ions react with electron-pair donors to form:

Complex Ions

Coordination Compounds

In this case, ligands are ions or molecules that form covalent bonds with cations by donating a pair of electrons which are then shared by the ligand and the cation. The number of bonds formed per molecule is referred to as a “**dentate**” (meaning tooth-like). Unidentate reagents form a single bond per

molecule, hexadentate form six, and so on... The chemical species formed as a result of these reactions leading to the formation of a covalent bond are called **inner-sphere complexes**.

Outer-Sphere Complexes: In this case the attraction between “metals” (cations) and “ligands” (anions) is purely electrostatic and result in a new compound where each of the initial species retain part of or all of their water coordination shells. These type of complexes are also called ion pairs.

Chelation (from the greek “claw”) is based on the formation of complex ligands

LIGANDS AND METALS

In general, metal ions prefer specific donor atoms of the ligands and also some specific geometry, *i.e.*, stereochemistry, in their binding. Hence, ligands can be devised to satisfy these selective requirements, but more generally, a metal ion imposes the geometry on a set of small ligands.

On the other hand some multidentate ligands of rigid geometry, *e.g.*, proteins, do impose the stereochemistry on the metal ion contrary to its geometric preference. This imposed geometry is called an “entatic” state (from the greek “under strain”), and it generates catalysis in many enzyme reactions. Metal toxicity, in short, can be view as the result of the replacement, at the level of a specific metal center, of a metal ion that activates properly

the protein of interest by a metal ion that perturb the biological function of the enzyme. One can decide about the selectivity of metal-ligand associations using the Hard Soft Acid Base (HSAB) theory, that provides empirical rules based on the classification of acids (metals) and bases (ligands). Here the terms Acid and Bases are used in a more generic sense -Lewis. The softness is related to the electronegativity of the species, *i.e.*, the ability of the ligand donor atoms to become better electron donors.

Hard (Predominantly, having the electron configuration of inert gases)

Acids: Li^+ , Na^+ , K^+ , Be^{2+} , Mg^{2+} , Ca^{2+} , Al^{3+} , Cr^{3+} , Fe^{3+} , Co^{3+}

Bases: NH_3 , RNH_2 , H_2O , OH^- , CO_3^{2-} , SO_4^{2-} , F^-

Boderline (Intermediate character)

Acids: Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Sn^{2+}

Bases: Br^- , Cl^-

Soft (Electron configuration in the outer shell similar to Ni^0 , Pb^0 , Pt^0)

Acids: Cu^+ , Ag^+ , Cd^{2+} , Hg^{2+} , Au^+

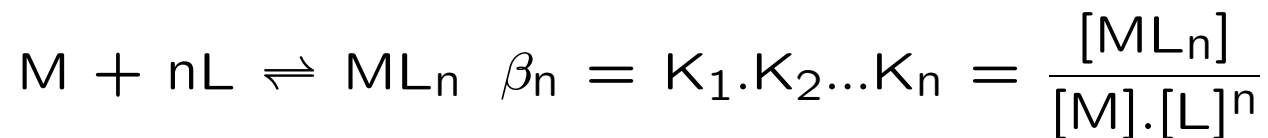
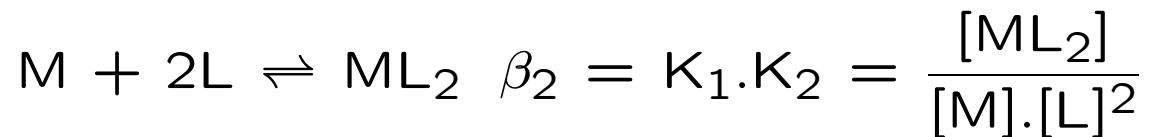
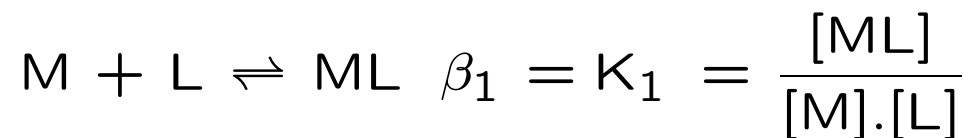
Bases: CN^- , SCN^- , RSH , RS^-

The hard and soft characters are not absolute but gradually vary.

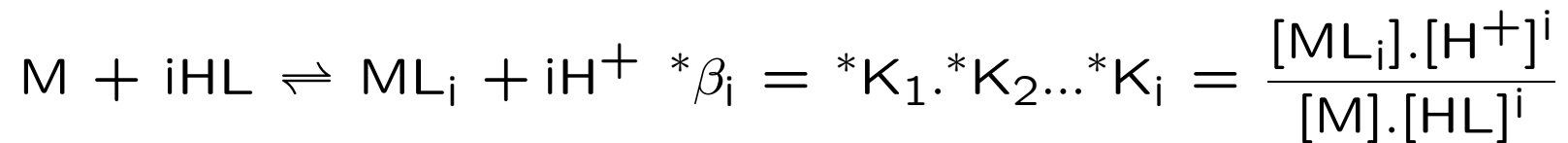
HSAB RULES: *Thermodynamic equilibrium:* **Hard acids prefer to associate with hard bases and soft acids with soft bases.** *Kinetics:* Hard acids react readily with hard bases and soft acids with soft bases.

NOTATION FOR COMPLEXATION REACTIONS

For dealing with complexation reactions it is convenient to use overall equilibrium constants (β) as opposed to the successive equilibrium constants (K) that we have used so far. For mononuclear complex we write:



For complexation reactions involving a protonated ligand:



And for the general case of a complexation reaction

