


 University
of Idaho

GEOL578
Advanced Geochemistry of Natural Waters

LESSON 5
Aqueous Complexes
(Coordination Chemistry)

MODULE 3
Theoretical Concepts of Complexation

Start Audio Lecture!

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PEARSON HARD-SOFT ACID-BASE (HSAB) THEORY

<ul style="list-style-type: none"> • Hard ions (class A) <ul style="list-style-type: none"> • small • highly charged • d^0 electron configuration • electron clouds not easily deformed • prefer to form ionic bonds 	<ul style="list-style-type: none"> • Soft ions (class B) <ul style="list-style-type: none"> • large • low charge • d^{10} electron configuration • electron clouds easily deformed • prefer to form covalent bonds
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Pearson's Principle - *In a competitive situation, hard acids tend to form complexes with hard bases, and soft acids tend to form complexes with soft bases.*

In other words - metals that tend to bond covalently preferentially form complexes with ligands that tend to bond covalently, and similarly, metals that tend to bond electrostatically preferentially form complexes with ligands that tend to bond electrostatically.

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Classification of metals and ligands in terms of Pearson's (1963) HSAB principle.

Hard	Borderline	Soft
Acids H^+ $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ $Al^{3+} > Ga^{3+}$ $Sc^{3+} > Y^{3+}; REE^{3+} (Lu^{3+} > La^{3+});$ $Ce^{4+}; Sn^{4+}$ $Ti^{3+} > Ti^{2+}; Zr^{4+} \approx Hf^{4+}$ $Cr^{6+} > Cr^{3+}; Mo^{6+} > Mo^{5+} >$ $Mo^{4+}; W^{6+} > W^{5+}; Nb^{5+}; Ta^{5+};$ $Re^{7+} > Re^{6+} > Re^{4+}; V^{6+}; V^{5+} >$ $V^{4+}; Mn^{4+}; Fe^{3+}; Co^{3+}; As^{5+}; Sb^{5+};$ $Th^{4+}; U^{6+} > U^{4+}$ $PGE^{6+} > PGE^{4+}, etc. (Ru, Ir, Os)$	Acids $Fe^{2+}; Mn^{2+}; Co^{2+}; Ni^{2+};$ $Cu^+; Zn^{2+}; Pb^{2+}; Sn^{2+};$ $As^{3+}; Sb^{3+}; Bi^{3+}$	Acids $Au^+ > Ag^+ > Cu^+$ $Hg^{2+} > Cd^{2+}$ $Pt^{2+} > Pd^{2+}$ other PGE ²⁺ $Tl^+ > Tl^0$
Bases $F^-; H_2O; OH^-; O^{2-}; NH_3; NO_2^-;$ $CO_3^{2-} > HCO_3^-; SO_4^{2-} > HSO_4^-;$ $PO_4^{3-} > HPO_4^{2-} > H_2PO_4^-;$ carboxylates (i.e., acetate, oxalate, etc.); $MoO_4^{2-}; WO_4^{2-}$	Bases Cl ⁻	Bases $I^- > Br^-; CN^-; CO;$ $S^{2-} > HS^- > H_2S;$ organic phosphines (R ₃ P); organic thiols (RS); polysulfide (S _n S ²⁻); thiosulfate (S ₂ O ₃ ²⁻); sulfite (SO ₃ ²⁻); $HSe^-; Se^{2-}; HTe^-; Te^{2-};$ $AsS_2^-; SbS_2^-$

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ION PAIRS VS. COORDINATION COMPLEXES

<ul style="list-style-type: none"> • ION PAIRS <ul style="list-style-type: none"> • formed solely by electrostatic attraction • ions often separated by coordinated waters • short-lived association • no definite geometry • also called outer-sphere complexes 	<ul style="list-style-type: none"> • COORDINATION COMPLEXES <ul style="list-style-type: none"> • large covalent component to bonding • ligand and metal joined directly • longer-lived species • definite geometry • also called inner-sphere complexes
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STABILITY CONSTANTS OF ION PAIRS CAN BE ESTIMATED FROM ELECTROSTATIC MODELS

For 1:1 pairs (e.g., NaCl⁰, LiF⁰, etc.)
 $\log K \approx 0 - 1 (I = 0)$

For 2:2 pairs (e.g., CaSO₄⁰, MgCO₃⁰, etc.)
 $\log K \approx 1.5 - 2.4 (I = 0)$

For 3:3 pairs (e.g., LaPO₄⁰, AlPO₄⁰, etc.)
 $\log K \approx 2.8 - 4.0 (I = 0)$

Stability constants for covalently bound coordination complexes cannot be estimated as easily.
