E 5 Lewis Acids and Bases: Complexation

1. ACIDITY OF CATIONS (Part 1)

- Cations are Lewis acids and exist as aquo complex ions in aqueous solution.
  Example: $[Al(HOH)_6]^{3+}$, $[Cu(HOH)_4]^{2+}$
- Aquo Complex cations may react with water. During reaction proton/s is/are released from the aquo complex ion and bond to water molecule/s to form hydronium ions.
  Example: $[Cu(HOH)_4]^{2+}$ + HOH = $[Cu(HOH)_3(OH)]^+$ + H• HOH^+

- Acidic properties of cations in aqueous solution differ and are related to the position of the metal ion's element in the periodic table and its charge and charge density and resulting attraction for electrons (oxidizing agent strength)
  - Lewis acid strength: Post-transition > transition > alkaline earth > alkali
  (e.g. $Mg^{2+}_{(aq)}$ is better Lewis acid than $Na^+_{(aq)}$; $Al^{3+}_{(aq)}$ is better Lewis acid than $Mg^{2+}_{(aq)}$)
  - Lewis acid strength is related to charge density of the cation
  (e.g. $Mg^{2+}_{(aq)}$ has greater charge density than Ca^{2+} since the ionic radius of the former is smaller than the latter and thus $Mg^{2+}_{(aq)}$ is more acidic than Ca^{2+}.
  - As period # *decreases* within a family, acid strength of cation *increases*:
  (e.g. $Mg^{2+}_{(aq)}$ is more acidic than $Ca^{2+}_{(aq)}$)

2. LEWIS ACID-BASE REACTIONS.

- Lewis acids = electron pair seekers (such as cations) react with (coordinate to) a Lewis base = electron pair donor.
- Lewis bases are also called ligands.
- Lewis acid-base reactions are also called complexation reactions.
- Lewis acid-base reactions are equilibrium systems.

3. RXN OF AQUO COMPLEX CATIONS WITH LEWIS BASES (Part 2)

- A Lewis *acid* (base) reacts with (bonds to) the BEST Lewis *base* (acid) and therefore Ligand/base exchange may occur
  Example: $[Cu(HOH)_4]^{2+}$ + 4 NH_3 = $[Cu(NH)_3)_4]^{2+}$ + 4 HOH
- Reaction extent (i.e. equilibrium point) of aquo complex cations is related to the position of the cation's element in the Periodic Table and its Lewis acid strength.
- Reaction extent differs with different bases (e.g. OH^- vs. NH_3) and is predictable from the position of the cation's element in the Periodic Table.
  - Class data shows only transition cation's reacted extensively with NH_3.*
  Example:
  $[Ni(H_2O)_6]^{2+}$ is green in aqueous solution. If NH_3 is added, violet $[Ni(NH_3)_6]^{2+}$ is formed. The post-transition cation Pb^{2+} ($[Pb(H_2O)_4]^{2+}$) does not react with NH_3, but instead reacts with OH^- present in the ammonia solution to form a

hydroxide ppt. ($[Pb(H_2O)_2(OH)_2]$). There is a small concentration of OH^- ions in the basic ammonia solution.

*Note: When NH_3, is added to any solution containing a cation and reaction occurs, the product $[M(NH_3)_x]^{x+}$ will always be charged (the same as the reacting metal ion) and soluble (since NH_3 has no charge). If a precipitate forms upon addition of ammonia to a solution containing a cation, you may conclude that it is likely a hydroxide ppt. due to reaction with the small amount of OH- ions in the ammonia,

- **Class data shows only post-transition cation's reacted extensively with OH^-.**

Note: When cations react with OH^-, the cation product's charge and solubility alter as it bonds to the charged hydroxide ion.

Example: Reaction of OH^- ions with aquo complex metal ions:

$$\text{Equilibrium: } [M(HOH)_x]^{2+} + xOH^- = [M(OH)_x]^{2-} + xHOH$$

Cation Family	Example	Primary Class Observations
I	**$[Na(HOH)_6]^+$** (lousy Lewis acids; equilibrium pt. far left)	**no reaction**
II	**$[Ca(HOH)_6]^{2+}$** (weak Lewis acids; rxn does not proceed to any great extent)	**ppt.** $[Ca(HOH)_4(OH)_2]$ **or no change** $[M(HOH)_5(OH)]^+$
Transition	**$[Co(HOH)_6]^{2+}$**	**solution color change# or ppt.** $[Co(HOH)_5(OH)]^+ \ldots [Co(HOH)_4(OH)_2]$
	# (Cation with unfilled d electron subshell).	
PostTrans.	**$[Pb(HOH)_4]^{2+}$** (strong Lewis acids; equilibrium pt. far right)	**ppt. forms** $[Pb(HOH)_2(OH)_2]$ **and dissolves** $[Pb(OH)_4]^{2-}$

4. **COMPLEXATION AND SOLUBILITY EQUILIBRIA** (Part 3)**.**

- Dissolving of precipitates upon addition of base (OH^- or NH_3) is predictable from the position of the cation's element in the periodic table.
- A precipitate (complex) will dissolve upon addition of OH^- or NH_3 if the cation comprising the ppt. reacts with the added base to forms a soluble complex ion:
  - A ppt. containing a transition metal ion will likely dissolve upon addition of NH_3.
  - A ppt. containing a post-transition metal ion will likely dissolve upon addition of OH^- (e.g., upon addition of NaOH).
  - A ppt. containing a metal ion other than transition of post-transition will NOT dissolve upon addition of OH^- or NH_3.

Cation Family	**Primary Observation**	**Interpretation**
II	ppts. did NOT dissolve	Cations = weak Lewis acids (i.e. **do not react extensively with OH^- or NH_3**)
Trans.	ppts. dissolve in NH_3	**Trans. cations react (bond) well to Lewis base NH_3** and convert to soluble ammine complex ion.
	some dissolve in NaOH.	Some cations reacted with OH^- to form a soluble hydroxo complex ion. Most do not react extensively with OH^- and therefore the ppt. does not dissolve.
Post-trans.	ppts. dissolve in OH^- ppts. do NOT dissolve in NH_3	**Post trans. cations react extensively with OH^-** and ppts tend to dissolve as metal ion converts to a soluble hydroxo complex ion. Post trans.cations do NOT react well with NH_3.

QUESTIONS EXPERIMENT 5 (LEWIS ACIDS AND BASES)

Part 1. Acidity of Cations and the Periodic Table

1. The aquated form of the Cd^{2+} ion is $Cd(H_2O)_6^{2+}$. When $CdCl_{2(s)}$ is added to water (pH 7), the pH drops to about pH 5 and the aqueous solution remains clear. Write a balanced equation that supports the observations. Include only the reactants and not spectator ions.

__________ + ____________ $\longrightarrow$ ____________ + _____________

2. You have solutions of 0.10 M $CaCl_2$, $NiCl_2$, and $GaCl_3$. Arrange these in order of *decreasing* pH values:

highest pH		lowest pH
________ >	________ >	_________

(now try Dec'04, 4A-B, April'05, 1A; Dec.05, 1B, 2A, April'06, 4A; Dec.06, 1B-C; April'07, 1B)

Part 2 Acid-Base Reactions and Complexation

3. **Circle** any compound that is soluble in water and is likely to form a hydroxide precipitate that dissolves upon addition of 1M NaOH.

KNO_3	$Ba(NO_3)_2$	$Pb(NO_3)_2$

4. Concentrated NaOH is added dropwise to a solution of 0.1M $ZnCl_2$. After 5 drops a cloudy white precipitate forms. The precipitate dissolves after the addition of 15 drops. What is the principal zinc containing species in solution after the addition of 15 drops of NaOH?

Circle the white precipitate formed after the addition of 5 drops of NaOH:

$[Zn(H_2O)_4]^{2+}$ $[Zn(OH)_4]^{2-}$ $[Zn(H_2O)_2(OH)_2]$ $[Zn(H_2O)_2(Cl)_2]$

Circle the species present after the addition of 15 drops of NaOH:

$[Zn(H_2O)_4]^{2+}$ $[Zn(OH)_4]^{2-}$ $[Zn(H_2O)_2(OH)_2]$ $[Zn(H_2O)_3(OH)]^{+}$

5.

Circle any 0.10 M solution that forms a precipitate that dissolves upon addition of 1.0 M NH_3.

$CaCl_2$ $NiCl_2$ $GaCl_3$

Question 6 deals with your investigations of the Lewis acid-base interactions of the metal ions Cu^{2+}, Co^{2+}, Cd^{2+}, and Ca^{2+}. Below are your experimental data:

Aquo Complex Ion	**REAGENT**	**REAGENT + 5M NaOH**	**REAGENT + 5M $NH_{3(aq)}$**
$[Cu(H_2O)_4]^{2+}$	$Cu(NO_3)_2$ clear, blue	blue-white ppt.	blue-white ppt.→ ppt. dissolves clear, prussian blue.
$[Co(H_2O)_6]^{2+}$	$Co(NO_3)_2$ clear, rose	rose-red ppt.	rose-red ppt.→ ppt. dissolves clear, yellow
$[Cd(H_2O)_4]^{2+}$	$Cd(NO_3)_2$ clear, colorless	white ppt.→ ppt.dissolves clear, colorless	white ppt.→ ppt. dissolves clear, colorless
$[Ca(H_2O)_4]^{2+}$	$Ca(NO_3)_2$ clear, colorless	white ppt.	white ppt.

A. Based on the above data which one or more of the cations Cu^{2+}, Co^{2+}, Cd^{2+}, and Ca^{2+} can act as a Lewis acid and complex with the Lewis base, NH_3?

> **Circle** any cation that acts as a Lewis acid and complexes with the Lewis base NH_3.
>
> Cu^{2+} Co^{2+} Cd^{2+} Ca^{2+}

B. According to the above data, the addition of 5 NH_3 to $Co(NO_3)_2$ results ultimately in a "clear, yellow" solution. Identify the principal cobalt species in the "clear, yellow" solution.

> **Circle** the principal cobalt containing species in the clear yellow solution:
>
> $[Co(H_2O)_6]^{2+}$ $[Co(OH)_6]^{4-}$ $[Co(NH_3)_6]^{2+}$ $[Co(OH)_2(NH_3)_4]$

(try Dec'04, 3, April'05, 1C, 3A; Dec.05, 2, 5; April 2006, 4B, 4C; Dec.06, 6; April'07, 1D, 4A)

Part 3 Complexation & Solubility Equilibria

6. (continued)

C. In another experiment, you precipitate $Co(OH)_2$, $Cd(OH)_2$, and $Ca(OH)_2$. Based **upon the above observations**, which *one or more* of these precipitates will dissolve upon addition of 5M NaOH?

> **Circle** any precipitate which will dissolve upon addition of 5M NaOH or circle "NONE":
>
> $Co(OH)_2$ $Cd(OH)_2$ $Ca(OH)_2$ NONE

(Try Dec'04, 4C-D, 5A#3; April'05, 3; Dec.05,7; April'06, 1D, 4C; Dec.06, 1B, 2C#2; April'07, 1C, 4B, 5B1)