

E5 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: $[\text{Al}(\text{HOH})_6]^{3+}$, $[\text{Cu}(\text{HOH})_4]^{2+}$
- 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: $[\text{Cu}(\text{HOH})_4]^{2+} + \text{HOH} = [\text{Cu}(\text{HOH})_3(\text{OH})]^+ + \text{H} \bullet \text{HOH}^+$
- 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. $\text{Mg}^{2+}_{(\text{aq})}$ is better Lewis acid than $\text{Na}^+_{(\text{aq})}$; $\text{Al}^{3+}_{(\text{aq})}$ is better Lewis acid than $\text{Mg}^{2+}_{(\text{aq})}$)
 - **Lewis acid strength is related to charge density of the cation**
(e.g. $\text{Mg}^{2+}_{(\text{aq})}$ has greater charge density than Ca^{2+} since the ionic radius of the former is smaller than the latter and thus $\text{Mg}^{2+}_{(\text{aq})}$ is more acidic than Ca^{2+} .)
 - **As period # decreases within a family, acid strength of cation increases:**
(e.g. $\text{Mg}^{2+}_{(\text{aq})}$ is more acidic than $\text{Ca}^{2+}_{(\text{aq})}$)

2. LEWIS ACID-BASE REACTIONS.

- Lewis acids = electron pair seekers (such as cations) react with (coordinate/bond 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 if a new Lewis base is added to a reaction mixture, ligand/base exchange will occur if the added base is better – forms a stronger bond with the Lewis acid.



- Reaction extent (i.e. equilibrium point) 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:

$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is green in aqueous solution. If NH_3 is added, violet $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is formed. The post-transition cation Pb^{2+} ($[\text{Pb}(\text{H}_2\text{O})_4]^{2+}$) does not react with NH_3 , but instead reacts with OH^- present in the ammonia solution to form a

hydroxide ppt. ($[\text{Pb}(\text{H}_2\text{O})_2(\text{OH})_2]$) due to the fact that 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 amine complex ion product $[\text{M}(\text{NH}_3)_x]^{x+}$ will always 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 where the reaction stoichiometry between the metal ion and the hydroxide ion is such that the overall charge on the complex product is neutral.

- **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:



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

4. COMPLEXATION AND SOLUBILITY EQUILIBRIA (Part 3).

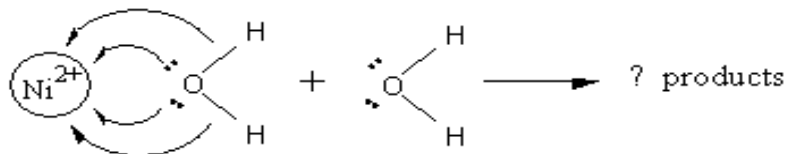
- Dissolving of precipitates upon addition of base (OH^- or NH_3) is predictable from the position of the cation's element in the periodic table. For example, transition metal ion precipitates dissolved upon addition of NH_3 while post-transition and pre-transition metal ion precipitates did not dissolve.
- 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.
 - If the cation comprising the ppt. reacts with the NH_3 a soluble complex ion will be formed since any metal ion bonded to NH_3 retain its charge.
 - If the cation comprising the ppt. reacts with OH^- a soluble complex ion or an insoluble complex will be formed depending on reaction stoichiometry.

<u>Cation</u> <u>Family</u>	<u>Primary Observation</u>	<u>Interpretation</u>
II	ppts. did NOT dissolve	Cations = weak Lewis acids (i.e. do not react extensively with OH⁻ or NH₃)
Trans.	ppts. dissolve in NH ₃ <i>some</i> dissolve in NaOH.	Trans. cations react (bond) well to Lewis base NH₃ and convert to soluble ammine complex ion. 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. Ni^{2+} exists in aqueous solution as $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$. When you dissolve $\text{Ni}(\text{Cl})_{2(s)}$ in a sample of water = pH 6.8, the pH drops to pH 4.5. The picture below represents the Lewis acid Ni^{2+} reacting with a sample of the Lewis base HOH:



Circle the correctly completed and balanced Lewis acid–base equation showing the products in the **acidic** solution.

- | | | | | | | |
|----|---|----------------------------------------|---|------------------------|---|----------------------|
| 1. | → | $[\text{Ni}(\text{OH})]^+$ | + | H^+ | + | OH^- |
| 2. | → | $[\text{NiO}]$ | + | 2H^+ | + | H_2O |
| 3. | → | $[\text{Ni}(\text{OH})]^+$ | + | H_3O^+ | | |
| 4. | → | $[\text{Ni}(\text{H}_3\text{O})]^{2+}$ | + | OH^- | | |
| 5. | → | $[\text{Ni}(\text{OH})]^{2+}$ | + | H_3O^+ | | |

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 April'06, 4A; Dec.06, 1B-C; April'07, 1B; Dec.07, 1(3), 4A; April'08 1A, 2A; Dec.'08 1-#1, 6A)

Part 2 Acid-Base Reactions and Complexation

3. **Circle** one combination of species from the three combinations of species given below that will likely react in a Lewis acid-base reaction.

Br^- and I^-

Ni^{2+} and NH_3

Hg^{2+} and Sn^{2+}

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

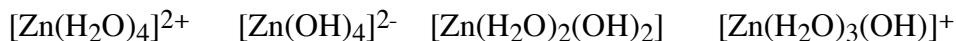
KNO_3

$\text{Ba}(\text{NO}_3)_2$

$\text{Pb}(\text{NO}_3)_2$

5. 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?

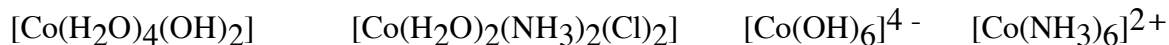
Circle the species present after the addition of 15 drops of NaOH:



6. Co^{2+} exists as $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ in aqueous solution. To 2 mL of a red solution of 0.10 M $\text{Co}(\text{Cl})_2$, you add 2 mL of 1.0 M NH_3 and observe:

→ red precipitate forms and dissolves and clear yellow solution results.

A. Identify (**circle**) the correct formula for the red precipitate initially formed upon reaction.



B. Identify (**circle**) the primary cobalt species present in the clear yellow solution.



(try April'06, 4B, 4C; Dec'06, 6; April'07, 1D, 4; Dec.'07, 1(4 -5), 4B; April'08, 5, 7; Dec.08, 1-#4, 4, 6 B&C)

Part 3 Complexation & Solubility Equilibria

7. Cu^{2+} exists as $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ in aqueous solution. If 2 mL of 1.0 M NaOH is added to 2 mL of 0.10 M $\text{Cu}(\text{Cl})_2$, copper hydroxide precipitates.

If $\text{HNO}_{3(\text{aq})}$ is added to a portion of the precipitated sample, reaction occurs and the precipitate dissolves. If $\text{NH}_{3(\text{aq})}$, is added to another portion of the precipitated sample, reaction again occurs and the precipitate dissolves! The reactivity of the copper hydroxide precipitate upon the addition of acid or base can be explained using Lewis acid-base theory.

Identify the reacting species (Lewis acid or base) in the copper hydroxide equilibrium system upon the addition of acid or base.

The species reacting upon addition of $\text{HNO}_{3(\text{aq})}$ = _____

The species reacting upon addition of $\text{NH}_{3(\text{aq})}$ = _____

8.

Circle any precipitate which will dissolve upon addition of 5M NaOH or circle "NONE":



NONE

(Try April'06, 1D, 4C; Dec.06, 1B, 2C#2; April'07, 4, 5B(1); Dec.07, 4B; April'08 1C, 5; Dec'08, 6C)