

BC2001x Lab Lecture 12 QUALITATIVE ANALYSIS IV SOLID UNKNOWN C: The Cation



Chemistry Lab at Barnard's first campus, 345 Madison Ave.
Could they be finding Unknown C? (from the BEATL Archive)

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CATION ANALYSIS

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H	THE 14 CATIONS that might be PRESENT																He
Li	Be											B	C	N	O	F	Ne
Na ⁺	Mg ²⁺	TRANSITION METALS										Al ³⁺	Si	P	S	Cl	Ar
K ⁺	Ca ²⁺	Sc	Ti	V	Cr	Mn	Fe ³⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺	Ga	Se	As	Se	Br	Kr
Rb	Sr ²⁺	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba ²⁺	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb ²⁺	Bi	Po	At	Rn

NH₄⁺

< here as "honorary alkali": shares most solubility properties

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Chemical tests: treatment with strong base

1	2	3	4	5	6	7	8	9	10	11	12	13	14
	Does an insoluble hydroxide salt form?												
		(gray = yes; the ppts are mostly white.)											
Na ⁺	Mg ²⁺	TRANSITION METALS										Al ³⁺	
K ⁺	Ca ²⁺						Fe ³⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺		
	Sr ²⁺												
	Ba ²⁺												Pb ²⁺

NH₄⁺

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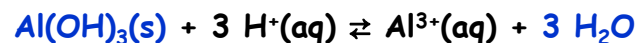
Alkaline earth hydroxide salts are sparingly soluble

Salt	K _{sp}	Result of test with strong base
Mg(OH) ₂	1.5 × 10 ⁻¹¹	fine white precipitate
Ca(OH) ₂	7.9 × 10 ⁻⁶	no precipitate unless [OH ⁻] is rather large
Sr(OH) ₂	3.2 × 10 ⁻⁴	no precipitate unless [OH ⁻] is quite large
Ba(OH) ₂	3.0 × 10 ⁻⁴	no precipitate unless [OH ⁻] is quite large

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Do hydroxide salts dissolve in strong acid?

Al(OH)_3 ($K_{\text{sp}} = 1.9 \times 10^{-33}$).



Al^{3+} and H^+ compete for OH^- , similar to competitions discussed previously.

$$K_{\text{eq}} = \frac{[\text{Al}^{3+}][\text{OH}^-]^3}{[\text{H}^+]^3} \times \frac{K_{\text{sp}}(\text{Al(OH)}_3)}{[\text{K}_w(\text{HOH})]^3} = \frac{(1.9 \times 10^{-33})}{(1.0 \times 10^{-14})^3} = 1.9 \times 10^9 \gg 1$$

The acid-base reaction goes forward easily
Insoluble hydroxides dissolve in strong acid.

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Disolving Al(OH)_3 in weak acid? $\text{Al(OH)}_3(\text{s}) + 3 \text{HOAc} \rightleftharpoons \text{Al}^{3+} + 3 \text{H}_2\text{O} + 3 \text{OAc}^-$

Again, a competition between Al^{3+} and H^+ for OH^- , plus competition between OAc^- and OH^- for H^+

$$K = \frac{[\text{Al}^{3+}][\text{OAc}^-]^3}{[\text{HOAc}]^3} \times \frac{[\text{OH}^-]^3}{[\text{OH}^-]^3} \times \frac{[\text{H}^+]^3}{[\text{H}^+]^3} = \frac{K_{\text{sp}}(\text{Al(OH)}_3) \times \{\text{K}_a(\text{HOAc})\}^3}{\{\text{K}_w(\text{H}_2\text{O})\}^3}$$

$$= \frac{(1.9 \times 10^{-33}) \times (1.76 \times 10^{-5})^3}{(1.0 \times 10^{-14})^3} = 1.04 \times 10^{-5} \ll 1$$

The reaction does not go forward to any great extent. Insoluble hydroxides are usually hard to dissolve in weak acid. They can dissolve if the weak acid is made concentrated enough, say 6 M.

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Caution: If a basic solution is not freshly made, it may be contaminated with carbonate.



In water, very little CO_3^{2-} forms:
both equilibria favor reactants.

In base, OH^- reacts with H^+ , driving both reactions to the right. The net reaction:



Basic solutions open to the air
(which contains CO_2) become contaminated with small amounts of carbonate.
Worse in a lab full of breathing people.

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Practical consequences of CO_3^{2-} contamination

If you see a little precipitate form when you add (contaminated) OH^- solution, you might incorrectly think it is an insoluble hydroxide, when it is actually an insoluble carbonate.

This is called a false positive test.

This is also possible (but less likely) with contaminated NH_3 solution.

Hydroxide solutions have to be kept protected from contamination by atmospheric CO_2 or by CO_2 from your breath.

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FURTHER treatment with strong base something *interesting* may happen...

1 2 3 4 5 6 7 8 9 10 11 12 13 14

AMPHOTERIC? Does the hydroxide salt dissolve in excess OH⁻?

(green = dissolves, not green color!)

Na ⁺	Mg ²⁺												Al ³⁺	
K ⁺	Ca ²⁺					Fe ³⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺				
	Sr ²⁺													
	Ba ²⁺													Pb ²⁺

NH₄⁺

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AMPHOTERIC hydroxides dissolve in *either* acid or base. How does this work?

OH⁻ acts as a **ligand** forming a soluble **complex anion** with the **metal**. Example:



Precipitate **dissolves** in excess OH⁻:



Or written is one step (no ppt shown):



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AMPHOTERIC hydroxides dissolve in *either* acid or base. How does this work?

Precipitate forms:



Precipitate dissolves in excess OH⁻:



Practical problems in observing this:

- 1) If you add the strong base too fast, you might miss the initial precipitation.
- 2) Some amphoteric hydroxides are hard to dissolve.

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Treatment with **ammonia** {NH₃(aq)}
Basic: so hydroxide ppt may form, but..

1 2 3 4 5 6 7 8 9 10 11 12 13 14

does the hydroxide salt dissolve in ammonia?

approximate color, metal-ammine complex ion

Na ⁺	Mg ²⁺												Al ³⁺	
K ⁺	Ca ²⁺					Fe ³⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺				
	Sr ²⁺													
	Ba ²⁺													Pb ²⁺

NH₄⁺

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Treatment with ammonia $\text{NH}_3(\text{aq})$
 {bottles labeled NH_4OH should be labeled $\text{NH}_3(\text{aq})$ }

Ammonia is a weak **base**, so OH^- is present:



Insoluble hydroxide precipitates **may** form,
but some cations also **react with $\text{NH}_3(\text{aq})$** :

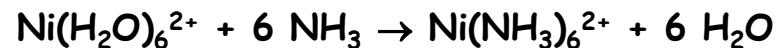
NH_3 is also a good **ligand**: can form soluble
metal-ammine complex ions: $\text{M}(\text{NH}_3)_n^{m+}$.

The hydroxide precipitate **may form and then**
dissolve in excess NH_3 , **or it may not form**.

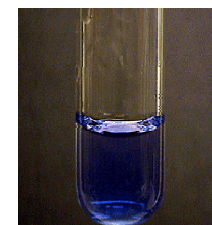
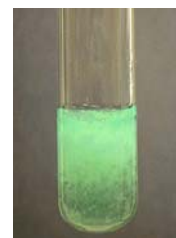
The solution may change color: see below.

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**colors of metal-water and
 metal-ammine $\text{Ni}(\text{II})$ complex ions**



green to **blue**



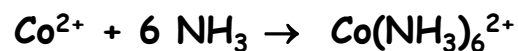
Note a little $\text{Ni}(\text{OH})_2$ ppt

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**colors of metal-water and
 metal-ammine complex ions**



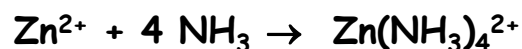
green to **blue**



pink to **yellow brown**



aqua to **dark blue**



colorless to **colorless**

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CATION ANALYSIS: summary

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Li	Be	Flame tests										B	C	N	O	F	Ne
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Rb	Sr ²⁺	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba ²⁺	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb ²⁺	Bi	Po	At	Rn

NH_4^+

Colored Ammine
Complexes

Amphoteric hydroxides/
Hydroxide complexes

Insoluble Hydroxides

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