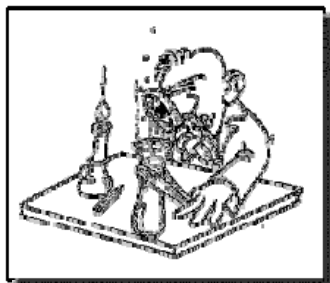




Chemistry BC2001x
Lab lecture 10
QUALITATIVE ANALYSIS II



Elimination Tests 5, 6, 7:

The formation and dissolution of precipitates and **Unknown A**

Long experiment, so this lecture will end early.

1

Elimination Tests 5, 6, 7:

The formation and dissolution of precipitates.

Asking, in effect, two questions:

Q1: Does a precipitate form, or not, when the specific cation reagent is added?

Q2: If a precipitate does form, is it soluble in strong acid, or not?

ET-6 is *not* actually carried out in this way, with the two steps **in this order**, but the underlying principles are the same. Read ET-6 carefully to see the distinction.

2

In effect, we are completing this chart (for all anions):

anion	(5) Ag ⁺ TEST		(6) Ca ²⁺ TEST		(7) Ba ²⁺ TEST	
	ppt?	dissolve?	ppt?	dissolve?	ppt?	dissolve?
CO ₃ ²⁻						
NO ₃ ⁻						
Cl ⁻						
SO ₃ ²⁻						
SO ₄ ²⁻						

3

**ET-5, ET-6, and ET-7:
Ag⁺, Ca²⁺ and Ba²⁺**

For most anions, solubility rules could be used to fill in the first column ("does ppt form?")

Two anions **not** included in rules given in rules:

F⁻ and **NO₂⁻**

Use your **OBSERVATIONS** for them

4

**ET-5, ET-6, and ET-7
Ag⁺, Ca²⁺ and Ba²⁺: Predictions**

Are carbonates soluble?

no, most are insoluble.

→ ppt will form with Ag⁺, Ba²⁺, and Ca²⁺

Are nitrates soluble?

yes, always. → No ppt will form.

Are chlorides soluble?

most are, but not salts with four cations:

Ag⁺, Cu⁺, Pb²⁺, and Hg₂²⁺

→ precipitate will form with Ag⁺,
but not with Ba²⁺ and Ca²⁺

5

**ET-5, ET-6, and ET-7
Ag⁺, Ca²⁺ and Ba²⁺: predictions (2)**

Are sulfites soluble?

no, most are insoluble.

→ ppt will form with Ag⁺, Ba²⁺, and Ca²⁺

Are sulfates soluble?

most are soluble, except Pb²⁺, Sr²⁺, Ba²⁺.

Ca²⁺, Ag⁺, Hg₂²⁺ sulfates slightly soluble

→ Definite ppt with Ba²⁺,
possible ppt with Ca²⁺ and Ag⁺
(depends on how much is added.)

6

**The formation and dissolution of precipitates:
predictions for some anions**

anion	(5) Ag ⁺ TEST		(6) Ca ²⁺ TEST		(7) Ba ²⁺ TEST	
	ppt?	dissolve?	ppt?	dissolve?	ppt?	dissolve?
CO ₃ ²⁻	Y		Y		Y	
NO ₃ ⁻	N		N		N	
Cl ⁻	Y		N		N	
SO ₃ ²⁻	Y		Y		Y	
SO ₄ ²⁻	?		?		Y	

7

**Will the precipitate dissolve in acid?
General rules**

Consider the possible reaction



["-?→" means the reaction may or may not proceed]

What will make this reaction proceed
(i.e. have a large K_{eq}, favoring products)?

First:

When will it definitely NOT proceed?

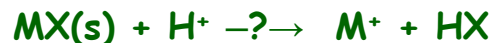
When HX is a strong acid!

→ halide salts do NOT dissolve in acid

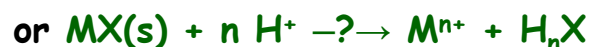
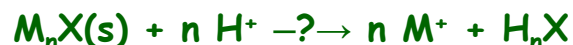
8

Will the precipitate dissolve in acid?

The reaction we consider is

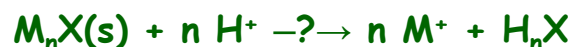


or if anion has charge X^{n-} , then $n H^+$'s add:



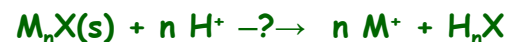
In strongly acidic solution, X^{n-} is **fully protonated** (unless H_nX is a strong acid)

equation used generically below:



9

Will the precipitate **dissolve in acid**?



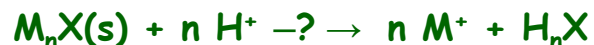
Dissolving the insoluble salt M_nX **competes** with forming the weak acid H_nX (H^+ and M^+ compete for X^{n-}).

What will make this reaction favor **products**, so the salt dissolves?

In general, both K_{sp} and K_a values are needed to answer this, but there are special cases where we can answer it without them.

10

Precipitates with some anions will **always dissolve** in acid



One property will cause this reaction to proceed 100%. What is this?

The acid H_nX is unstable!

Use **Le Chatelier's principle**:

if H_nX is destroyed, the equilibrium shifts to produce more H_nX ; this process continues until the salt dissolves completely!

11

Which precipitates will **always** dissolve in acid?

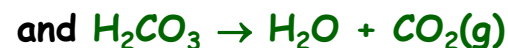
The salt dissolves if the acid H_nX is **unstable**.

Which acids are unstable?

from **ET-2**: H_2CO_3 and H_2SO_3

All **carbonates** and **sulfites** dissolve in acid.

Reaction (e.g. $BaCO_3$):



12

What about **volatile** acids? H_2S ?
 Will **sulfide** salts dissolve in acid?

Usually the answer is NO (a few sulfides will).

K_{sp} values for sulfides are VERY small.

Even though H_2S is quite weak, the reaction



proceeds VERY little.

The issue is the solubility of gas H_2S :
 usually $H_2S(aq)$ is so small so the solution
 is not **saturated**: thus $H_2S(g)$ will not form.

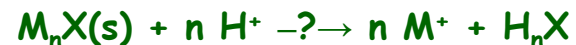
Evidence: **no rotten egg smell** !

13

ET-5, ET-6, ET-7: Summary

1) Will precipitate form with the test reagent?

2) If so, will it dissolve in strong acid?



NO if the salt's anion is conjugate to strong acid.

YES for **sulfite** salts and **carbonate** salts. Even
 with small K_{sp} values, they dissolve in strong acid,
 since the corresponding acids H_2X are unstable.

OTHERWISE, it depends on the K_{eq} value, which can
 be obtained by combining K_{sp} for the insoluble salt
 with K_a 's for the weak acid. See class notes.

14

(almost) completed partial chart

anion	(5) Ag ⁺ TEST		(6) Ca ²⁺ TEST		(7) Ba ²⁺ TEST	
	ppt?	dissolve?	ppt?	dissolve?	ppt?	dissolve?
CO ₃ ²⁻	Y	Y	Y	Y	Y	Y
NO ₃ ⁻	N	-	N	-	N	-
Cl ⁻	Y	N	N	-	N	-
SO ₃ ²⁻	Y	Y	Y	Y	Y	Y
SO ₄ ²⁻	?	?	?	?	Y	?

ET-6 actually done by adding CH_3COOH first,
 then adding Ca^{2+} to see if precipitate **forms in acidic solution**.

15