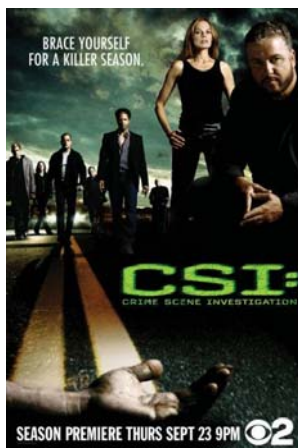


Chemistry BC2001x Lab lecture 9 QUALITATIVE ANALYSIS: Week I



1

ANALYTICAL CHEMISTRY

Quantitative experiments asked

"What is the value of...?"

Qualitative chemical analysis asks
"What is it?" Huge important question!

Many important applications:

forensic chemistry
environmental chemistry
food and cosmetics
pharmaceuticals

Many job opportunities



2

Overview of next few weeks' work

In a four-week series of experiments you will work with a limited set of **inorganic salts**

To identify a salt, you need to identify both the **cation** and the **anion**

Weeks 1-2: identifying anions.

First learn tests using **knowns**

Then determine an **unknown**

3

Overall strategy

Use physical and chemical properties
Color of salt or solution, reactivity...

Use careful logical argument

Use process of deduction

like the game "20 questions"

Make a tentative assignment, then

Verify with a specific ID test



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We focus on **eleven anions**

Location of the eleven anions according to their position on the periodic chart (oxyanions with parent)

14	15	16	17
CO_3^{2-}	NO_2^- NO_3^-		F^-
	PO_4^{3-}	S^{2-} SO_3^{2-} SO_4^{2-}	Cl^-
			Br^-
			I^-

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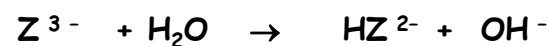
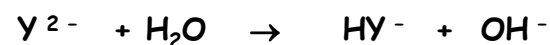
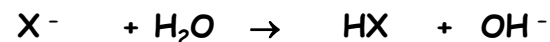
ELIMINATION TEST 1 (ET-1): Test for STRONGLY basic anions

Procedure: test with wide-range pH indicator paper. Look for $\text{pH} > 10$



Strongly basic means there is a large $[\text{OH}^-]$ in solution. **Where does this OH^- come from?**

The **anion** reacts with WATER:



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ELIMINATION TEST 1 (ET-1) Test for STRONGLY basic anions

Which anions are basic? Start with another question:

What are the six common strong acids? Know these!

HClO_4 (anion ClO_4^- not in our group)

HCl , HBr , HI , HNO_3 , H_2SO_4

The five anions conjugate to these acids are not even slightly basic!

Cl^- , Br^- , I^- , NO_3^- , HSO_4^-

note: ion conjugate to H_2SO_4 is HSO_4^- (not SO_4^{2-})

All the other anions in the test group are at least **slightly basic**: they are conjugate to **weak acids**.

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ELIMINATION TEST 1 (ET-1) Test for STRONGLY basic anions

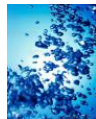
But which are **strongly basic**? The reaction of the anion with water proceeds significantly only if the conjugate acid is **quite weak**. Which of the eleven anions have very weak conjugate acids?

	Acid	K_a	Base	
strong	HCl etc.	very large	Cl^- etc.	not basic at all
moderately	HSO_4^-	1.2×10^{-2}	SO_4^{2-}	very
strong	HF	7.2×10^{-4}	F^-	weak
weak acids	HNO_2	4.5×10^{-4}	NO_2^-	weak bases
intermediate	HSO_3^-	6.2×10^{-8}	SO_3^{2-}	intermediate
very	HCO_3^-	4.7×10^{-11}	CO_3^{2-}	rather
weak	HPO_4^{2-}	4×10^{-13}	PO_4^{3-}	strong
weak acids	HS^-	1.3×10^{-13}	S^{2-}	weak bases

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ELIMINATION TEST 2 (ET-2)

Does the anion react to form a *volatile* or *unstable* acid when treated with strong acid?



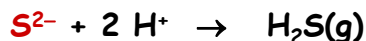
Procedure: treat with strong acid.

Look for formation of **gas**.

(H₂SO₄ used: no odor or competing reactions.)

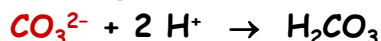
Positive tests with **S²⁻**, **CO₃²⁻**, **SO₃²⁻**, **NO₂⁻**

REACTIONS



H₂S(g) is **volatile**.

H₂S(g) is **colorless** and *smells* like rotten eggs



H₂CO₃ is **unstable** → H₂O + CO₂(g)

CO₂(g) is **colorless** and *odorless*

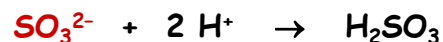


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ELIMINATION TEST 2 (ET-2)

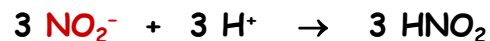
Does the anion react to form a *volatile* or *unstable* acid when treated with strong acid?

REACTIONS (continued)



H₂SO₃ is **unstable** → H₂O + SO₂(g)

SO₂(g) is **colorless**, with a sharp, choking *odor*



HNO₂ is **unstable** → H₃O⁺ + NO₃⁻ + 2 NO(g)

Then 2 NO(g) + O₂(g) → 2 NO₂(g)

NO₂(g) is **reddish-brown**; sharp, acrid *odor*

A positive ET-2 test thus identifies the anion also.

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OXIDATION-REDUCTION CHEMISTRY: ELECTRON TRANSFER REACTIONS

REVIEW

An **electron donor** is a **reducing agent**.

It loses n electrons, and is itself **oxidized**:



If M loses electrons *easily* it is a **strong** reducing agent

An **electron acceptor** is an **oxidizing agent**.

It gains m electrons, and is itself **reduced**:



If X gains electrons *easily* it is a **strong** oxidizing agent.

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OXIDATION-REDUCTION CHEMISTRY: ELECTRON TRANSFER REACTIONS

Loss of electrons is **oxidation**. (LEO)

Gain of electrons is **reduction**. (GER)

Electrons appear in half-reactions but **never appear in the net chemical equation**.

Electrons are always transferred **directly** between the reacting species in solution.

Since you have not yet studied how to write half-reactions, most are supplied in the manual as needed for this week's experiment; your job is to **combine them** properly into net reactions.

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OXIDATION-REDUCTION CHEMISTRY: ELECTRON TRANSFER REACTIONS

Combining half-reactions into net reactions:

Electrons are not free species in aqueous solution so **no electrons in the balanced overall reaction**

Multiply the half reactions and add so that the electrons lost in the oxidation exactly cancel those gained in the reduction.

Sometimes the combined reaction has H^+ or OH^- or H_2O (or even something else) on both sides: eliminate the excess so each appears as reactant or product only.

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ELIMINATION TEST 3 (ET-3) Test for STRONG reducing agents

Procedure: Take solution containing anion, acidify, add $FeCl_3$, then add $K_3Fe(CN)_6$.
Look for precipitate of *Prussian blue*:



Look at reactant: $K_3Fe(CN)_6 = 3 K^+$ and $Fe(CN)_6^{3-}$

$Fe(CN)_6^{3-}$ is a **complex ion** (metal + ligands)

Six CN^- ligands are tightly bound to the core Fe^{3+}

The reduction happens within this complex ion:



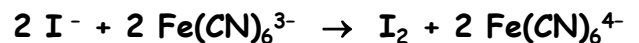
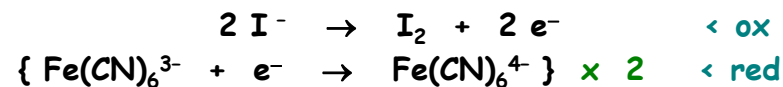
The iron in this complex is now Fe^{2+}

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ELIMINATION TEST 3 (ET-3) Test for STRONG reducing agents

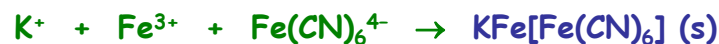
Strong reducing agents: I^- , S^{2-} , SO_3^{2-} , NO_2^-

Redox equations. Start with the half-reactions:



all species are in solution, aqueous

Formation of **Prussian Blue**:



an insoluble potassium salt!

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ELIMINATION TEST 4 (ET-4) Test for STRONG oxidizing agents

Procedure: Add saturated $MnCl_2$ in 12 M HCl.
Warm the solution. Look for **yellow** or **brown** color.

Strong oxidizing agents: NO_2^- and NO_3^-

Mn^{2+} is oxidized to Mn^{3+}

Half-reaction:



What is the reduction involving NO_2^- or NO_3^- ?
see your lab manual

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