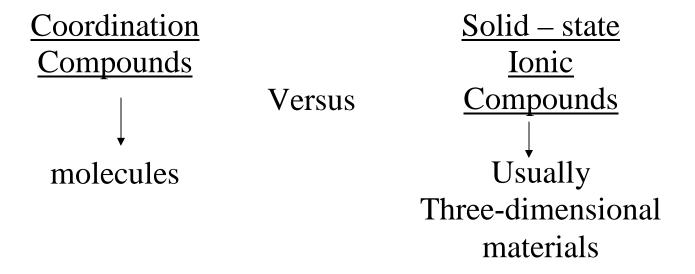
Chapter 5

Chemistry of Selected Anions

Anions are very important ligands in molecules as well as solids.



<u>Ligand</u> – an atom or molecule that coordinates to a metal ion (where the word "coordinates" means to attach in a bonding sense).

Classifications of anions

1. Simple anions

 O^{2-} , F-, CN- etc.

2. OXO anions (discrete)

NO₃-, SO₄²-, CO₃²- etc.,

3. OXO anions (polynuclear or polymeric)

"SiO₂ based"

"BO₃ based"

Silicates

Borates

PO₄ based

Phosphates

4. Complex anions which are themselves metal complexes

 $[AlCl_4]^-$, $[PF_6]^-$, $[TaF_6]^-$, $[Fe(CN)_6]^{3-}$, etc.,

Some of the anions can exist freely in solution, while others exist only in the solid state

For example:

O²- only in solid state – unstable in solution

Cl exists in solution as well as the solid state

Main Categories of Anions

- A. Oxides, Hydroxides, Alkoxides (Discrete, molecular species)
- B. Polymeric Oxides(also includes larger polynuclear ones)
- C. Halogen Containing Anions
- D. Sulfide and Hydrosulfide Anions

Oxides, Hydroxides, Alkoxides

O²- is unstable in solution whereas OH and OR (alkoxides) can exist in solution

$$O^{2-}(s) + H_2O \longrightarrow 2OH^-(aq)$$
 $K_{eq} > 10^{22}$

Example:

$$CaO + H_2O \rightarrow Ca^{2+}(aq) + 2OH^{-}$$

Some oxides are not soluble in water so these will not react of course!

They can be dissolved in acids however:

$$MgO(s) + 2H^{+}(aq) \rightarrow Mg^{2+}(aq) + H_2O$$

Oxides

ALL ELEMENTS except Noble gases form oxides <u>Three Categories</u>:

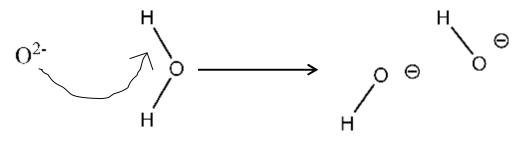
- Basic. Ionic oxides (these form with metals)
- Acidic. Covalent oxides
 (these form with non-metals, metalloids, some metals also)
- Amphoteric. Can be ionic or covalent (these form with metals)

Basic or Ionic Oxides

- Form OH in H₂O
- Groups I, IIA (except Be) some transition metals

Examples:

$$Na_2O(s) + H_2O \rightarrow 2 NaOH(aq)$$



$$MgO(s) + H_2O \rightarrow Mg(OH)_2(s)$$
 (insoluble hydroxide)

Acidic or Covalent Oxides

- Form acids in water
- All non-metals except noble gases. SO₃, SO₂, NO,
- NO₂, SiO₂, Sb₂O₃, etc., and some transition elements

Examples:

$$SO_3 + H_2O \rightarrow H_2SO_4(aq)$$

$$CrO_3 + H_2O \rightarrow H_2CrO_4(aq)$$

Amphoteric Oxides

- Can be either acidic or basic
- Al, Ga, Sn, Pb and most transition metals
- They can neutralize acid or base

Example:
$$Al_2O_3$$
(amphoteric)

Reacts with acids:

a.
$$Al_2O_3(s) + 6H^+(aq) + 9H_2O \rightarrow 2[Al(H_2O)_6]^{3+}(aq)$$

and Reacts with bases:

b.
$$Al_2O_3(s) + 2OH^-(aq) + 7 H_2O \rightarrow 2[Al(H_2O)_2 (OH)_4]^-(aq)$$

In reaction a, Al₂O₃ is a base In reaction b, Al₂O₃ is an acid

- Q. How can you predict if a transition metal oxide will be acidic, basic or amphoteric?
- **A.** There are Two Trends

Trend 1

The <u>higher</u> the <u>oxidation</u> <u>state</u> of the metal, the more covalent (acidic) it will be.

Trend 2

The <u>lower</u> the <u>oxidation</u> <u>state</u> of the metal, the more ionic (basic) it will be.

Consider: Cr⁺²O, Cr₂⁺³O₃, Cr⁺⁶O₃ The most ionic is CrO (lowest ox. state) The most covalent is CrO₃ (highest ox. state)

• • CrO is basic, CrO₃ is acidic and Cr₂O₃ is amphoteric

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