Chapter 5

Chemistry of Selected Anions

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

Coordination Compounds		**Solid – state Ionic Compounds**
↓	Versus	↓
molecules		Usually Three-dimensional materials

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

<u>Classifications of anions</u>

1. **Simple anions**
   O^{2-}, F^-, CN^- etc.

2. **Oxo anions (discrete)**
   NO_3^-, SO_4^{2-}, CO_3^{2-} etc.,

3. **Oxp anions (polynuclear or polymeric)**
   "SiO_2^- based" "BO_3^- based"
   Silicates Borates
   PO_4^- based
   Phosphates

4. **Complex anions which are themselves metal complexes**
   $[AlCl_4]^-$, $[PF_6]^-$, $[TaF_6]^-$, $[Fe(CN)_6]^{3-}$, *etc*.,

<u>Some of the anions can exist freely in solution, while others exist only in the solid state</u>

For example:

O^{2-} 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

O^{2-} is unstable in solution whereas OH^- and OR^- (alkoxides) can exist in solution

$$O^{2-}(s) + H_2O \rightleftharpoons 2\,OH^-(aq)$$

$$K_{eq} > 10^{22}$$

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

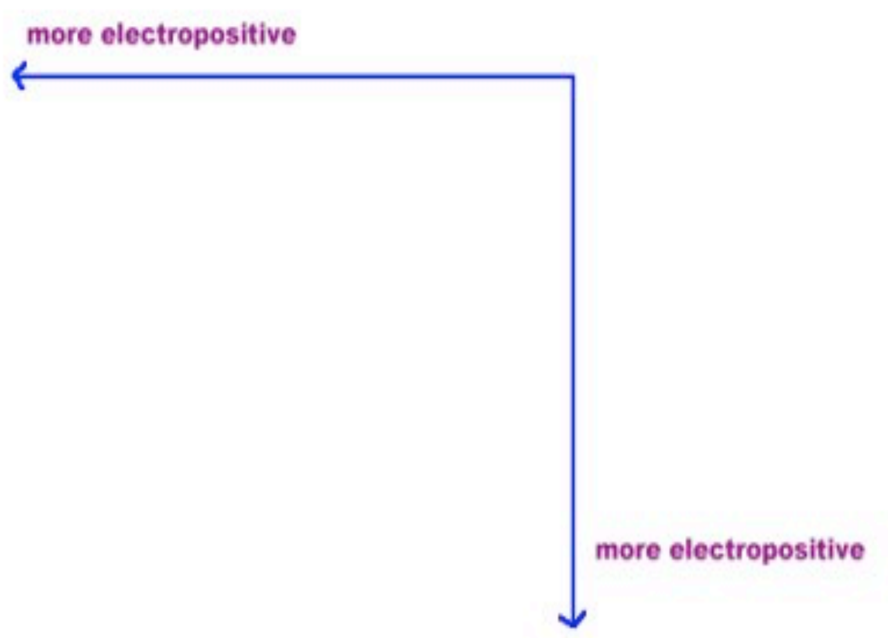
ALL ELEMENTS **except Noble gases form oxides**

Three Categories:

- 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)

General Rules

In general, the electropositive character of the oxide's central atom will determne whether the oxide will be acidic or basic. The more electropositive the central atom the more basic the oxide. The more electronegative the central atom, the more acidic the oxide. Electropositive character increases from right to left across the periodic table and increases down the column.



A resultant borderline between basic and acidic oxides occurs along a diagonal.

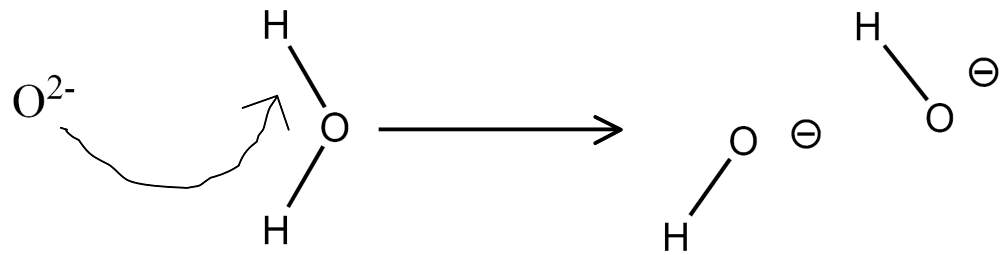
Properties of *s*- and *p*-Block Elements						
Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl
K	Ca	Ga	Ge	As	Se	Br
Rb	Sr	In	Sn	Sb	Te	I
Cs	Ba	Tl	Pb	Bi	Po	At
Basic Oxides			Amphoteric Oxides		Acidic Oxides	

Basic or Ionic Oxides

- Form OH^- in H_2O
- 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.
- SO_3, SO_2, NO,
- NO_2, SiO_2, Sb_2O_3, 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, Al_2O_3 is a base

In reaction b, Al_2O_3 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 higher the oxidation state of the metal, the more covalent (acidic) it will be.

Trend 2

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

Consider: $Cr^{+2}O$, $Cr_2{}^{+3}O_3$, $Cr^{+6}O_3$

The most ionic is CrO (lowest oxidation state)

The most covalent is CrO_3 (highest oxidation state)

∴ CrO is basic, CrO_3 is acidic and Cr_2O_3 is amphoteric

There are three nonmetal oxides from the upper right portion of the periodic table, CO, NO, and N_2O, which have such low oxidation numbers for the central atom that they give neutral aqueous solutions.

Since the acidity of a cation rises rapidly with charge, *d*-block elements which exhibit a wide variety of oxidation numbers may have one or more oxides that exhibit only basic properties and one or more oxides that exhibit only acidic properties. The higher the oxidation number the more acidic the corresponding oxide. Chromium is an example of such an element.

Oxide	Oxidation Number	Category
CrO	Cr^{2+}	basic
Cr_2O_3	Cr^{3+}	amphoteric
CrO_3	Cr^{6+}	acidic

Basic oxides react with acidic oxides to produce salts of oxo anions.

Since there is no water involved salts of oxo anions which are too basic to persist in water can be formed. These reactions of acidic and basic anions have important practical applications such as in the control of gaseous acidic oxides that when released into the atmosphere result in acid rain.

$$Ca(OH)_2 + SO_2 + 1/2\ O_2 \longrightarrow CaSO_4 + H_2O$$

These reactions are also used in the production of materials such as concrete, glass and ceramics.

Basic Oxides

PERIODIC TABLE OF ELEMENTS

some basic oxides throughout transition series

	1	2											3	4	5	6	7	8
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Hn (262)	106 Unh (263)	107 Ns (262)	108 Hs (265)	109 Mt (266)									

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (256)

PERIODIC TABLE OF ELEMENTS

acidic oxides

Some acidic oxides throughout transition series

	1	2											3	4	5	6	7	8
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Hn (262)	106 Unh (263)	107 Ns (262)	108 Hs (265)	109 Mt (266)									

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (256)

Amphoteric Oxides

PERIODIC TABLE OF ELEMENTS

many oxides of transition elements are amphoteric

Period	1	2											3	4	5	6	7	8
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Hn (262)	106 Unh (263)	107 Ns (262)	108 Hs (265)	109 Mt (266)									

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (256)

THESE ARE <u>JUST</u> BASIC TRENDS BECAUSE TRANSITION METALS CAN BE BOTH BASIC AND ACIDIC

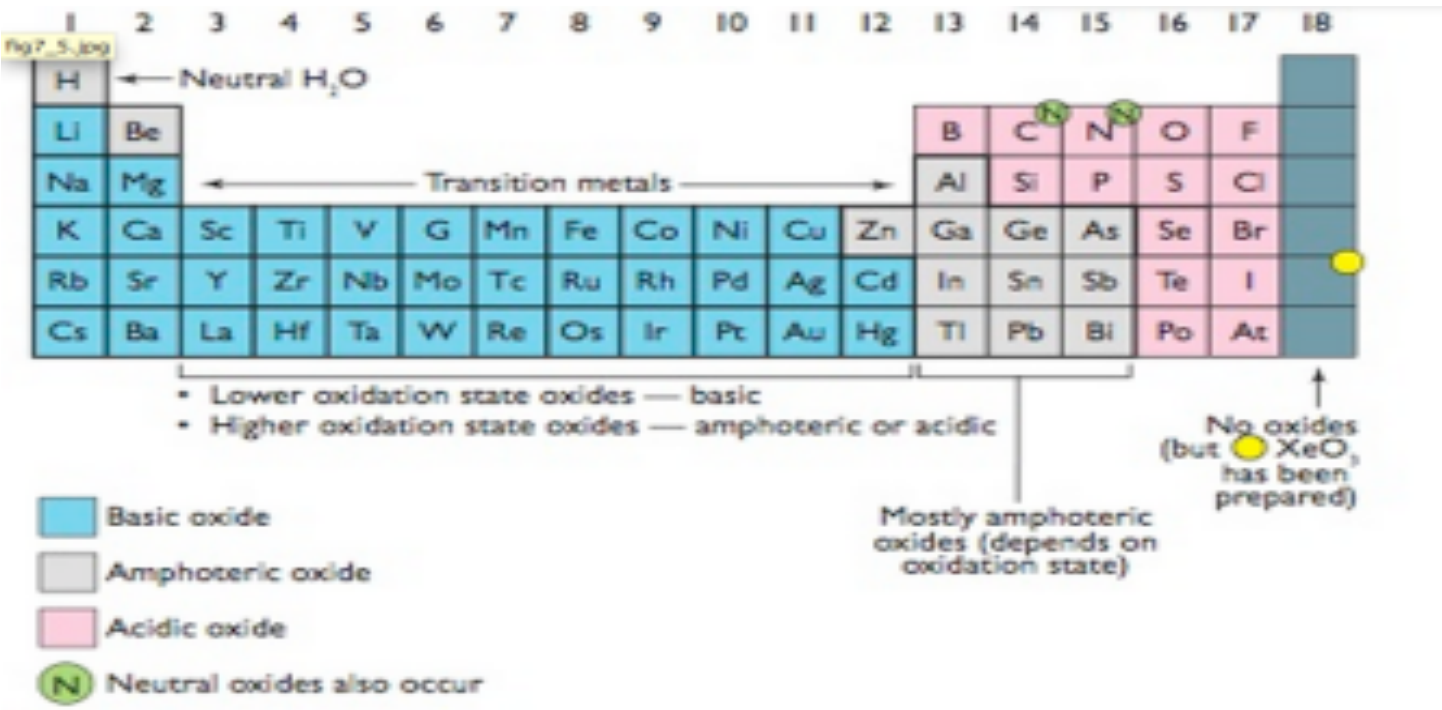
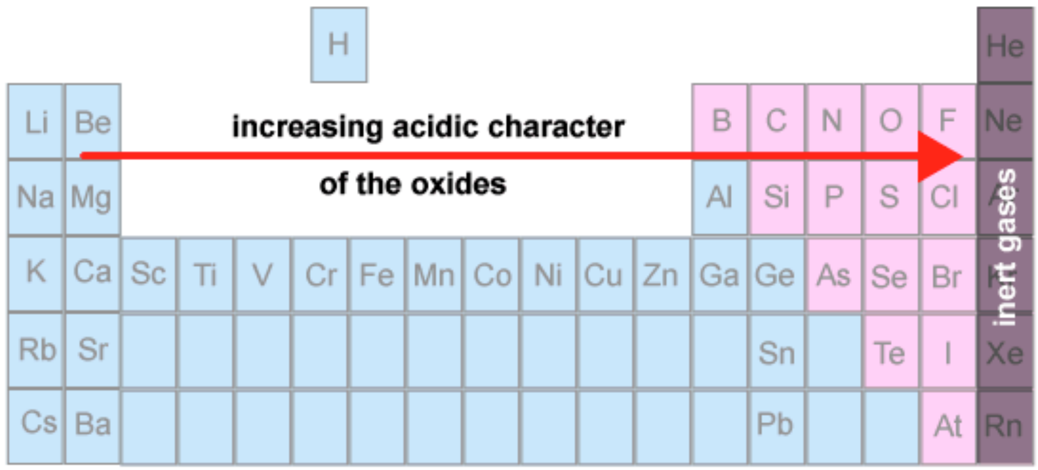


Figure 7.5
The periodic table shows that metallic oxides are mostly basic and that non-metallic oxides are mostly acidic. The elements with amphoteric oxides lie between these two groupings.

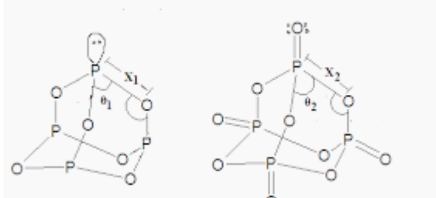


- Metal oxides are basic
- Aluminium oxide is amphoteric (reacts with both acids and bases)
- Non-metal oxides are acidic (they may also be referred to as 'acid anhydrides')
- Certain non-metal oxides do not display any acid - base character - eg N_2O and CO

Summary of the period 3 oxides

	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10} (or P_4O_6)	SO_3 (or SO_2)	Cl_2O_7
Adding H2O	$Na_2O + H_2O \rightarrow 2NaOH$	$MgO + H_2O \rightarrow Mg(OH)_2$	Insoluble	Insoluble	$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$	$SO_3 + H_2O \rightarrow H_2SO_4$	$Cl_2O_7 + H_2O \rightarrow HClO_4$
Adding HCl	$Na_2O + H^+ \rightarrow 2Na^+ + H_2O$	$MgO + 2H^+ \rightarrow Mg^{2+} + H_2O$	$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$	No reaction	No reaction	No reaction	No reaction
Add NaOH	No reaction	No reaction	$Al_2O_3 + 2OH^- + 3H_2O \rightarrow 2Al(OH)_4$	$SiO_2 + 2OH^- \rightarrow SiO_3^{2-} + H_2O$	$P_4O_{10} + 12OH^- \rightarrow 4PO_4^{3-} + 6H_2O$	$SO_3 + OH^- \rightarrow SO_4^{2-} + H_2O$	$Cl_2O_7 + OH^- \rightarrow 2ClO_4^- + H_2O$
Nature	Basic Oxide	Basic Oxide	Amphoteric Oxide	Acidic Oxide	Acidic Oxide	Acidic Oxide	Acidic Oxide

comment Comparing the two compounds P_4O_6 and P_4O_{10} phosphorus is +5 state in P_4O_{10} and +3 state in P_4O_6 so P_4O_{10} is more acidic.



Phosphorous trioxide P_4O_6 Phosphorous pentaoxide P_4O_{10}

Hydroxides

$$M^{+}OH^{-}_{(s)} + nH_2O \rightarrow M^{+}_{(aq)} + OH^{-}_{(aq)}$$

for metals with more ionic bonds → Base

$$MOH + nH_2O \rightleftharpoons MO^{-}_{(aq)} + H_3O^{+}_{(aq)}$$

for more covalent M-O bonds of the non-metals → Acid

and Amphoteric Hydroxides also exist

Alkoxides

The basic formula of an alkoxide is OR^- where R is an organic group such as an alkyl group.

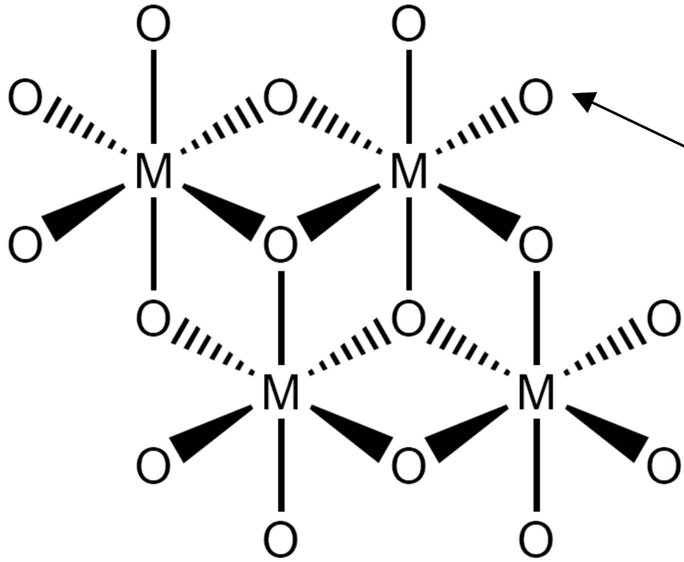
They are very reactive in water and hydrolyze quickly… very basic

$$OR^{-} + H_2O \rightleftharpoons OH^{-} + ROH$$

(forms an alcohol)

$M(OR)_4$ is a common metal alkoxide type of compound (or we also say "complex").
e.g., $Ti(OR)_4$

It has an interesting molecular structure that stabilizes the molecule.

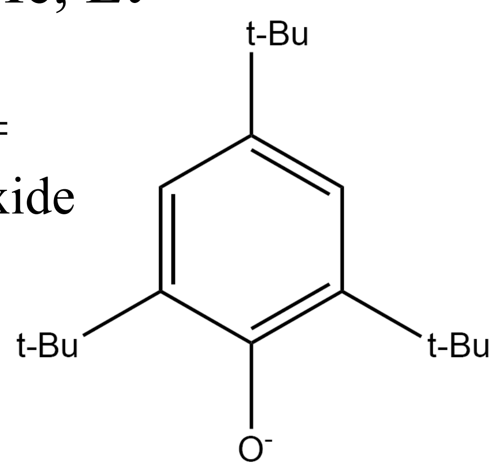


These represent OR^- groups

the more bulky R groups on OR^- ligands lead to compounds with low coordination numbers

$M(OR)_4$ when R = Me, Et

"$M(OR)_2$" when R =
2,3,5-tritetrabutylphenoxide



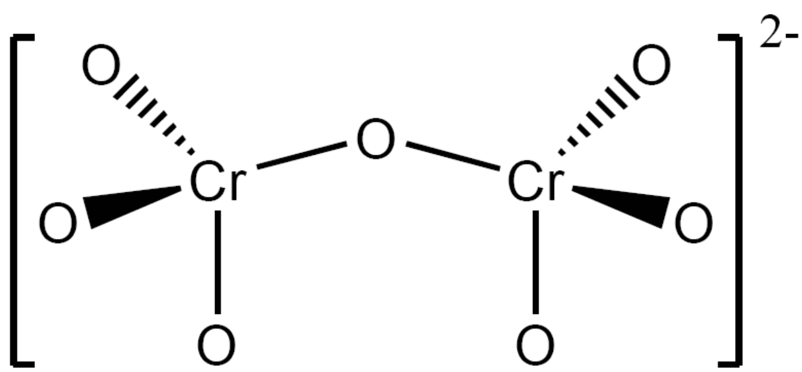
Polynuclear or Polymeric Oxides/Hydroxides

- dimers, trimers, cages, etc.
- cyclic structures
- chains
- sheets

Polynuclear Oxo Anions

oxygen atoms shared between various polyhedra

Ex #1 dichromate

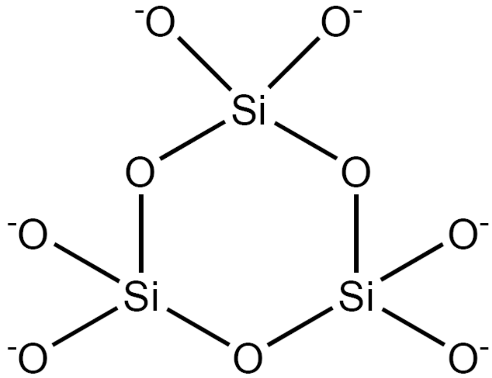


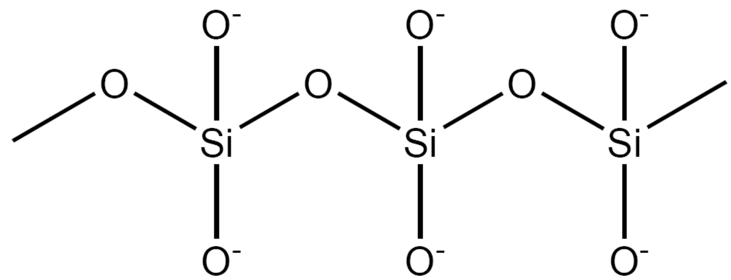
Dimer

$Cr_2O_7^{2-}$

(two tetrahedra sharing one atom)

Ex #2





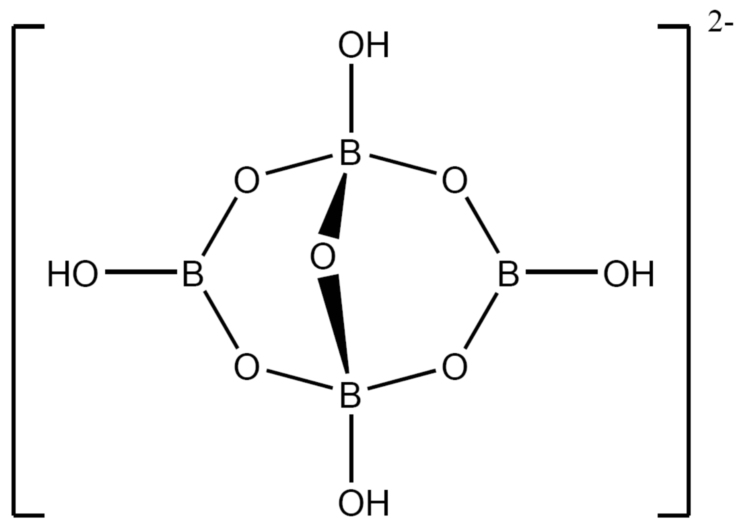
(tetrahedra sharing an edge)

<u>**Ring anion**</u>
$Si_3O_9^{6-}$

<u>**Chain**</u>
SiO_3^{2-}

Ex #3

<u>**tetramer**</u>
$B_4O_5(OH)_4^{2-}$



Common anion in borates

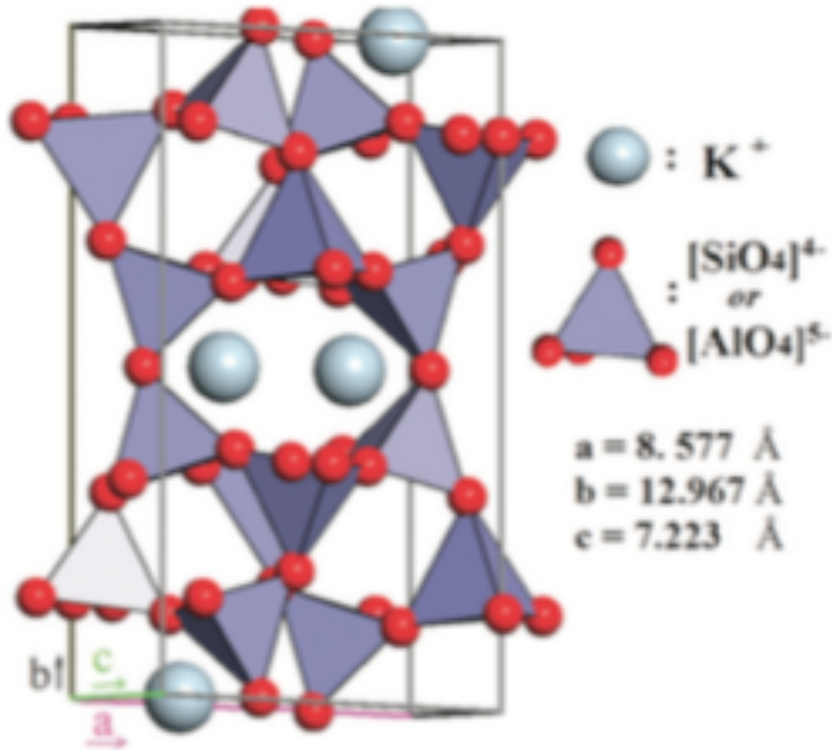
Basic Idea:

- Silicates are minerals composed of different types of shared tetrahedral SiO_4 units
- Borates are minerals in the same vein, but with BO_4 units shared in various ways

The structure that results is based on a complicated interplay of concentrations, pH, temperature and pressure (which affect solubilities).

- Eventually, if all oxygen atoms are shared in a SiO_4^{n-}, solid, it becomes silica, SiO_2

- replace some Si^{4+} ions with Al^{3+}, and it is possible to make structures like the silicates, except now there is an anion charge:
  "SiO_2" neutral
  "$SiAlO_2$" is negatively charged



-

→ **Zeolites**

$[(Al,Si)O_2]_n$ frameworks

Microporous Minerals with open frameworks that can allow molecules to pass through

Ion exchangers (solution)

Molecular sieves (gas)

Catlaysts

Basic composition of Zeolites is:

$$M_{x/n}[(AlO_2)_x(SiO_2)_y] \cdot z\,H_2O$$

number of AlO_2^+ units

charge of metal cation

number of SiO_2 units

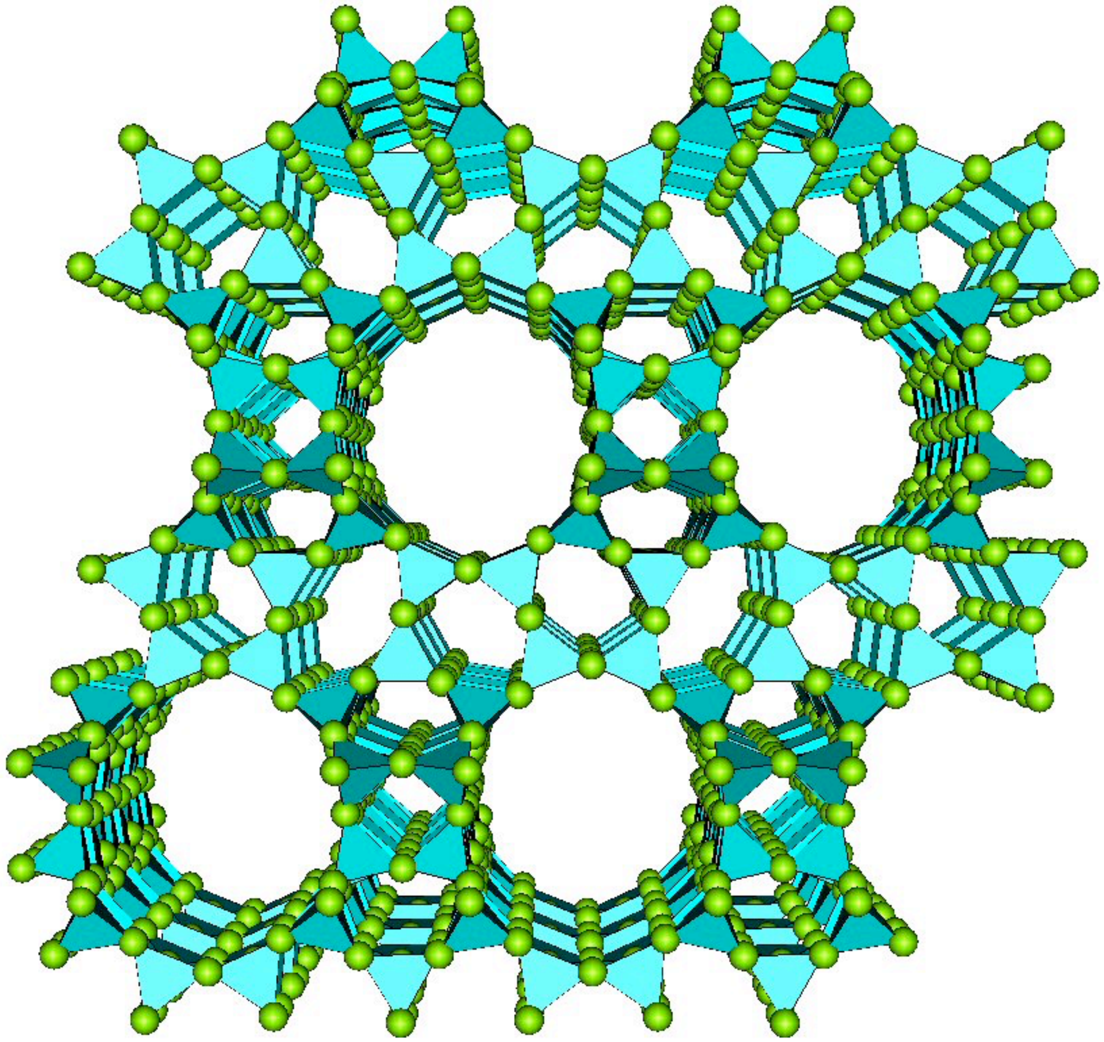
z – degree of hydration

lots of water can fill void space

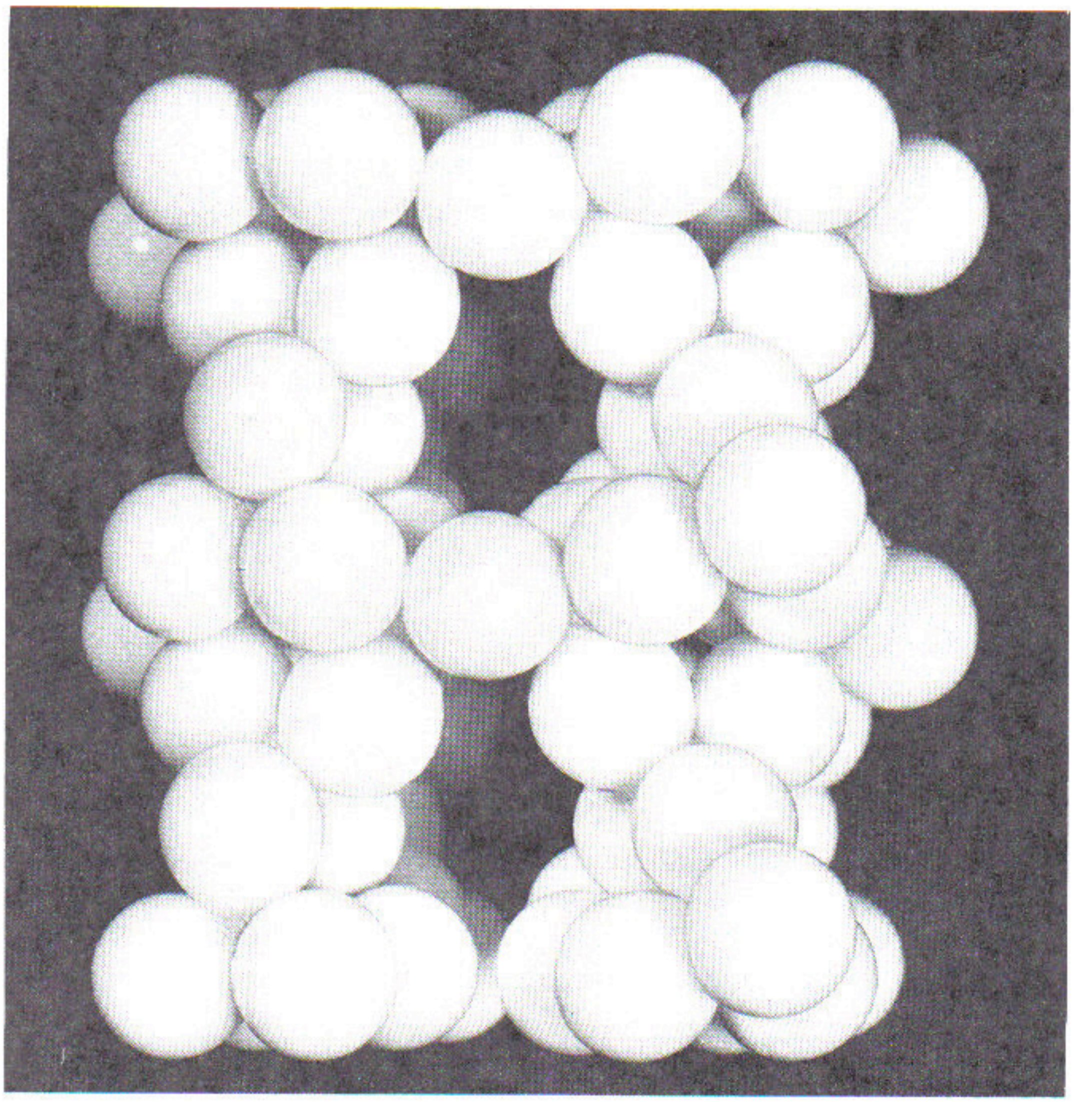
Zeolites are hydrated aluminosilicate minerals made from interlinked tetrahedra of alumina (AlO_4) and silica (SiO_4). In simpler words, they're solids with a relatively open, three-dimensional crystal

Zeolites are very stable solids that resist the kinds of environmental conditions that challenge many other materials. High temperatures don't bother them because they have relatively high melting points (over 1000°C), and they don't burn. They also resist high pressures, don't disssolve in water or other inorganic solvents, and don't oxidize in the air.

An important use for zeolites is as catalysts in drug (pharmaceutical) production and in the petrochemical industry, where they're used in **catalytic crackers** to break large hydrocarbon molecules into gasoline, diesel, kerosene, waxes and all kinds of other byproducts of petroleum. Again, it's the porous structure of zeolites that proves important. The many pores in a zeolite's open structure are like millions of tiny test tubes where atoms and molecules become trapped and chemical reactions readily take place. Since the pores in a particular zeolite are of a fixed size and shape, zeolite catalysts can work selectively on certain molecules, which is why they're sometimes referred to as **shape-selective catalysts** (they can select the molecules they work on in other ways beside shape and size, however). Like all catalysts, zeolites are reusable over and over again. Structures built from the elements aluminum, oxygen, and silicon, with alkali or alkaline-Earth metals (such as sodium, potassium, and magnesium) plus water molecules trapped in the gaps between them. Zeolites form with many different crystalline structures, which have large open pores (sometimes referred to as cavities) in a very regular arrangement and roughly the same size as small molecules.

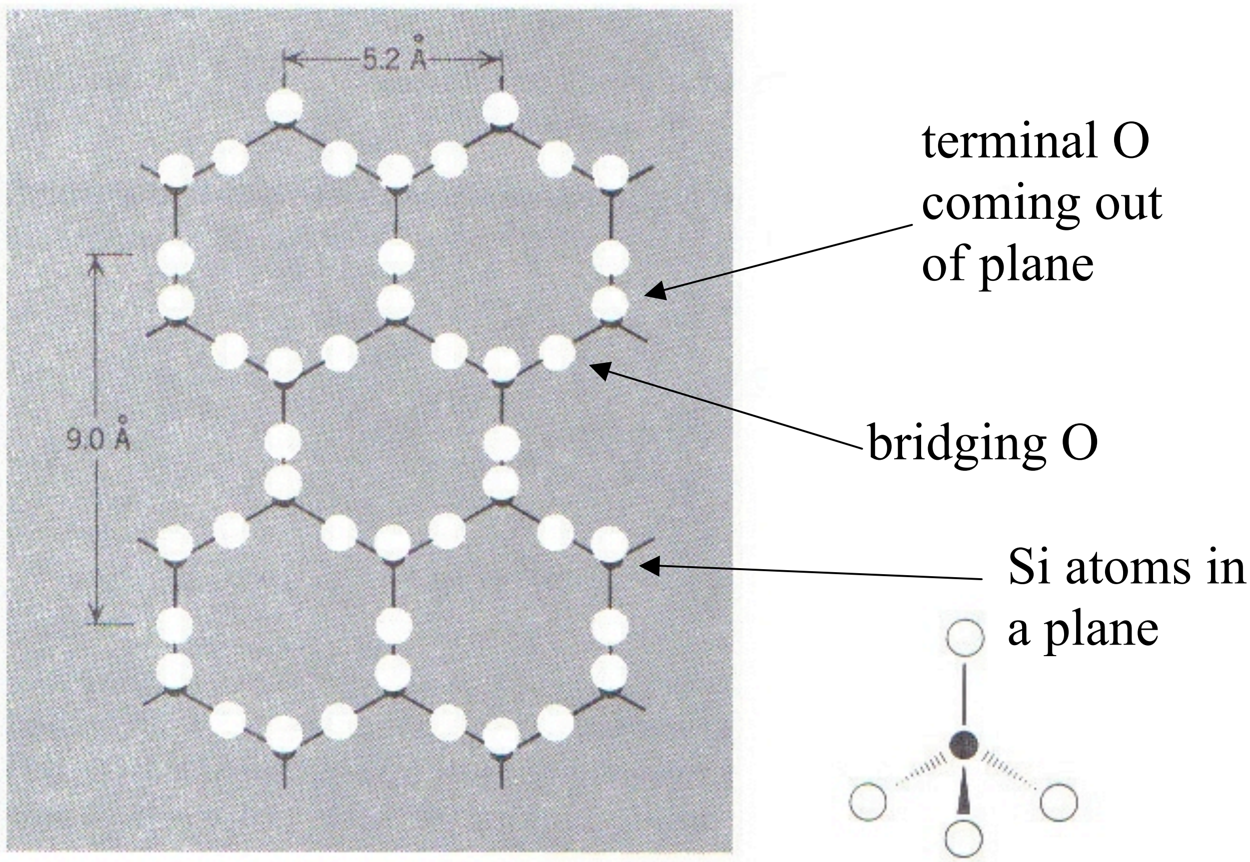


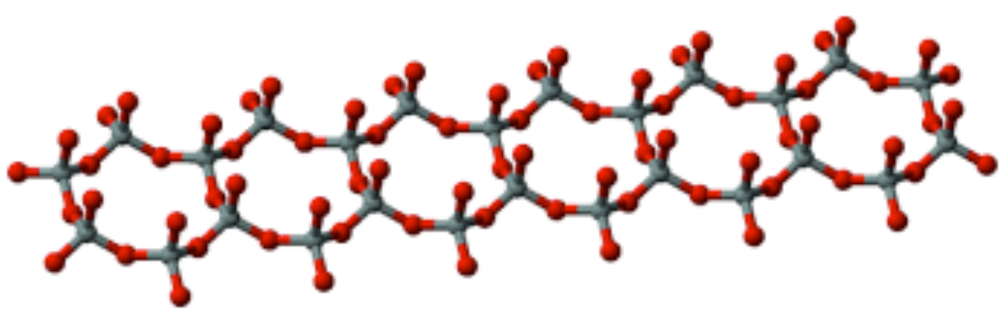
Model of a zeolite showing the channels in the structure. The spheres are O atoms. The Si and Al atoms lie at the centers of the O_4 tetrahedra and cannot be seen



$Si_2O_5^{2-}$ sheets

Si atoms are in a plane connected by 3 oxygen atoms to give a hexagonal motif
one oxygen on each Si is not used to bridge





sheets are bonded to cations between the layers
…. mica and talc for example

Polynuclear Oxo Anions continued

"Polyoxoanions" of Transition Metals

V^{V}, Nb^{V}, Ta^{V}, Mo^{VI}, W^{VI}

form anions with shared MO_6 octahedra where corners and edges are shared

Excellent example is $[CrMo_6O_{24}H_6]^{3-}$

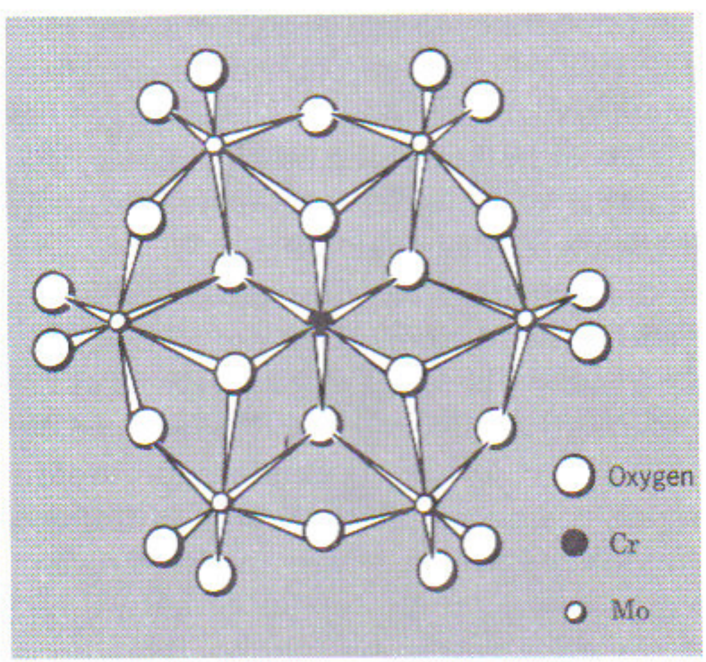
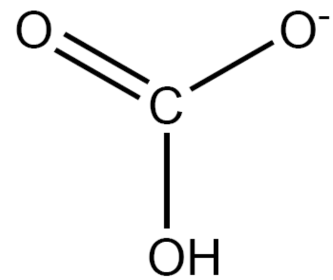


Figure 5-5 The structure of $[CrMo_6O_{24}H_6]^{3-}$. The hydrogen atoms are probably bound to oxygen atoms of the central octahedron.

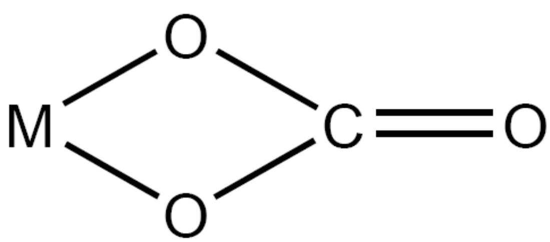
Miscellaneous oxo anions that are worth mentioning specifically because they are ubiquitious are as follows:

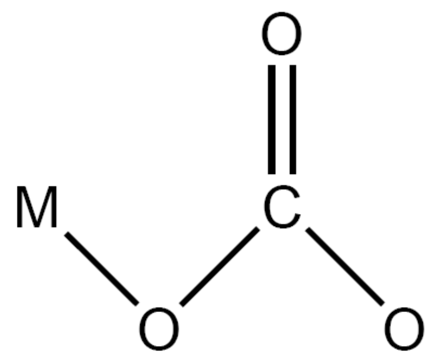
<u>Carbon-based</u>

CO_3^{2-} HCO_3^-



coordination modes:

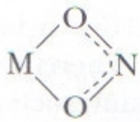




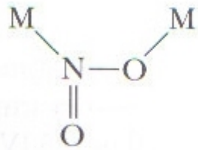
<u>Nitrogen-based</u>

NO_2^- nitrite NO_3^- nitrate

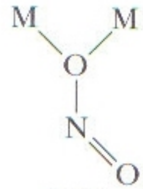
Various binding modes are depicted on page 152-153 of textbook



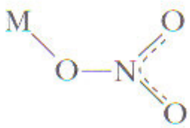
5-X



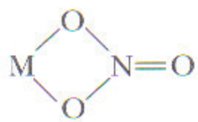
5-XI



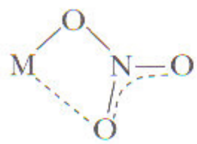
5-XII



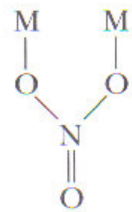
5-XIII



5-XIV



5-XV

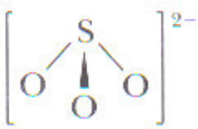


5-XVI

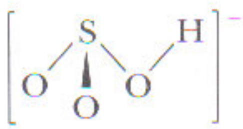
<u>Sulfur-based</u>

SO_3^{2-} sulfite; HSO_3^- bisulfite

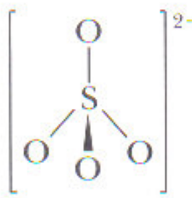
SO_4^{2-} sulfate; HSO_4^- bisulfate



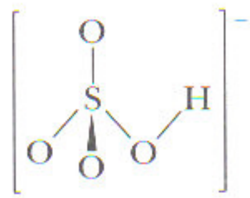
5-XVII



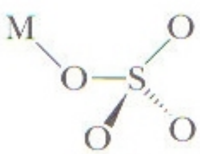
5-XVIII



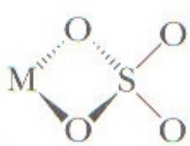
5-XIX



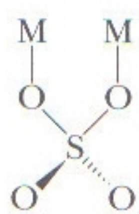
5-XX



5-XXI



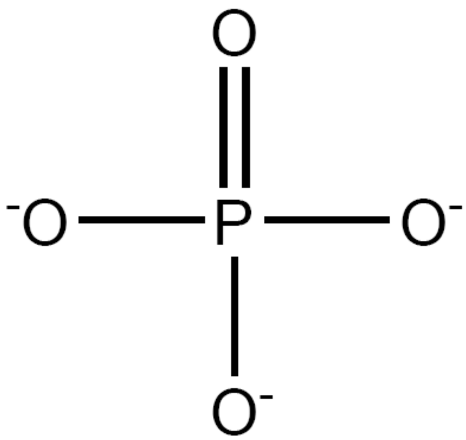
5-XXII



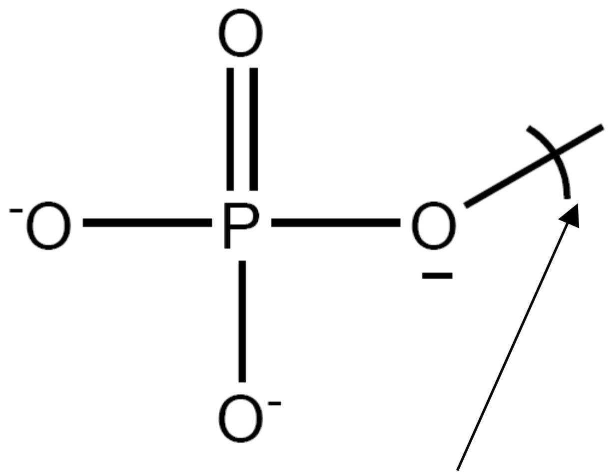
5-XXIII

Phosphates

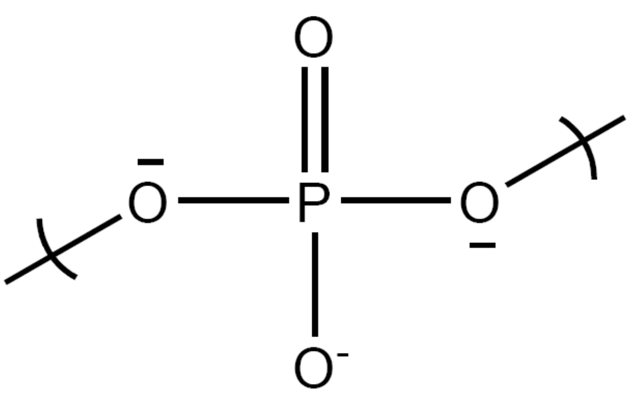
Also important in chemistry as discrete anions and in condensed (polymeric) phases as minerals



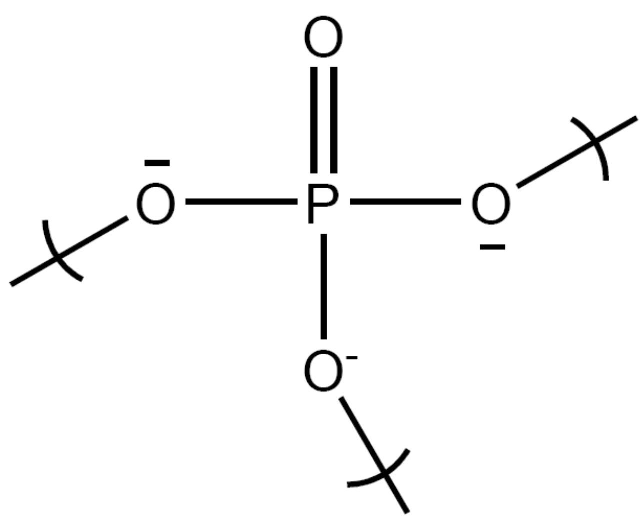
PO_4^{3-}
(one of four resonance forms)



binds as an end unit at one O

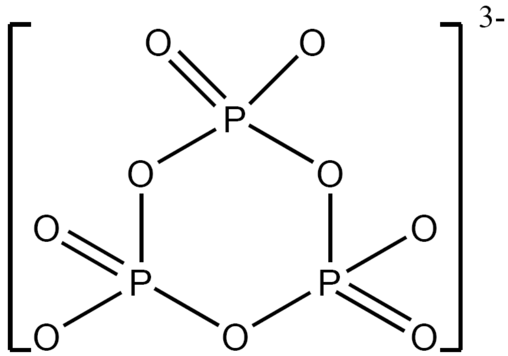


binds as a middle unit

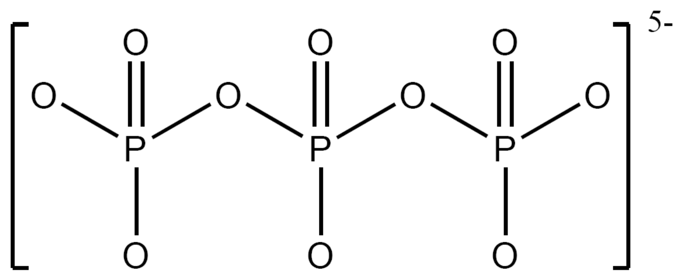


binds as a branching unit

These "Building Blocks" can assemble into linear or cyclic structures



$P_3O_9^{3-}$
metaphosphates



$P_3O_{10}^{5-}$
polyphosphates

widely used as water softeners due to their ability to stabilize Ca^{2+}, Mg^{2+} and other ions that make water "hard" ($MgCO_3$, $CaCO_3$ scum)

<u>Other types of Oxo Anions</u>

- Halogen-Containing Anions
  Halogen-Oxides
  (1) XO_3^- halates (X formal ox. state = ?)
  e.g. ClO_3^- chlorate
  (2) XO_4^- perhalates (X formal ox. state = ?)
  ClO_4^- perchlorate is most well-known

XO_4^- not particularly stable, especially as in the perchlorate anion, ClO_4^-

→ these are strong oxidizing agents stabilized in water, dangerous when dry and especially with organic compounds around

- Transition Metal Oxides (Discrete)

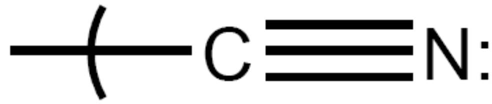
Tetrahedral MO_4^{n-} is very common for the highest oxidation state of the metal (or next to highest)

e.g.	OsO_4^-	$Os^?$	← What is formal ox. state?
	ReO_4^-	$Re^?$	←
Excellent oxidizing agents!	MnO_4^-	$Mn^?$	
	CrO_4^-	$Cr^?$	

<u>Halides and "Pseudohalides"</u>

- Pseudohalides such as CN^- act like halides OCN^-, SCN^- (all are good ligands)

Most important one is cyanide anion CN^-



Binds through C atom first

- Halides - ionic versus covalent – ionic are discussed in Chapter 5 (covalent analogs are in Chapter 20) ionic halides are with metals in +1, +2, +3 oxidation states

Sulfide and Hydrosulfide

- S^{2-} Ionic sulfide compounds are formed with alkali and alkaline earth (they are not stable in H_2O)

- S_n^{2-} polysulfides very important ligands for transition metals

Complex Anions

Complex Halides

$$AlCl_3 + Cl^- \rightleftharpoons AlCl_4^-$$

Lewis Acid ($AlCl_3$)   Lewis Base (Cl^-)

$$PF_5 + F^- \rightleftharpoons PF_6^-$$

general stability is F > Cl > Br > I
due to strength of A-F
vs A-Cl interactions
vs A-Br
vs A-I

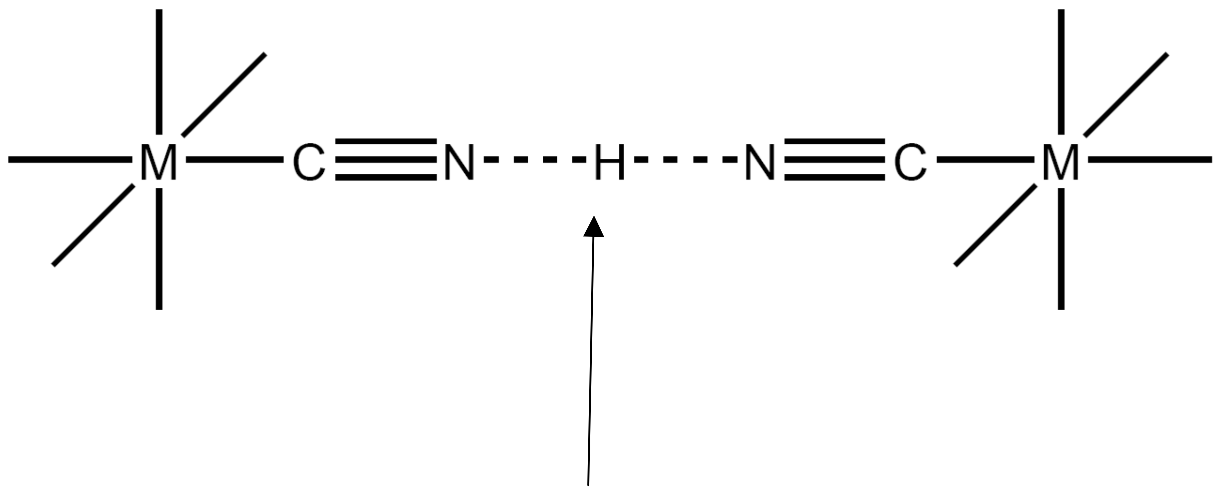
<u>Complex Transition Metal Anions</u>

CN^- forms many complex anions in a variety of oxidation states from low to high

$[Fe^{II}(CN)_6]^{4-}$ versus $[Mo^{V}(CN)_8]^{3-}$

Most of these anions are quite stable in H_2O, and, indeed, the acid form of some of them can be made, without releasing HCN.

For example $H_4[Fe(CN)_6]$ exists



H^+ is stabilized by H-bonding between molecules