Chapter 5

Chemistry of Selected Anions

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

Coordination Compounds	Versus	Solid – state Ionic Compounds
↓		↓
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).

Classifications of anions

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

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

3. **OXO 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*.,

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

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:

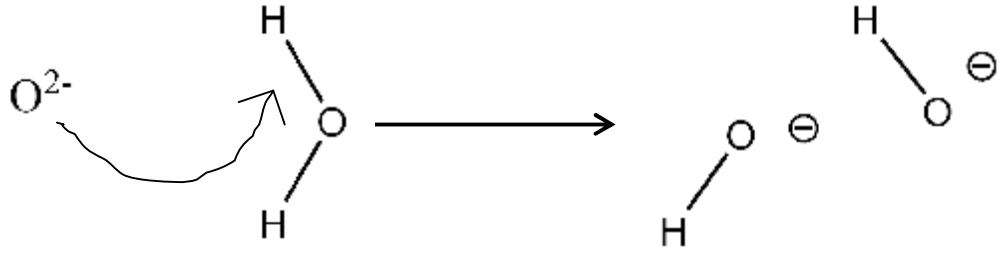
- Basic. Ionic oxides
  (these form with metals)
- Acidic. Covalent oxides
  (these form with non-metals, metalloids, some metals also)
- Amphoteric. Can be ionic or covalent
  (these form with metals)

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 ox. state)
The most covalent is CrO_3 (highest ox. state)

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

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												3	4	5	6	7	8
1	1 H 1.008	2																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

	1												3	4	5	6	7	8
1	1 H 1.008	2																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)