Chemical Reactions & Periodicity

- In the next sections periodicity will be applied to the chemical reactions of hydrogen, oxygen, and their compounds.

Hydrogen and the Hydrides

- Hydrogen gas, H_2, can be made in the laboratory by the reaction of a metal with a nonoxidizing acid.

$$\mathbf{Mg + 2\ HCl \rightarrow MgCl_2 + H_2}$$

•Hydrogen is commercially prepared by the thermal cracking of hydrocarbons.

$$\mathbf{C_4H_{10} \rightarrow 2\ C_2H_2 + 3\ H_2}$$

Reactions of Hydrogen and the Hydrides

- Hydrogen reacts with active metals, groups IA and IIA, to yield hydrides.

$$2\,K + H_2 \rightarrow 2\,KH$$

$$Ba + H_2 \rightarrow BaH_2$$

Reactions of Hydrogen and the Hydrides

- The H^- reacts with water to produce H_2 and OH^-.

$$\mathbf{H^- + H_2O \rightarrow H_2 + OH^-}$$

•For example, the reaction of LiH with water proceeds in this fashion.

$$LiH_{(s)} + H_2O_{(\ell)} \rightarrow H_{2(g)} + OH^-_{(aq)} + Li^+_{(aq)}$$

Reactions of Hydrogen and the Hydrides

- Hydrogen reacts with nonmetals to produce covalent compounds.

$$H_2 + F_2 \rightarrow 2\,HF$$
$$H_2 + Br_2 \rightarrow 2\,HBr$$

$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$
$$8\,H_2 + S_8 \rightarrow 8\,H_2S$$

Reactions of Hydrogen and the Hydrides

- The hydrides of Group VIIA and VIA hydrides are acidic.

$$HCl \rightarrow H^{+}_{(aq)} + Cl^{-}_{(aq)} \qquad \text{(a strong acid)}$$

$$H_2S \rightleftarrows H^{+}_{(aq)} + HS^{-}_{(aq)} \qquad \text{(a weak acid)}$$

Reactions of Hydrogen and the Hydrides

- There is an important periodic trend evident in the ionic or covalent character of hydrides.

1. ***Metal hydrides*** are ionic compounds and form basic aqueous solutions.
2. ***Nonmetal hydrides*** are covalent compounds and form acidic aqueous solutions.

IA	IIA	IIIA	IVA	VA	VIA	VIIA
LiH	BeH_2	B_2H_6	CH_4	NH_3	H_2O	HF
NaH	MgH_2	$(AlH_3)_x$	SiH_4	PH_3	H_2S	HCl
KH	CaH_2	Ga_2H_6	GeH_4	AsH_3	H_2Se	HBr
RbH	SrH_2	InH_3	SnH_4	SbH_3	H_2Te	HI
CsH	BaH_2	TlH	PbH_4	BiH_3	H_2Po	HAt

Oxygen and the Oxides

- Joseph Priestley discovered oxygen in 1774 using this reaction:

$$2\ HgO_{(s)} \rightarrow 2\ Hg_{(\ell)} + O_{2(g)}$$

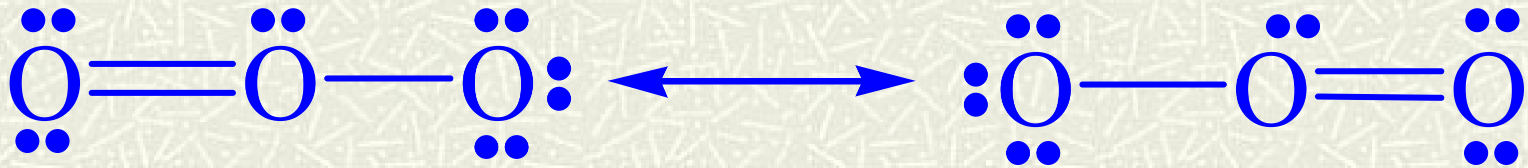
•A common laboratory preparation method for oxygen is:

$$2\ KClO_{3\ (s)} \rightarrow 2\ KCl_{(s)} + 3\ O_{2(g)}$$

•Commercially, oxygen is obtained from the fractional distillation of liquid air.

Oxygen and the Oxides

- Ozone (O_3) is an **allotropic** form of oxygen which has two resonance structures.



•Ozone is an excellent UV light absorber in the earth's atmosphere.

$$2\ O_{3(g)} \rightarrow 3\ O_{2(g)}$$

in presence of UV

Reactions of Oxygen and the Oxides

- Oxygen is an extremely reactive element.
  - O_2 reacts with most metals to produce normal **oxides** having an oxidation number of –2.

$$4\ \mathrm{Li_{(s)}} + \mathrm{O_{2(g)}} \rightarrow 2\ \mathrm{Li_2O_{(s)}}$$

- However, oxygen reacts with sodium to produce a **peroxide** having an oxidation number of –1.

$$2\ \mathrm{Na_{(s)}} + \mathrm{O_{2(g)}} \rightarrow \mathrm{Na_2O_{2(s)}}$$

Reactions of Oxygen and the Oxides

- Oxygen reacts with K, Rb, and Cs to produce **superoxides** having an oxidation number of -1/2.

$$2\ Na_{(s)} + O_{2(g)} \rightarrow Na_2O_{2(s)}$$

TABLE 6-4 *Oxygen Compounds of the IA and IIA Metals**

	IA					IIA				
	Li	Na	K	Rb	Cs	Be	Mg	Ca	Sr	Ba
normal oxides	Li_2O	Na_2O	K_2O	Rb_2O	Cs_2O	BeO	MgO	CaO	SrO	BaO
peroxides	Li_2O_2	Na_2O_2	K_2O_2	Rb_2O_2	Cs_2O_2			CaO_2	SrO_2	BaO_2
superoxides		NaO_2	KO_2	RbO_2	CsO_2					

The shaded compounds represent the principal products of the direct reaction of the metal with oxygen.

Class	Contains Ions	Oxidation No. of Oxygen
normal oxides	O^{2-}	-2
peroxides	O_2^{2-}	-1
superoxides	O_2^{-}	$-\frac{1}{2}$

Reactions of Oxygen and the Oxides

- At high oxygen pressures the IIA metals can form peroxides.

$$Ca_{(s)} + O_{2(g)} \rightarrow CaO_{2(s)}$$

- Metals that have variable oxidation states, such as the *d*-transition metals, can form variable oxides.
  - For example, in limited oxygen:

    $$2\ Mn_{(s)} + O_{2(g)} \rightarrow 2\ MnO_{(s)}$$

  - In excess oxygen:

    $$4\ Mn_{(s)} + 3\ O_{2(g)} \rightarrow 2\ Mn_2O_{3(s)}$$

Reactions of Oxygen and the Oxides

- Oxygen reacts with nonmetals to form covalent nonmetal oxides.
  - In limited oxygen

$$2\,C_{(s)} + O_{2(g)} \rightarrow 2\,CO_{(g)}$$

  - In excess oxygen

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$$

Reactions of Oxygen and the Oxides

- Phosphorous reacts similarly to carbon forming two different oxides depending on the oxygen amounts:
  - In limited oxygen

    $$P_{4(s)} + 3\ O_{2(g)} \rightarrow P_4O_{6(s)}$$

  - In excess oxygen

    $$P_{4(s)} + 5\ O_{2(g)} \rightarrow P_4O_{10(s)}$$

Reactions of Oxygen and the Oxides

- Similarly to the nonmetal hydrides, nonmetal oxides are ***acidic***.
  - They react with water to produce ternary acids.
    - For example:

$$CO_{2(g)} + H_2O_{(\ell)} \rightarrow H_2CO_{3(aq)}$$

$$Cl_2O_{7(s)} + H_2O_{(\ell)} \rightarrow 2\ HClO_{4(aq)}$$

$$As_2O_{5(s)} + 6\ H_2O_{(\ell)} \rightarrow 4\ H_3AsO_{4(aq)}$$

Reactions of Oxygen and the Oxides

- Similarly to the hydrides, metal oxides are ***basic***.
  - These are called basic anhydrides.
  - They react with water to produce ionic metal hydroxides (bases)

$$Li_2O_{(s)} + H_2O_{(\ell)} \rightarrow 2\ LiOH_{(aq)}$$

$$CaO_{(s)} + H_2O_{(\ell)} \rightarrow Ca(OH)_{2(aq)}$$

- Metal oxides are usually ***ionic*** and ***basic***.
- Nonmetal oxides are usually ***covalent*** and ***acidic***.

	Metal Oxide + Water	$\longrightarrow$	Metal Hydroxide (base)	
sodium oxide	$Na_2O(s)$ + $H_2O(\ell)$	$\longrightarrow$	$2\ NaOH(aq)$	sodium hydroxide
calcium oxide	$CaO(s)$ + $H_2O(\ell)$	$\longrightarrow$	$Ca(OH)_2(aq)$	calcium hydroxide
barium oxide	$BaO(s)$ + $H_2O(\ell)$	$\longrightarrow$	$Ba(OH)_2(aq)$	barium hydroxide

	Nonmetal Oxide	+ Water	$\longrightarrow$	Ternary Acid	
carbon dioxide	(+4) $CO_2(g)$	$+ H_2O(\ell)$	$\longrightarrow$	(+4) $H_2CO_3(aq)$	carbonic acid
sulfur dioxide	(+4) $SO_2(g)$	$+ H_2O(\ell)$	$\longrightarrow$	(+4) $H_2SO_3(aq)$	sulfurous acid
sulfur trioxide	(+6) $SO_3(\ell)$	$+ H_2O(\ell)$	$\longrightarrow$	(+6) $H_2SO_4(aq)$	sulfuric acid
dinitrogen pentoxide	(+5) $N_2O_5(s)$	$+ H_2O(\ell)$	$\longrightarrow$	(+5) $2HNO_3(aq)$	nitric acid
tetraphosphorus decoxide	(+5) $P_4O_{10}(s)$	$+ 6H_2O(\ell)$	$\longrightarrow$	(+5) $4H_3PO_4(aq)$	phosphoric acid

Increasing acidic character →

Increasing base character ↓

IA	IIA	IIIA	IVA	VA	VIA	VIIA
Li_2O	BeO	B_2O_3	CO_2	N_2O_5		OF_2
Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
K_2O	CaO	Ga_2O_3	GeO_2	As_2O_5	SeO_3	Br_2O_7
Rb_2O	SrO	In_2O_3	SnO_2	Sb_2O_5	TeO_3	I_2O_7
Cs_2O	BaO	Tl_2O_3	PbO_2	Bi_2O_5	PoO_3	At_2O_7

Reactions of Oxygen and the Oxides

- Nonmetal oxides react with metal oxides to produce salts.

$$Li_2O_{(s)} + SO_{2(g)} \rightarrow Li_2SO_{3(s)}$$

$$Cl_2O_{7(s)} + MgO_{(s)} \rightarrow Mg(ClO_4)_{2(s)}$$

	Metal Oxide	+	Nonmetal Oxide	$\longrightarrow$	Salt	
	(+2)		(+6)		(+2) (+6)	
calcium oxide + sulfur trioxide	$CaO(s)$	+	$SO_3(\ell)$	$\longrightarrow$	$CaSO_4(s)$	calcium sulfate
	(+2)		(+4)		(+2) (+4)	
magnesium oxide + carbon dioxide	$MgO(s)$	+	$CO_2(g)$	$\longrightarrow$	$MgCO_3(s)$	magnesium carbonate
	(+1)		(+5)		(+1) (+5)	
sodium oxide + tetraphosphorus decoxide	$6Na_2O(s)$	+	$P_4O_{10}(s)$	$\longrightarrow$	$4Na_3PO_4(s)$	sodium phosphate

Combustion Reactions

- Combustion reactions are exothermic redox reactions
- One example of extremely exothermic reactions is the combustion of hydrocarbons.

$$2\ C_4H_{10(g)} + 13\ O_{2(g)} \rightarrow 8\ CO_{2(g)} + 10\ H_2O_{(g)}$$

$$C_5H_{12(g)} + 8\ O_{2(g)} \rightarrow 5\ CO_{2(g)} + 6\ H_2O_{(g)}$$

Fossil Fuel Contaminants

- When fossil fuels are burned, they frequently have contaminants in them.
- Sulfur contaminants in coal are a major source of air pollution.
  - Sulfur combusts in air.

$$S_{8(g)} + 8\ O_{2(g)} \rightarrow 8\ SO_{2(g)}$$

- Next, a slow air oxidation of sulfur dioxide occurs.

$$2\ SO_{2(g)} + O_{2(g)} \rightarrow 2\ SO_{3(g)}$$

- Sulfur trioxide is a nonmetal oxide, i.e. an acid anhydride.

$$SO_{3(g)} + H_2O_{(\ell)} \rightarrow H_2SO_{4(aq)}$$

Fossil Fuel Contaminants

This combustion reaction occurs in a car's cylinders during combustion of gasoline.

$$N_{2(g)} + O_{2(g)} \rightarrow 2\ NO_{(g)}$$

- After the engine exhaust is released, a slow oxidation of NO in air occurs.

$$2\ NO_{(g)} + O_{2(g)} \rightarrow 2\ NO_{2(g)}$$

Fossil Fuel Contaminants

- NO_2 is also an acid anhydride.
  - It reacts with water to form acid rain and, unfortunately, the NO is recycled to form more acid rain.

$$\mathbf{3\ NO_{2(g)} + H_2O_{(\ell)} \rightarrow 2\ HNO_{3(aq)} + NO_{(g)}}$$

Chemistry is fun!