

# Chem 241

## Lecture 33

# Exam Stata

High: 104

Low : 62

Avg:85

SD :11



# Announcement

## Grading

Come on Wednesday for evals.

Mistake we have class on the 3<sup>rd</sup> not 4<sup>th</sup>  
May 3<sup>rd</sup> no lecture, review session

APRIL/MAY

| M  | T  | W  | T  | F  | S  | S  |
|----|----|----|----|----|----|----|
| 19 | 20 | 21 | 22 | 23 | 24 | 25 |
| 26 | 27 | 28 | 29 | 30 | 1  | 2  |
| 3  | 4  | 5  | 6  | 7  | 8  | 9  |
| 10 | 11 | 12 | 13 |    |    |    |



# Recap

Al

Ga

In

Tl

Hydrides

Halides

Oxides

Sulfides

Semiconductors

Organometallics

Boranes



# Rest of the Table

Standardized Tests – GRE, cumes, entrance  
General Chemical Edification

Popular

C, Si, N, P, O, S → some reactions but mostly different forms

Halogens, talked about most. Halogen-Halogen complexes.

Nobel Gases → mostly inert few complexes



# Group 14

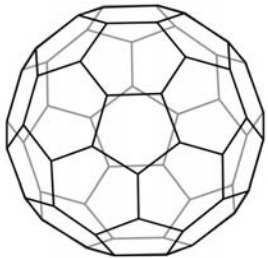
- I. Properties of the Elements
  - A. Electronic Configuration:  $ns^2np^2$ 
    - 1. Increasing metal character down the group can be understood as a consequence of decreasing IE.
    - 2. most common oxidation state is +4, with the exception of Pb, where the most common oxidation state is +2 (inert pair effect), however Pb(IV) compounds are known (Similar to Tl in Gp 13) and the +2 oxidation state is also common for Sn.
    - 3. All the elements in Gp14 have at least one solid phase with the diamond structure (ccp with C in alt. Td holes.).



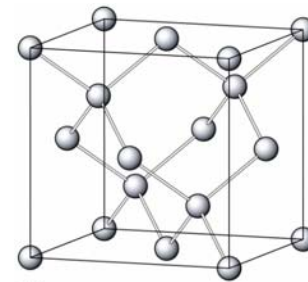
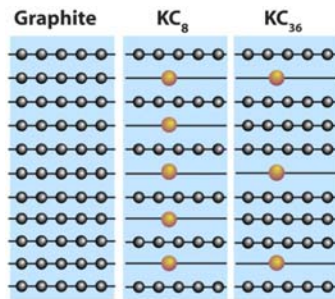
# Occurrence, Sources and Uses

## 1. C

- a. two allotropes of C can be mined, diamond and graphite. A third, fullerenes, are formed when an electric arc is discharged between two C electrodes in an inert atmosphere (Nobel to Smalley, Curl and Kroto in 1996 for  $C_{60}$ , buckminsterfullerene.)
- b. Diamond
  - Cubic structure
  - Hardest known natural substance (used as abrasive and for cutting tools)
    - High refractive index (gemstone)
    - Electrical insulator
    - Highest thermal conductivity (detect fakes by measuring)
    - Conversion of diamond to graphite is spontaneous at STP, ( $\Delta G = -2.90$ )



1  $C_{60}$



# Si

- 2.
  - a. Si makes up 26% of the Earth's crust (quartz, sand, amethyst, agate, opal asbestos, feldspar, clays, mica, are a few silicates)
  - b. elemental Si is produced from  $\text{SiO}_2$  by high-temperature reduction with C in an electric arc furnace:  $\text{SiO}_2 + 2 \text{C} \rightarrow \text{Si(s)} + 2 \text{CO}_2$
  - c. Uses include applications that take advantage of the semiconductor properties of Si; integrated circuits, computer chips, solar cells;  $\text{SiO}_2$  is the major raw material in glass manufacture.





# Group 14

- 3. Ge
  - a. low abundance in nature
  - b. Element is obtained by reduction of  $\text{GeO}_2$  with CO or  $\text{H}_2$ .
  - c. Ge was the first widely used material for the construction of transistors because it is easier to get highly purified Ge, and it has a smaller band gap (0.72 eV vs. 1.11 eV for Si), making it a better intrinsic semiconductor.
- 4. Sn
  - a. found in the mineral cassiterite as  $\text{SnO}_2$
  - b. element is obtained by reduction of  $\text{SnO}_2$  with coke in an electric furnace.
  - c. Tin is resistant to corrosion and is used to plate steel for use in tin cans. Bronze is an alloy of Sn and Cu. Solder is an alloy of Sn and Pb.
  - d. float glass manufacture
  - e. Trialkyl and triaryl Sn compds are fungicides and biocides

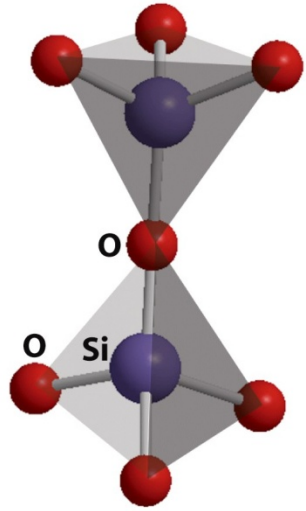


# Chapter 14

- 5. Pb
  - a. softness and malleability led to use in plumbing, which is now illegal in many places because of the concerns about lead poisoning.
    - Paint and tetraethyl lead were other sources of Pb in the environment
    - Pb is absorbed in the intestines, stored in bones where it replaces Ca, impairs growth, hearing, metal development
  - b. low m.p. makes it useful in solder
  - c. high density makes it useful in ammunition.
  - d. PbO is used in glass to raise the refractive index.

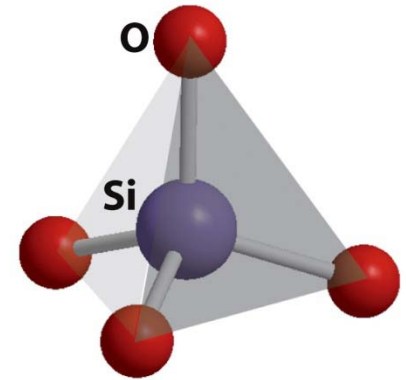


# Silicates



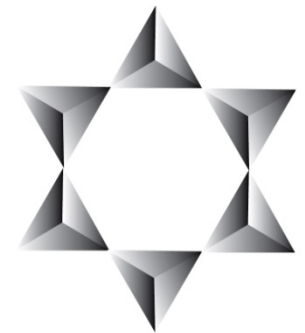
**15**  $[\text{Si}_2\text{O}_7]^{6-}$

- b. Si ( $\text{SiO}_2$ , silicates, silicones)
- silicates are polymers formed of  $\text{SiO}_4^{4-}$  (orthosilicate) tetrahedra.

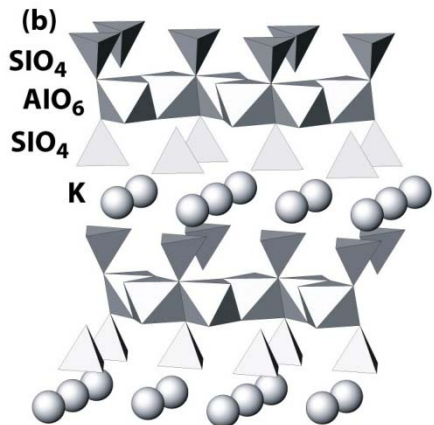


meta silicates are chains and rings with 2 shared O atoms,  $[\text{SiO}_3^{2-}]_n$ , as in  $\text{Si}_6\text{O}_{18}^{12-}$  found in beryl. Chain metasilicates include jadeite,  $\text{NaAl}(\text{SiO}_3)_2$ , and the double chains found in asbestos.

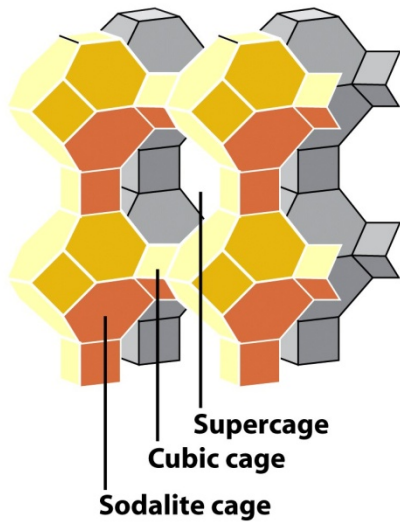
- aluminosilicates are formed when Al substitutes for Si, or is added in holes in the silica lattice. Since Al(III) has one less + charge, a cation is added for each Al in the framework ( $\text{H}^+$  etc.) Layered aluminosilicates are found in clays, mica. Many minerals, such as feldspar, have a 3 dimensional network.



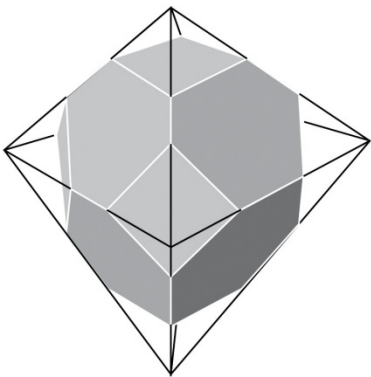
**16**  $[\text{Si}_6\text{O}_{18}]^{12-}$



# Group 14



- Zeolites are aluminosilicates with large open cavities and channels that are useful in ion-exchange and molecular absorption (molecular sieves) and shape-selective heterogeneous catalytic applications. (ZSM-5 is a zeolite used to synthesize 1,2-dimethylbenzene (o-xylene) for an octane booster in gasoline. Other isomers are not formed in the process because the catalysis is controlled by the size and shape of the zeolite cavities.



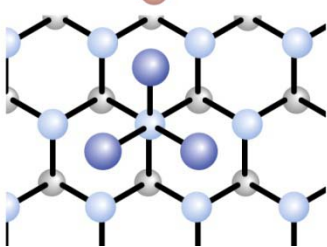
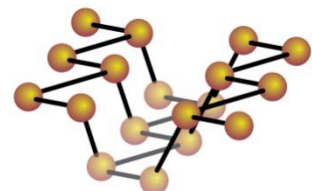
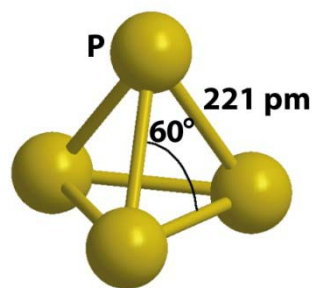
- Zeolites occur naturally and can be made synthetically including several not found in nature.
- Structure is often based on the sodalite cage—a truncated octahedral structure.



# Group 15

## I. General features of the Elements

- A. Electron configuration  $ns^2np^3$ . Oxidation sts. -III to V.
- B. Elemental forms
  - 1. N is exceptional in that it is a gas ( $N_2$ ) in the elemental form, and makes up nearly 80% of the Earth's atmosphere. All other members of Gp15 are solids @ STP



- 2. P exists as several allotropes. White P (std. state), a reactive waxy solid consisting of  $P_4$  tetrahedra.  $P_2$  exists in the gas phase above 800 C. Heating white P to to 300 C in an inert atm. converts it to red amorphous P, which is less reactive. Heating under pressure converts it to black P, which has several polymorphs including a layered structure consisting of puckered six-memebered rings.

- 3. As exists in two forms: yellow As, and metallic As. Yellow (and gas phase) As is  $As_4$  tetrahedra. Metallic has a structure similar to black P.

- 4. The structures of Sb and Bi are similar to metallic As.

Bi recently found to be radioactive. 13



# Occurrence and Recovery

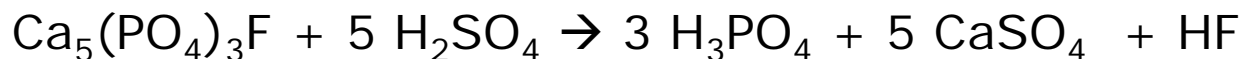
a. N<sub>2</sub> prepared on large scale by distillation of liquid air.

- chemistry of N<sub>2</sub> is limited by three factors: 1) the strength of the N-N triple bond, 2) the large HOMO-LUMO gap (little redox) and 3) the low polarizability (poor ligand)

b. P was originally isolated by Hennig Brandt in 1669, who was trying to extract gold from urine, and instead obtained a white solid that glowed in the dark.

- found in the minerals fluorapatite, Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F and apatite, Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH, which are materials from seashells and found in bones and teeth.

- used to produce phosphoric acid (bulk chemical) and white phosphorus.

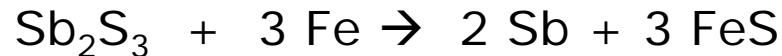


# Group 15

- c. As is found in sulfide ores and as the minerals realgar,  $\text{As}_4\text{S}_4$ , orpiment,  $\text{As}_2\text{S}_3$ , arenolite,  $\text{As}_2\text{O}_3$ , and arsenopyrite,  $\text{FeAsS}$ .
  - Often extracted from flue dust of Cu and Pb smelters
  - Also obtained by heating sulfides anerobically



- d. Sb occurs natually as Stibnite,  $\text{Sb}_2\text{S}_3$  and ullmanite,  $\text{NiSbS}$ . It is extracted by heating with scrap Fe.



- e. Bi occurs as bismite,  $\text{Bi}_2\text{O}_3$  and bismuthinite,  $\text{Bi}_2\text{S}_3$ . The element is produced bas a by-product of Cu, Sn, Pb, and Zn production in the same manner as Sb.



# Group 16: The Chalcogens

- I. Properties of the Elements (Chalcogens, Gr., bronze.)
  - A. General Properties: Electronic Configuration:  $ns^2np^4$ 
    - 1. The maximum oxidation state, VI, is not achieved by O, but is for others, particularly S. The lowest oxidation state, -II, is common, particularly for O.
    - 2. All have several allotropes; S has more allotropes than any other element.
    - 3. O is distinct
      - a. Is a gas, all others are solids
      - b. Second most electronegative element (doesn't like + ox sts)
      - c. 2 allotropes, dioxygen and ozone.
      - d. Have discussed electronic structure of  $O_2$  and why it is paramagnetic.





# Occurrence

- B.
- 1. O

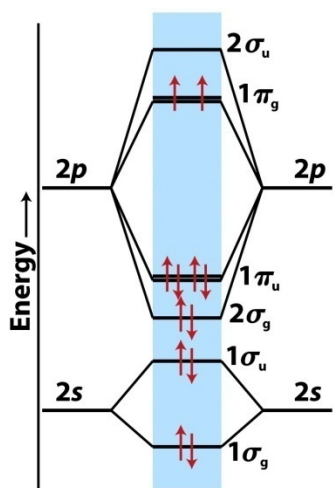
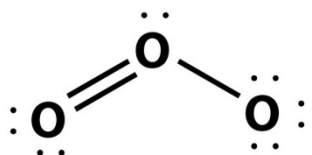
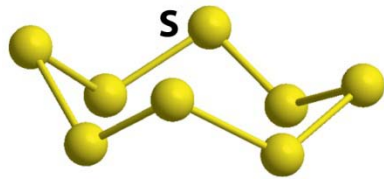


Figure 15-1  
 Shriver & Atkins Inorganic Chemistry, Fourth Edition  
 © 2006 by D. F. Shriver, P. W. Atkins, T. L. Overton, J. P. Rourke, M. T. Weller, and F. A. Armstrong

- a. 21 % of air, most abundant element in Earth's crust (silicates etc.) , ave. person is 2/3 O by mass (mostly water).
- b. obtained by distillation of liquid air.
- c. primary use is in steel production to make CO, which is used to reduce iron oxides to metal.
- d. ground state triplet, two excited state singlets:  $^1\Delta_g$  has e-(s) paired in the same  $\pi^*$  orbital and lasts long enough to be used in chemical reactions.  $^1\Sigma_g$  is higher in energy, has e- in the same orbitals as g.s., but paired.
- e. all elements for oxides except He, Ne, and Ar.
- f. The other allotrope is O<sub>3</sub> (ozone, Gr. Ozein, to smell). It is diamagnetic, and is produced by electrical discharges or UV irradiation of O<sub>2</sub>



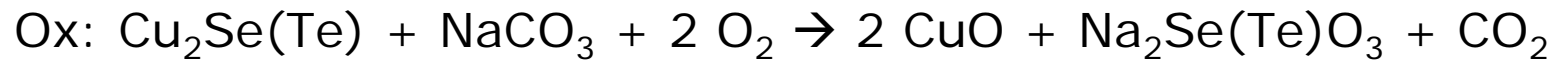
# S



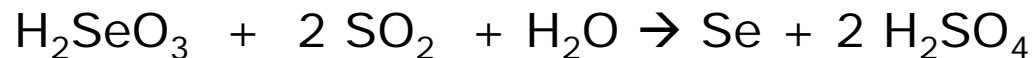
- S occurs as the element,  $S_8$ , and also as sulfide and sulfate ores, such as galena,  $PbS$ , barite,  $BaSO_4$ , etc. It also occurs as  $H_2S$  in natural gas, and in organic compounds in crude oil.
- Deposits of the element are extracted by the Frasch process in which superheated water, steam and compressed air are used to force it to the surface.
- Alternatively obtained from Claus process, which involves oxidation of  $H_2S$  to  $SO_2$  in air at 1000 – 1400 C., which reacts with  $H_2S$  to form S over a catalyst.
- Catenates. Unlike  $O_2$ , which forms double bonds, S (and others) make multiple single bonds. (S-S is third strongest single bond, 265 kJ/mol, after H-H (435) and C-C (330).) In the gas phase, S forms  $S_2$  molecules that are paramagnetic like  $O_2$ .
- Most stable form is yellow, orthorhombic  $\alpha$ - $S_8$ , composed of rings.
- Most S is used to make  $H_2SO_4$ , largest quantity bulk chemical. Also used to make gun powder and in the vulcanization of rubber.

# Se, Te, Po

- a. The stable allotrope of Se and Te consists of helical chains. Several allotropes of Se exist; 3 allotropes have Se<sub>8</sub> rings, (red, α-, β-, γ-) as well as the gray helical structure. Also black amorphous Se, and another amorphous form obtained by deposition of vapor in photocopying. Se is an essential element, but required only in small amounts.
- b. Se and Te are found in metal sulfide ores, mostly obtained electrolytic refining of Cu.



Acidification with H<sub>2</sub>SO<sub>4</sub> causes pptn of TeO<sub>2</sub> leaving H<sub>2</sub>SeO<sub>3</sub> in solution. The solution is then treated with SO<sub>2</sub>:



Te is prepared from the oxide by dissolving in NaOH and electrolyzing.



# Uses

- e. Se exhibits both photovoltaic action (light converted to electricity) for solar cells, and photoconductive action, resulting from the excitation of  $e^-$  across a small band gap (p-type semiconductor) for photocells. Also used to make red glasses.
- f. Po and Te are very toxic; worse for Po, which is also radioactive.
- g. Po crystallizes in a primitive cubic structure. (only element that does so at STP)
- h. Po has more isotopes than any other element, 29, all are radioactive.
- i. Po is produced by neutron radiation of Bi.

