

BRING YOUR REG CARD OR PICTURE ID TO THE FINAL EXAM

FINAL: TUESDAY, JUNE 11, 8 – 11 AM

**A – D
E – Z**

**Buchanan 1920
Chem 1179**

Office Hours: PSBN 3670 B Monday, 11 – 12 and 3 – 4 PM

The final will cover Ch. 13, 14, 16-20, 22, and 23 comprehensively. You are allowed to use one 8.5 x 11 inch page of notes during the exam. It is not useful to microfilm too much information onto the page, it will slow you down. The goal of the page of notes is to help you figure out what is important. If you can figure out what is important it will help you understand the material. Equations, conversion factors, constants, structures of amino acids, a periodic table and other useful information will be provided. Be sure to **WORK THE ASSIGNED HOMEWORK PROBLEMS AGAIN**. Work problems on the midterms, quizzes as well as the review questions handed out before each midterm.

Chapters 18-19. Periodic trends, Representative Elements, Groups 1 – 8

Representative Elements are elements in Groups 1 through 8, whose chemical properties are determined by the valence-level *s* and *p* electrons. The similarities and differences between members of a given periodic group and the trends in properties that occur among elements of neighboring groups are considered.

There is a marked resemblance between elements of groups 1 and 2. As we go down a group of representative elements the metallic properties of the elements increase. As we proceed across the periodic table from left to right, the metallic properties are modified and then disappear. This trend correlates directly with atomic size (see Figure 18.2, Page 831). Atomic size increases down a given group and decreases across a given row. All the non-metals have atomic radii less than ~1.4 Å. In smaller atoms, the electrons are closer to the nucleus and more energy is required to remove electrons. Non-metals are generally not willing to give up electrons, and generally form covalent bonds with other non-metals. The more metallic the element, the more willing it gives up one or more electrons to make a positive ion.

The resemblance between elements of the same group becomes less obvious in groups 3 and 4. Groups 5, 6, 7 and the noble gases, group 8, include most of the non-metallic elements. The chemical behavior of each of these elements is in general more complicated than the chemistry of the metals, and in some cases a nonmetallic element may show only slight resemblance to the other members of the family. Nevertheless, it is possible to detect a number of regularities, particularly among the structural features of the compounds of the nonmetals, that aid in remembering and understanding the chemistry of the elements. [References: 1) Bruce Mahan, College Chemistry 2) Cotton and Wilkinson, Advanced Inorganic Chemistry 3) Oxtoby, Gillis, Nachtrieb Principles of Modern Chemistry.]

Hydrogen: The hydrogen atom is the smallest in the periodic table, atomic radius = 0.37 Å. The very small size means that its electron is very close to the nucleus and is therefore strongly bound (the energy required to remove the electron is very high). As a result, when hydrogen bonds to other nonmetals, it typically does so by sharing electrons (forming a covalent bond) rather than by losing its electron to form H⁺ (in an ionic bond). H⁺ is formed in aqueous solution because the energy required to remove the electron is compensated for by energy of hydration of such ions in solution, H⁺(aq) or H₃O⁺(aq).

Group 1: Alkali Metals (Li, Na, K, Rb, Cs, Fr)

- React rapidly and completely with non-metals => elemental form of alkali metals not found in nature
- Na and K are abundant in nature, other Group 1 metals are more rare. Fr decays radioactively.
- Strong reducing agents => useful as reductants in industry
- Electrolysis is used to recover alkali metals from their compounds.
- Good conductors of electricity and heat.
- Soft metals, you can cut them with a knife => weak bonding. Li is the hardest (Li is more strongly bound) Cs is the softest. Li (s) has the highest melting point.
- Alkali metal ions: e.g. Na⁺, K⁺ and Li⁺ are important for biological systems to function properly, e.g. nerves and muscles. Lithium is used to treat manic-depressive patients

Group 2: Alkaline-Earth Metals (Be, Mg, Ca, Sr, Ba, Ra)

- Active reductants, react rapidly with non-metals => not found in metallic form in nature
- **Beryllium** is the smallest of the group and has unique chemical behavior with predominantly covalent chemistry. Notice how small Be²⁺ is (ionic radius = 0.31 Å) relative to Be (atomic radius = 1.13 Å). In fact, Be²⁺ is smaller than H (atomic radius = 0.37 Å). The small size of Be²⁺ with its large charge density (charge/volume) causes an attraction for electrons to itself and when Be bonds to nonmetals it typically does so by sharing electrons, forming covalent rather than ionic bonds. For example, BeCl₂ is covalently bound whereas CaCl₂ is ionic because Ca²⁺ is significantly larger in size relative to Be²⁺.
- **Mg** is the second most abundant metallic element in the ocean. The chemistry of Mg is between that of Be and the heavier elements. Mg has considerable tendency for covalent bonding, consistent with its high charge density (charge per unit volume). The boiling points of the metal chlorides as well as the solubility of the metal hydroxides shows the switch from covalent to ionic bonding as the atomic number of the metal increases.

	<u>Boiling Point (°C)</u>	<u>Bonding</u>		<u>K_{sp}</u>	<u>Solubility in water (to produce ions)</u>
BeCl ₂	490	Covalent	Be(OH) ₂	1.6 x 10 ⁻²⁶	Insoluble (does not produce ions)
MgCl ₂	1400	Covalent/Ionic	Mg(OH) ₂	8.0 x 10 ⁻¹²	Slightly Soluble
CaCl ₂	1600	Ionic	Ca(OH) ₂	1.3 x 10 ⁻⁶	Moderately Soluble
		Ionic	Sr(OH) ₂	3.2 x 10 ⁻⁴	Moderately Soluble
		Ionic	Ba(OH) ₂	5.0 x 10 ⁻³	Soluble

- **Ca** occurs naturally as CaCO_3 (marble, limestone, chalk)
- **Ba** and **Sr** are found as BaSO_4 and SrSO_4 . Ra is formed in a radioactive decay series and decays radioactively.
- Group 2 metals are considerably harder than alkali metals (stronger bonding) but relatively soft, they can be hammered and rolled into sheets. Group 1 and 2 metals become increasingly softer as we go down the group.
- Mg alloyed with Al, Zn, and Mn forms a light weight, moderately strong material used for aircraft construction. Photographic flashbulbs: $2 \text{Mg}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow 2 \text{MgO}(\text{s}) + \text{light}$
- Ca^{2+} and Mg^{2+} are essential for human life: Ca^{2+} in bones and teeth, Mg^{2+} plays a vital role in metabolism and in muscle functions
- Ca^{2+} and Mg^{2+} are found in natural water supplies, they make water "hard" and interfere with the action of detergents. Water softeners work through ion exchange processes: $2 \text{NaSO}_3 + \text{Ca}^{2+} \longrightarrow \text{Ca}(\text{SO}_3)_2 + 2 \text{Na}^+$

Group 3: (B, Al, Ga, In, Tl)

- **Boron**: non-metal, smallest atom of the group. The first ionization energy of boron is high (800.6 kJ/mol) and the next two are much higher. B^{3+} is extremely small, has a large charge density (charge/volume) and strongly attracts electrons to itself from neighboring atoms which results in the formation of covalent bonds rather than ionic bonds. B^{3+} ions are not observed in solution. The hydration energy of B^{3+} is not sufficient to compensate for the high ionization energy.
- **Aluminum**: most abundant metal on earth, it has a high strength/weight ratio and is therefore useful for aircraft construction, bicycle components, etc.
Al is a strong reducing agent: $6 \text{H}_2\text{O} + 2 \text{Al}(\text{s}) \longrightarrow 2 \text{Al}^{3+}(\text{aq}) + 3 \text{H}_2 + 6 \text{OH}^- \quad \mathcal{E}^\circ = 0.83 \text{ V}$
The positive cell potential indicates aluminum should dissolve in water. Aluminum also oxidizes in air. Why do we observe Al to be highly resistant to corrosion? In air, Al forms a protective oxide coating: $\text{Al}_2\text{O}_3(\text{s})$
 Al_2O_3 is a dense, tough, transparent coating which protects the metal from further chemical attack.
- **Gallium**: < 1% in Al and Zn ore. Similar chemistry to Al. Relatively strong reducing agent. Forms protective oxide coating, $\text{Ga}_2\text{O}_3(\text{s})$ Unusually low melting point for Ga (29.8°C). Ga melts in your hand (this is much lower than the melting point for Al which is 660°C). There is no simple explanation why the melting point for Ga is so low.
Boiling point for Ga: ~ 2400°C => very large liquid range, useful as a thermometer liquid
- **Indium**: << 1% in Al and Zn ore. Rare and soft, => no important structural uses. Forms protective oxide coating: In_2O_3 Takes a high polish => used in construction of special mirrors
- **Thallium**: Rare and soft, no protective oxide coating => oxidizes readily in air

Group 4: (C, Si, Ge, Sn, Pb)

Carbon and silicon are two of the most important elements on earth. Carbon is a fundamental constituent of molecules necessary for life (biology). Silicon is the basis for the geological world.

Why is life based on carbon chemistry and not silicon chemistry? Consider the relative bond energies in kJ/mol:

C – C	347	C – H	413	Si – Si	222	Si – H	393
C = C	615	C – O	358			Si – C	360
C – C	812	C – N	292			Si – O	452

IMPORTANT POINT: When bonds are formed energy is released. The stronger the bond the more energy is released. In an exothermic reaction, the products are lower in energy than the reactants because the bonds in the products are stronger (the products are more stable). Thus, the stronger the bond, the more stable the compound and the more likely it is formed.

- **Carbon**: Carbon chemistry is unique. It forms unlimited compounds containing C–C bonds both in chains and rings. e.g. in hydrocarbons, diamond, graphite, and biomolecules. Why is carbon unique? Carbon can form bonds to itself because C–C bonds are strong and similar to other bond strengths, e.g. C–H, C–N, C–O etc. Thus, C – C bond formation can compete effectively with the formation of other bonds. This is why many compounds contain long chains or rings of C – C bonds, single, double and triple bonds as found in biomolecules. The bond strengths for Group 4 are observed to decrease in the order C–C, Si–Si, Ge–Ge, Sn–Sn, and Pb–Pb. Thus, Si–Si bonds are significantly weaker than Si–O bonds which is why Si–O bonds dominate silicon chemistry rather than Si–Si bonds.
- Because of its small size, carbon can form π -bonds due to effective overlap between 2p-orbitals. Strong π -bonds are formed between C and C, C and O and C and N. Other group 4 elements do not show this behavior.
- A **pi (π)-bond** is a covalent bond in which parallel p-orbitals share an electron pair occupying the space above and below the line joining the atoms (above and below the inter nuclear axis).
- A **sigma (σ)-bond** is a covalent bond in which the electron pair is shared in an area centered on a line running between the atoms (the inter nuclear axis).
- Because carbon can form π -bonds the chemical and physical properties of $\text{CO}_2(\text{g})$ are very different from the rest of the group, $\text{SiO}_2(\text{s})$, $\text{GeO}_2(\text{s})$, $\text{SnO}_2(\text{s})$ and $\text{PbO}_2(\text{s})$. CO_2 is a linear, non-polar molecule which satisfies the octet rule for both the carbon and the oxygen. CO_2 is a stable molecule all by itself, it has no need for further bonding. The molar mass of CO_2 is relatively small and London Dispersion Forces are the only intermolecular forces which draw CO_2 molecules together so it is not surprising that CO_2 is a gas at room temperature and pressure. Si on the other hand can not form π -bonds and the structure O – Si – O does not satisfy the octet rule. Si forms additional bonds with oxygen to satisfy the octet rule. The structure of quartz has the empirical formula SiO_2 and contains chains of SiO_4 tetrahedra that share oxygen atoms. See Figure 18.3, pg. 832 of your text. $\text{SiO}_2(\text{s})$, $\text{GeO}_2(\text{s})$, $\text{SnO}_2(\text{s})$ and $\text{PbO}_2(\text{s})$ are all non-volatile solids with relatively complicated crystal structures.

NOTE: Valence shell expansion is not observed for second row elements. Second row elements generally obey the octet rule with the exception of B and Be which can be electron deficient in their compounds.

Group 5, 6: (N, P, O, S)

- **Nitrogen** and **Oxygen** form strong π -bonds using p-orbitals. **Phosphorous** has a larger atomic radius than nitrogen and does not form π -bonds using its p-orbitals. Phosphorous does form π -bonds using d-orbitals. **Sulfur** has a smaller atomic radius than phosphorous and a larger atomic radius than oxygen. As a result, sulfur makes only weak π -bonds in compounds such as SO_2 , but does not make π -bonds in elemental sulfur compounds. At room temperature and pressure, N_2 and O_2 are stable gases because they can form π -bonds. P_2 and S_2 are not stable gases under these conditions. Phosphorous is a solid, red, white or black. Sulfur is stable as cyclic S_6 (s) or S_8 (s). S_2 (g) is observed only at very high temperatures, 2200°C.

Group 7: (F, Cl, Br, I)

- **Halogens**: non-metals. **Fluorine** is the most **electronegative** element in the periodic table. It wants one electron to complete its valence shell. Fluorine does not form double bonds. Why not? Because of its high electronegativity, fluorine is not willing to share more than one electron.

Acid strength: $\text{HF}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{F}^-(\text{aq}) \quad K_a = 7 \times 10^{-4}$ The small K_a value indicates the equilibrium position lies on the left, HF is a weak acid.

HCl, HBr and HI are all strong acids. Why? Two factors drive a reaction, ΔH and ΔS . **Reaction spontaneity is determined by the equation:** $\Delta G = \Delta H + T \Delta S$. If $\Delta G < 0$ the reaction is spontaneous. When $\Delta H < 0$ and $\Delta S > 0$, then $\Delta G < 0$ at all temperatures. A more negative ΔG value \Rightarrow the reaction is more spontaneous. The bond energy decreases down the group: $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$. The reaction, $\text{HF}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{F}^-(\text{aq})$, is less exothermic relative to that of HCl, HBr and HI and the entropy change is more negative. F^- is smaller than Cl^- , Br^- and I^- . Thus, $\text{F}^-(\text{aq})$ is more ordered because F pulls the water molecules in tighter. ΔG is positive for the dissociation of HF and therefore $K_a < 1$. K_a values are much larger for HCl, HBr and HI than for HF. **NOTE: In diluting concentrated acids:** Always add acid to water, slowly!

HCl used most (3 million tons, annually, in the US): to clean steel before galvanizing; to manufacture other chemicals.

Fluoride in toothpaste. Tooth enamel, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, dissolves in acidic solution. Eating sugar feeds bacteria and excretion of acid by the bacteria causes tooth decay. The fluoride in toothpaste, F^- , replaces OH^- in tooth enamel. $\text{Ca}_5(\text{PO}_4)_3\text{F}$ is a tougher enamel and less reactive (F^- is a weaker base than OH^-).

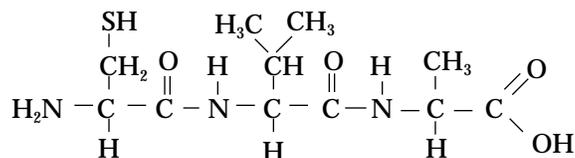
Review Problems

1. Circle the representative elements. Na, Mg, Zn, Cr, Mn, Fe, F, B
2. Circle the non-metals. C, Sn, Cl, Ga, B, Na
3. Based on its place in the periodic table, which element should have the most metallic character? Mg, Sb, Al
4. Based on its place in the periodic table, which element should have the most nonmetallic character? Tl, As, Li, Br
5. List two general ways in which the first member of groups 1 and 2 differ from subsequent members of the group.
6. Which elements most commonly form π -bonds?
7. Why does hydrogen act so differently from the metals in group 1?
8. Which has the higher boiling point BeCl_2 or CaCl_2 ? Why?
9. Which has the highest boiling point, BF_3 , BCl_3 , BBr_3 , BI_3 ? Why?
10. Why is BF_3 so reactive with NH_3 ?
11. What is the hybridization on carbon and in $\text{O}=\text{C}=\text{O}$?
12. Why do alkali metals react so well with nonmetals?
13. Circle the covalently bound compounds. BeCl_2 , $\text{Ba}(\text{OH})_2$, NaOH , Br_2
14. Why does hydrogen have such low boiling and melting points?
15. Write the balanced combustion reaction between hydrogen and oxygen to form water.
16. Write the balanced equation for the reaction between methane and water to produce hydrogen and carbon monoxide.
17. **Most ionic in character:** BeCl_2 MgCl_2 CaCl_2
18. Why does $\text{Ba}(\text{OH})_2$ dissociate to form ions in an aqueous solution and no ions are formed when $\text{Be}(\text{OH})_2$ is dissolved in water?
19. Circle the strongest bond. $\text{Ge}-\text{Ge}$ $\text{Sn}-\text{Sn}$ $\text{C}-\text{C}$ $\text{Si}-\text{Si}$ $\text{Pb}-\text{Pb}$
20. Write the Lewis dot structures for both CO and N_2 .
 - a) How many sigma bonds and pi bonds are in CO and N_2 ?
 - b) What does it mean when we say CO and N_2 are isoelectronic?
 - c) Both CO and N_2 are very strong bonds. Why is CO observed to be more reactive with O_2 than N_2 with O_2 ?
21. Highest boiling point. Explain. a) He, Ne, Ar, Kr, Xe b) CH_4 , SiH_4 c) NH_3 , PH_3 d) HF, HCl
22. Predict the boiling point of H_2O if H-bonding between water molecules did not occur (use Fig 16.4, p 732 text). Would water be a liquid at room temperature without H-bonding?
23. Which is the stronger acid: HNO_3 or H_3PO_4 (for the first ionization only). Explain why.
24. **One method to generate gaseous hydrogen involves the action of steam on iron to give iron oxide (Fe_3O_4).**
 - a) Write a balanced chemical equation for this reaction.
 - b) For this reaction $\Delta H^\circ = -151.1 \text{ kJ}$. To maximize the production of H_2 , should the temperature be high or low?
25. Why can't carbon form a compound such as CCl_6^{2-} while tin can form SnCl_6^{2-} ?
26. Why can carbon form π -bonds with carbon, nitrogen and oxygen while other group 4 elements, Si, Ge, Sn, and Pb. cannot?
27. Considering relative bond energies, why does the silicon to oxygen bond dominate silicon chemistry rather than the silicon to silicon bond?
28. What is the hybridization of P in PF_6^- ?

29. Why is nitrogen fixation important?
30. Draw the Lewis structures and assign the oxidation states of N for the following compounds: N_2 , NO, NH_3 , N_2H_4
31. a) H_3PO_3 is a diprotic acid. Draw the Lewis structure and circle the acidic hydrogens. b) H_3PO_2 is a monoprotic acid. Draw the Lewis structure and circle the acidic hydrogen.
32. Which is more stable O_2 or SO ? Explain why. 33. Which of the following compounds are ionic? HCl , Cl_2 , $NaCl$, $CaCl_2$
34. What are the characteristics of a useful and safe explosive?
35. Suppose the hydrogen atoms in phosphine (PH_3) are replaced by chlorine atoms to give PCl_3 . Do you expect PCl_3 to be a stronger or a weaker Lewis base than PH_3 ? Explain your reasoning.
36. What is the difference between the π -bonds formed in $C=O$ and $P=O$?
37. Do Chapter 23, problem 7, pg 1036 again.
38. Write the balanced equation for the condensation of glycine with dimethyl amine to produce an amide.
39. Draw the structure of Cys–Leu–Ala, in that order.
40. Write the complementary nucleic acid sequence for the following DNA sequence using the concept of complementary base pairing. G A C T C G A T

Solutions

1. Na, Mg, F, B 2. C, Cl, B 3. Mg 4. Br 5. The first member of the group is smaller than the rest of the group. They are generally non-metals forming covalent bonds with other non-metals. Other group 1 and 2 members are metallic, forming ionic bonds with non-metals. 6. Carbon, oxygen and nitrogen make strong π -bonds. Sulfur makes double bonds with oxygen, but sulfur-oxygen π -bonds are weaker than oxygen-oxygen π -bonds. Sulfur does not make double bonds with other sulfur atoms.
7. Hydrogen is a nonmetal that is very small and can either lose or gain an electron. When hydrogen bonds to other nonmetals, it typically does so by sharing electrons (forming a covalent bond) rather than by losing its electron to form H^+ (in an ionic bond). H^+ is formed in aqueous solution because the energy required to remove the electron is compensated for by energy of hydration of such ions in solution, $H^+(aq)$ or $H_3O^+(aq)$.
8. $CaCl_2$ is ionic and has a higher boiling point than $BeCl_2$ which is covalent. Ionic forces for $CaCl_2$ will be stronger than LDF for $BeCl_2$. 9. BI_3 has the highest boiling point. These molecules are all covalent non-polar and therefore the larger the molecule, the more polarizable, the stronger the LDF. 10. Boron is electron deficient and nitrogen donates its lone electron pair. 11. sp 12. See pg one of this review. 13. $BeCl_2$ and Br_2
14. H_2 has a low molar mass, it has only two electrons \Rightarrow low polarizability \Rightarrow weak LDF \Rightarrow low b.p.
17. $CaCl_2$ Explain why. 18. $Ba(OH)_2(aq) \rightarrow Ba^{2+}(aq) + 2 OH^-(aq)$ whereas $Be(OH)_2$ is covalently bound and does not ionize in water. 19. C–C bond is the strongest 20. See lecture
21. a) Xe is the largest in size, greatest LDF \Rightarrow higher b.p b) Both CH_4 and SiH_4 are non-polar covalent. SiH_4 is bigger, greater LDF \Rightarrow higher b.p. c) NH_3 has a higher b.p. due to H-bonding d) HF has a higher b.p. due to H-bonding
22. A straight line extrapolation, following the trend of other group members, H_2Te , H_2Se and H_2S , gives a boiling point of H_2O of ~ 200 K or $-73^\circ C$. Without H-bonding water would be a gas at room temperature and pressure.
23. K_{a1} is greater for HNO_3 than for H_3PO_4 (HNO_3 is a stronger acid) because N is more electronegative. See lecture, June 5.
24. a) $3 Fe(s) + 4 H_2O(g) \rightarrow Fe_3O_4 + 4 H_2 + \text{heat}$ b) low T 25. Carbon follows the octet rule; it is not able to expand its valence shell. Sn can expand its octet by putting electrons into d-orbitals.
26. Carbon has a small enough atomic radius to allow for effective overlap between the p-orbitals. The other group 4 elements are bigger and p-orbitals do not overlap effectively. 27. See above discussion, pg. 2 of this hand-out.
28. d^2sp^3 29. See text pg. 858-860 30. The oxidation state of nitrogen is: 0 in N_2 , +2 in NO, -3 in NH_3 , -2 in N_2H_4 .
31. Hydrogen must be bonded to an oxygen to be acidic. Because H_3PO_3 is a diprotic acid it must have two OH groups directly bonded to phosphorous. See text, pg. 868, Fig 19.14 a and b.
32. O_2 is more stable (stronger bond). O is smaller, the p-orbitals overlap more effectively, making stronger π -bonds than S.
33. $NaCl$ and $CaCl_2$ 34. See lecture or text pg. 857.
35. PH_3 will be a stronger Lewis base. Because Cl is more electronegative than H, the lone pair electrons on the P atom will be held more closely in PCl_3 than in PH_3 , so PCl_3 will be a weaker Lewis base (less willing to donate an electron pair).
36. In $C=O$ the π -bond is due to overlap between two p-orbitals. In $P=O$ the π -bond is due to the overlap between a d-orbital on P and a p-orbital on O. 37. See Solutions manual
38. This is a standard condensation reaction. It is similar to the reaction shown on page 1012.
39. Cys–Leu–Ala



40. C T G A G C T A

Good luck on the final and have a great summer!!

BRING YOUR REG CARD OR PICTURE ID TO THE FINAL EXAM