## Compounds and the Mole I

- 1. In this series of problems we will examine a few structures on the Crystallography Open Database (COD).
  - A. Visit <u>this link</u> and examine the three-dimensional structure that appears. Hover your mouse over each atom to see its chemical symbol. This structure contains both ionic and covalent bonds. List the different types of covalent bonds in the structure (e.g., C–C). Then, find the lone cation in the structure and determine its charge.
  - B. Visit <u>this link</u> and examine the three-dimensional structure that appears. Examine the  $AIF_5$  molecules. What is the net charge on each molecule? How do you know? What is the net charge on the  $HN(CH_2CH_2NH_3)_3$  molecule?
  - C. Visit <u>this link</u> and examine the three-dimensional structure that appears. The title of the paper reporting this structure mentions a "heavy alkaline earth" metal. What is the identity of this metal and what is its charge in the structure? What other charged atoms are in the structure?
- 2. Classify each of the following acids as a binary acid or an oxyacid and determine its name. As you generate the name, document your thought process in as much detail as you can.
  - A. HI
  - B. HBrO<sub>4</sub>
  - C. HBr
  - D.  $H_2S$
  - E. H<sub>3</sub>PO<sub>3</sub>
- 3. Each of the following compounds can be used as a source of phosphorus in the synthesis of H<sub>3</sub>PO<sub>3</sub>. Determine whether each is an ionic or covalent compound and name them. Separate the ionic compounds into their component ions.
  - A. K<sub>2</sub>HPO<sub>3</sub>
  - B. PCl₃
  - C. P<sub>4</sub>O<sub>6</sub>
- 4. The anion BF<sub>4</sub>- has acts in many ways like an oversized halide anion. The conjugate acid of this anion, HBF<sub>4</sub>, is of interest as a strong acid (similar to HCl, etc.).
  - A. The name of BF<sub>4</sub>- is "tetrafluoroborate." From this information, generate a name for the acid HBF<sub>4</sub>.
  - B. Pure HBF<sub>4</sub> decomposes to form HF and BF<sub>3</sub>. Provide chemical names for each of the products of this reaction.

# Compounds and the Mole II

- 1. The fact that a mole corresponds to  $6.022 \times 10^{23}$  (Avogadro's number,  $N_A$ ) objects is fairly well known. But where does this number come from? Through the following series of problems, we'll come to understand the mole better as a concept.
  - A. By definition, one carbon-12 atom has a mass of 12.00 atomic mass units (12.00 u). Using Wolfram Alpha, calculate the mass of Avogadro's number of carbon-12 atoms. (Wolfram Alpha is an intelligent calculator. You can type in "Avogadro's number" and it will understand what you mean quantitatively.)
  - B. Repeat the calculation for Avogadro's number of oxygen-16 atoms (15.99 u) and bromine-79 atoms (78.92 u). Do you notice a pattern in the masses of  $N_A$  atoms?
  - C. The pattern you're seeing is general for atoms and molecules. State the pattern as a general rule that relates mass on the atomic or molecular scale to mass on the scale of 1 mole.
- 2. In the video on <u>Mass Vocabulary</u>, Dr. Shepler distinguishes between the terms formula mass and molecular mass. While not profoundly different in practice, these terms refer to compounds that look very different on the sub-microscopic scale. For each compound below, indicate whether the term "formula mass" or "molecular mass" is more appropriate for describing the mass of the formula unit. Then, calculate that mass in atomic mass units (u).
  - A. CaTiO<sub>3</sub>
  - B. C<sub>21</sub>H<sub>23</sub>NO<sub>5</sub>
  - C. Al<sub>2</sub>O<sub>3</sub>
  - D. Be<sub>3</sub>Al<sub>2</sub>(SiO<sub>3</sub>)<sub>6</sub>
- 3. Desmopressin is a drug that promotes the re-uptake of water by cells, raising blood pressure and decreasing the frequency of urination.
  - A. Desmopressin contains 51.67% C, 6.03% H, 18.34% N, 17.96% O, and 6.00% S by mass. Determine the empirical formula of desmopressin from this data.
  - B. An independent experiment confirmed that a sample of 1.0692 g of desmopressin contains 1.000 mmol of desmopressin molecules. What is the molar mass of desmopressin? What is its molecular formula?
- 4. The combustion of an unknown hydrocarbon (a compound containing *only* carbon and hydrogen) produced 8.80 g of CO<sub>2</sub> and 4.50 g of H<sub>2</sub>O. The molar mass of the compound, determined in a separate experiment, is 58.124 g/mol. What is the molecular formula of the compound?

#### **Chemical Reactions and Aqueous Solutions I**

- 1. Classify each of the reactions below using the reaction classes described in the <u>Types of</u> <u>Chemical Reactions</u> videos.
  - A.  $Si(s) + 2 Cl_2(g) \rightarrow SiCl_4(I)$
  - B.  $2 C_4 H_{10}(g) + 13 O_2(g) \rightarrow 8 CO_2(g) + 10 H_2O(g)$
  - C.  $Pb(NO_3)_2(aq) + 2 KI(aq) \rightarrow PbI_2(s) + 2 KNO_3(aq)$
- 2. What is the driving force for reaction 1C?
- 3. To better understand and predict how and why reactions happen, we often think about what's going on at the molecular or sub-microscopic level. For each of the reactions below, draw molecular-scale pictures of the reactants and products. Make an effort to balance the elements in both pictures.
  - A.  $2 \operatorname{H}_2(g) + \operatorname{O}_2(g) \rightarrow 2 \operatorname{H}_2\operatorname{O}(I)$
  - B.  $Mgl_2(aq) + 2 AgNO_3(aq) \rightarrow 2 Agl(s) + Mg(NO_3)_2(aq)$
  - C.  $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
- 4. When aqueous sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) is mixed with an aqueous solution of acetic acid (HO<sub>2</sub>C<sub>2</sub>H<sub>3</sub>), a reaction occurs that produces carbon dioxide (CO<sub>2</sub>), water (H<sub>2</sub>O), and sodium acetate (NaO<sub>2</sub>C<sub>2</sub>H<sub>3</sub>).
  - A. This reaction occurs in two stages: an initial formation of carbonic acid (H<sub>2</sub>CO<sub>3</sub>) followed by the conversion of carbonic acid to water and carbon dioxide. *Unbalanced* equations showing these processes are below.

 $\underline{\text{Na}_2\text{CO}_3(aq) + \underline{\text{HO}_2\text{C}_2\text{H}_3(aq)} \rightarrow \underline{\text{NaO}_2\text{C}_2\text{H}_3(aq) + \underline{\text{H}_2\text{CO}_3(aq)} }$ 

Provide coefficients in both chemical equations so that the overall conversion of sodium carbonate to sodium acetate, water, and carbon dioxide is balanced.

- B. How would you classify the first reaction? What is its driving force?
- C. How would you classify the second reaction?
- 5. Melanoidins are complex structures formed when wet barley malt is heated in a kiln during the beermaking process. To model the formation of melanoidins, an  $\alpha$ -hydroxy acetaldehyde (C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>) was combined with methylamine (CH<sub>5</sub>N). The products were water (H<sub>2</sub>O) and an organic compound with the formula C<sub>6</sub>H<sub>10</sub>N<sub>2</sub>. Balance this chemical equation.

 $\underline{\quad} C_2H_4O_2 + \underline{\quad} CH_5N \longrightarrow \underline{\quad} C_6H_{10}N_2 + \underline{\quad} H_2O$ 

#### **Chemical Reactions and Aqueous Solutions II**

- 1. In the video <u>Compounds in Aqueous Solution</u>, Dr. Shepler discusses the difference between *dissolution* and *dissociation*.
  - A. Provide an example of a compound that does not undergo dissociation when dissolved in water. Write a balanced chemical equation with state indicators for the dissolution of this compound in water, looking up formulas where necessary.
  - B. Provide an example of a compound that *does* undergo dissociation when dissolved in water. Write separate balanced chemical equations for the dissolution and dissociation processes.
  - C. For your chosen compound in B, draw molecular-level pictures of the solution immediately following dissolution and following dissociation.
- 2. Determine whether each of the following compounds is a strong or weak electrolyte. Provide a justification in each case.
  - A. NaOH
  - B. NiBr<sub>2</sub>
  - $C. \quad H_2SO_4$
  - D.  $C_6H_{12}O_6$  (sucrose)
  - E.  $HO_2C_2H_3$  (acetic acid)
  - F. HCI
- 3. The solubility rules are qualitative guidelines that enable us to predict whether a given ionic solid is soluble in water or not.
  - A. Use the solubility rules to construct six ionic compounds involving different ions (i.e., twelve distinct ions in all) that are soluble in water.
  - B. Use the solubility rules to construct six ionic compounds involving different ions (i.e., twelve distinct ions in all) that are insoluble in water.
- 4. Lead(II) nitrate reacts with sodium chloride in aqueous solution to form a precipitate.
  - A. Write balanced molecular, ionic, and net ionic equations for this process with state indicators.
  - B. If you haven't already, identify the spectator ions in the reaction.

### Stoichiometry I

 In several problems spread out over the next week, we'll explore the process of creating a desmopressin solution outlined in <u>this video</u>. We previously encountered the anti-diuretic drug desmopressin (C<sub>46</sub>H<sub>64</sub>N<sub>14</sub>O<sub>12</sub>S<sub>2</sub>, 1069.2 g/mol) in Chapter 3.

This compound is commonly treated with acetic acid (HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, 60.1 g/mol) to produce desmopressin acetate (C<sub>48</sub>H<sub>68</sub>N<sub>14</sub>O<sub>14</sub>S<sub>2</sub>, 1129.3 g/mol). Desmopressin and acetic acid react in a 1:1 molar ratio.

- A. How many moles of desmopressin are present in a 120. mg sample?
- B. What mass of acetic acid is necessary to completely consume this amount of desmopressin?
- 2. The compound  $\alpha$ , $\alpha$ '-dibromo-o-xylene (C<sub>8</sub>H<sub>8</sub>Br<sub>2</sub>, 264.0 g/mol) reacts with lithium metal to give a product containing 16 carbons as well as lithium bromide. A balanced chemical equation for this process is given below.

 $2 C_8H_8Br_2 + 4 Li \rightarrow C_{16}H_{16} + 4 LiBr$ 

In <u>one synthesis</u> of  $C_{16}H_{16}$ , 101 g of  $C_8H_8Br_2$  were combined with 6.63 g of lithium metal.

- A. Determine the number of moles of each reactant.
- B. Determine the limiting reactant.
- 3. Barium nitride ( $Ba_3N_2$ ) and water react to form barium hydroxide ( $Ba(OH)_2$ ) and ammonia ( $NH_3$ ).
  - A. Write a balanced chemical equation for this process.
  - B. What is the maximum mass of barium hydroxide that can be produced from a mixture of 50.0 g of barium nitride and 20.0 g of water?
  - C. Under the conditions of the previous problem, assuming the reaction goes to completion, what mass of the excess reactant is left behind?
- Calcium hydroxide (Ca(OH)<sub>2</sub>) is formed from the reaction of calcium oxide (CaO) with water (H<sub>2</sub>O).
  - A. Write a balanced chemical equation for this process.
  - B. What mass of calcium hydroxide can be produced from a mixture of 25.0 g of calcium oxide and 12.0 g of water?
  - C. Under the conditions of the previous problem, assuming the reaction goes to completion, what mass of the excess reactant is left behind?

## Stoichiometry II

1. The diphosphorus pentoxide used to produce phosphoric acid for cola drinks is prepared by burning phosphorus in oxygen.

 $\mathsf{P}_4 + \mathsf{5} \mathsf{ O}_2 \longrightarrow \mathsf{P}_4\mathsf{O}_{10}$ 

- A. What is the limiting reactant when 0.200 mol  $P_4$  are combined with 0.200 mol  $O_2$ ?
- B. What is the percent yield of diphosphorus pentoxide if 10.0 grams of  $P_4O_{10}$  are obtained at the end of the reaction?
- 2. In the last set of problems we considered the reaction below.

 $2 C_8 H_8 Br_2 + 4 Li \rightarrow C_{16} H_{16} + 4 Li Br$ 

In <u>one synthesis</u> of  $C_{16}H_{16}$ , 101 g of  $C_8H_8Br_2$  were combined with 6.63 g of lithium metal. The actual yield of  $C_{16}H_{16}$  was 19.6 g. What is the percent yield of  $C_{16}H_{16}$ ?

- 3. Brewing water is commonly "treated" with one or more ionic salts to provide nutrients for yeast, adjust pH, or improve flavor. In one treatment, 0.058 moles of calcium in the form of calcium chloride (CaCl<sub>2</sub>) are dissolved in 4 gallons of water.
  - A. Write a balanced chemical equation for the dissolution of calcium chloride in water.
  - B. How many moles of chloride ions are added to the water in the process? What are the molarities of calcium and chloride ions?
  - C. What mass of calcium chloride is needed to create this solution?
- Let's continue to explore the process of creating a desmopressin solution outlined in this video. We previously encountered the anti-diuretic drug desmopressin (C<sub>46</sub>H<sub>64</sub>N<sub>14</sub>O<sub>12</sub>S<sub>2</sub>, 1069.2 g/mol) in Chapter 3.

If you haven't already, watch the complete video before tackling the problems below.

- A. A mass of 120. mg desmopressin acetate (C<sub>48</sub>H<sub>68</sub>N<sub>14</sub>O<sub>14</sub>S<sub>2</sub>, 1129.3 g/mol) is first dissolved in 100. mL of water. Assuming the final solution volume is 100. mL, what is the molarity of desmopressin in this solution?
- B. A volume of 1.0 mL of this solution is added to "vehicle," a mixture of simple and cherry syrup, to create a final solution with a volume of 60.0 mL. What is the molarity of desmopressin in the resulting solution?
- C. Verify that this molarity corresponds to 0.1 mg of desmopressin per 5 mL of solution as reported on the video.
- 5. Calculate each of the following quantities for additional practice with solutions.
  - A. Grams of solute in 175.8 mL of 0.0565 M calcium acetate

- B. Molarity of a 500. mL solution containing 3.38 g potassium iodide
- C. Moles of solute in 3.011 L of 0.850 M sodium cyanide
- 6. Arrange the solutions in order of increasing number of particles in solution assuming that the volumes of the solutions are the same: 0.50 M Na<sub>3</sub>PO<sub>4</sub>, 1.0 M C<sub>6</sub>H<sub>14</sub>, 1.0 M KCl, 1.0 M Ca(NO<sub>3</sub>)<sub>2</sub>.

## Stoichiometry III

- 1. The density of ethanol ( $C_2H_6O$ ) is 0.789 g/mL. Ethanol reacts with acetic acid ( $HC_2H_3O_2$ ) in a 1:1 molar ratio to yield ethyl acetate ( $C_4H_8O_2$ ) and water ( $H_2O$ ). What volume of a 2.0 M acetic acid solution is required to completely consume 500. mL of ethanol?
- The molar volume of an ideal gas at standard temperature and pressure is 22.4 L/mol. Determine the theoretical yield of water and the amount of excess reactant remaining when 18.0 L of H<sub>2</sub> gas and 12.0 L of O<sub>2</sub> gas are combined and react according to the balanced equation below.

 $2 H_2 + O_2 \longrightarrow 2 H_2 O$ 

3. The weak acid hydrazoic acid (HN<sub>3</sub>) can be titrated by sodium hydroxide (NaOH) to determine its concentration in solution. The two react according to the balanced chemical equation below.

 $HN_3 + NaOH \rightarrow NaN_3 + H_2O$ 

- A. What volume of 0.20 M NaOH is required to completely consume the hydrazoic acid in 25.0 mL of a 0.50 M HN $_3$  solution?
- B. After the two solutions have been combined and the reaction has run its course, what is the molarity of  $NaN_3$  in the resulting solution? Assume that the reaction goes to completion.
- C. What is  $[HN_3]$  in a 10.0-mL sample that requires 30.0 mL of 0.15 M NaOH to completely consume the  $HN_3$ ?
- 4. In a common medical laboratory determination of the concentration of free chloride ion in blood serum, a serum sample is titrated with a Hg(NO<sub>3</sub>)<sub>2</sub> solution.

 $2 \text{ Cl}^- + \text{Hg}(\text{NO}_3)_2 \longrightarrow 2 \text{ NO}_3^- + \text{HgCl}_2$ 

What is [Cl<sup>-</sup>] in a 0.25-mL sample of serum that requires 1.46 mL of 8.25 ×  $10^{-4}$  M Hg(NO<sub>3</sub>)<sub>2</sub> to fully consume the Cl<sup>-</sup> in the sample?

## Thermochemistry I

1. In aqueous solution, lithium sulfate (Li<sub>2</sub>SO<sub>4</sub>) reacts with barium chloride (BaCl<sub>2</sub>) to form solid barium sulfate (BaSO<sub>4</sub>) and aqueous lithium chloride (LiCl). Draw a diagram of this situation and label the system and surroundings, keeping in mind that, as chemists, we are interested in the energy change as the reactants become products.

 $Li_2SO_4(aq) + BaCl_2(aq) \rightarrow BaSO_4(s) + 2 LiCl(aq)$ 

- 2. Provide definitions and examples of the following types of systems.
  - A. An isolated system
  - B. A closed system that can exchange only heat with its surroundings
  - C. A closed system that can exchange heat or work with its surroundings
  - D. An open system
- 3. Inside a refrigerator, a refrigerant gas absorbs 80 cal of heat from the refrigeration compartment and its internal energy increases by 450 J.
  - A. Draw a diagram of this situation that includes the refrigerant gas line and the refrigeration compartment. Label the system and surroundings, keeping in mind that, as chemists, we are interested in the internal energy of the gas.
  - B. Calculate the work done on the gas during this process in Joules, considering the first law of thermodynamics.
- 4. Consider two identical cans of beans A and B starting at 20 °C. The cans are able to exchange energy with their surroundings but no particles can enter or leave the cans. A timer is started and can A is cooled to 5 °C and then heated to 80 °C. Simultaneously, can B is immediately heated to 80 °C. The timer is stopped when can A reaches 80 °C, at which point can B is already at this temperature.
  - A. Consider the processes for **A** and **B** that started when the timer was started and ended when the timer was stopped. List two examples of values that are *equal* for both processes and explain why they are equal. (*Hint:* the values depend only on the initial and final conditions and not on the process leading from one to the other.)
  - B. Consider the processes for **A** and **B** that started when the timer was started and ended when the timer was stopped. List two examples of values that are *unequal* for both processes and explain why they are unequal.

## Thermochemistry II

- Inside a refrigerator, an ideal gas expands through a valve at a constant pressure of 40 psi from 5.0 mL to 500.0 mL. At the same time, the gas absorbs 125 J of heat from its surroundings.
  - A. Draw a diagram of this situation that includes the gas line on either side of the valve, the valve, and the surroundings (the refrigeration compartment). Label the system and surroundings, keeping in mind that, as chemists, we are interested in the internal energy of the gas.
  - B. Label the directions of heat and work flows. What are the signs of heat and work from the perspective of the system?
  - C. Calculate the heat and work and use them to calculate the internal energy change of the gas during this process in Joules.
- 2. Imagine that the (tiny) refrigeration compartment in the last problem was filled with 0.010 L of water at 20.0 °C. What will the temperature of the water be when the process described in problem 1 is complete?
- 3. A sample of coal is burned in an apparatus with a calorimeter constant of 1.3 kJ/°C. When a sample weighing 0.367 g is used, the temperature change is +8.75 °C. What is the energy density of this coal in units of kJ/g?
- 4. A 61.0 g sample of hot metal, which initially has a temperature of 120.0 °C, is plunged into 100. g of water that is initially at 20.0 °C. The metal cools down and the water heats up until they reach a common temperature of 26.39 °C.
  - A. Draw a diagram of this situation, label the system and surroundings, and label the direction(s) of relevant heat flow(s).
  - B. Before doing any calculations, is the specific heat of the metal less than or greater than the specific heat of water?
  - C. Calculate the specific heat of the metal, using 4.184 J/g  $^{\circ}\text{C}$  as the specific heat of the water.
- 5. Predict whether each of the following processes is endothermic or exothermic. Consider the definition of enthalpy (*H*).
  - A. The temperature of an ideal gas increases inside a closed, rigid container.
  - B. An ideal gas is compressed at constant pressure and constant internal energy.
  - C. The temperature of an ideal gas decreases inside a closed, rigid container.
  - D. An ideal gas expands at constant pressure and constant internal energy.

## Thermochemistry III

- 1. When 4 moles of iron metal react with 3 moles of oxygen gas to form 2 moles of iron(III) oxide, the reaction releases 1652 kJ of heat at constant pressure.
  - A. Write a balanced thermochemical equation for this process.
  - B. How much heat is released when 10.0 g of iron metal and 3.00 g of oxygen gas react? Assume that the reaction goes to completion.
- 2. When solutions contain silver ions and chloride ions are mixed, silver chloride precipitates. One mole of reaction events releases 65.5 kJ of heat at constant pressure.

 $Ag^{+}(aq) + CI^{-}(aq) \rightarrow AgCI(s)$ 

- A. Write a balanced thermochemical equation for this process.
- B. Determine the change in enthalpy when  $9.25 \times 10^{-4}$  moles of AgCl solid dissolves in one liter of water.
- 3. Given the following data, calculate  $\Delta H^{o}_{rxn}$  for the target reaction below.

*Target:*  $H_2(g) + Br_2(I) \rightarrow 2 HBr(g)$ 

 $\begin{array}{ll} \mathsf{NH}_3(g) + \mathsf{HBr}(g) \to \mathsf{NH}_4\mathsf{Br}(s) & \Delta H^\circ_{rxn} = -188.32 \ \mathsf{kJ} \\ \mathsf{N}_2(g) + 3 \ \mathsf{H}_2(g) \to 2 \ \mathsf{NH}_3(g) & \Delta H^\circ_{rxn} = -92.22 \ \mathsf{kJ} \\ \mathsf{N}_2(g) + 4 \ \mathsf{H}_2(g) + \mathsf{Br}_2(I) \to 2 \ \mathsf{NH}_4\mathsf{Br}(s) & \Delta H^\circ_{rxn} = -541.66 \ \mathsf{kJ} \end{array}$ 

- 4. Inside an internal combustion engine, gaseous *n*-octane ( $C_8H_{18}$ ) reacts with oxygen gas ( $O_2$ ) to form carbon dioxide gas ( $CO_2$ ) and water vapor ( $H_2O$ ).
  - A. Write a balanced chemical equation for this process.
  - B. Use the <u>NIST Chemistry WebBook</u> to look up the enthalpies of formation of gaseous *n*-octane, gaseous carbon dioxide, and water vapor. Explain why looking up the enthalpy of formation of gaseous oxygen is unnecessary.
  - C. Use the enthalpies of formation you looked up and the balanced equation you wrote to calculate  $\Delta H^{o}_{rxn}$  for the combustion of gaseous *n*-octane.

#### Gases I

- 1. An understanding of gas laws is critical in the carbonation process. To "force-carbonate" beer, the liquid is placed in a sealed vessel (keg) and the headspace is filled with carbon dioxide at high pressure. This may be done at room temperature or after cooling the beer to refrigerator temperatures.
  - A. Imagine that 5 gallons of beer are force-carbonated using 50 psi of carbon dioxide at room temperature (20.0 °C). The keg is then placed in a refrigerator ("kegerator") and cooled to 3.0 °C. Assuming no change in the solubility of carbon dioxide in the liquid and no changes in volume or number of moles, what will the pressure of carbon dioxide be at the cold temperature?
  - B. After cooling, the pressure of carbon dioxide in a keg is *much* smaller than the value in part A because the solubility of a gas in water increases as the temperature drops. As the temperature falls, more carbon dioxide dissolves in the beer.

Imagine the headspace above the beer has a volume of 1 gallon (3.79 L). If the measured pressure at 3 °C is 12.1 psi, what amount in moles of additional carbon dioxide has dissolved in the beer upon cooling? You'll need to use the theoretical pressure from the last problem. The ideal gas constant is 0.319 psi·gallons/K·mol.

- 2. A gaseous mixture made from 10.0 g of oxygen and 5.0 g of methane is placed in a 10.0 L vessel at 25 °C. What is the partial pressure of each gas (in atm), and what is the total pressure in the vessel?
- 3. A mixture of 35.6 L of  $NH_3(g)$  and 40.5 L of  $O_2(g)$  are mixed at standard temperature and pressure (STP) and ignited. The reaction produces gaseous water and NO(g). After the products return to STP, how many grams of NO are present?
- 4. Check out the simulation of an ideal gas here: <a href="http://falstad.com/gas/">http://falstad.com/gas/</a>. The distribution of particle speeds is shown near the bottom of the simulation. Use the dropdown menu to explore different initial configurations of the gas molecules. Make sure to try out the "Two Gases" items. Determine whether each statement below is true or false.
  - A. The distribution of speeds at long simulation times depends profoundly on the initial configuration of gas molecules.
  - B. Heating the gas causes the distribution of speeds to "tighten up" or become "spikier."
  - C. Once the distribution of speeds converges to a Maxwell distribution, fluctuations above or below the theoretical distribution are not observed.
  - D. When two gases with different masses are mixed randomly in the same container, they converge to different speed distributions.
  - E. When two gases with different masses are mixed randomly in the same container, they converge to different energy distributions.

#### Gases II

- 1. Arrange the following samples of gas in order of increasing root mean square speed and explain your ordering.
  - A. O<sub>2</sub> at 700 K
  - B. 0<sub>2</sub> at 400 K
  - C.  $H_2$  at 700 K
  - D.  $H_2$  at 400 K
- 2. Arrange the following samples of gas in order of increasing kinetic energy and explain your ordering.
  - A.  $O_2 \mbox{ at } 700 \mbox{ K}$
  - B.  $O_2$  at 400 K
  - $C. \quad H_2 \text{ at } 700 \text{ K}$
  - D.  $H_{\rm 2} \mbox{ at } 400 \mbox{ K}$
- 3. Whoops—your toddler poked a tiny hole in your keg. Carbon dioxide, nitrogen, and oxygen gases in the headspace immediately started effusing through the hole. Which of the three gases effuses at the highest rate?
- 4. If it takes 67 minutes for a given volume of  $H_2$  to effuse, how long will it take an equal volume of UF<sub>6</sub> to effuse under the same conditions of temperature and pressure?
- 5. If it takes 67 minutes for a given volume of  $H_2$  to effuse at 25 °C, how long will it take the same volume to effuse if the temperature is increase to 37 °C?
- 6. An unknown gas effuses at a rate that is 1.5 times faster than chlorine gas (at the same temperature). What is the molar mass of the unknown gas?
- 7. What evidence could you supply to indicate that, unlike ideal gases, real gas particles do have some attractions to each other?

# Quantum Model of the Atom I

- The Voyager 1 spacecraft was launched in 1977 to explore the outer Solar System. In December 2012, it was 1.85 × 10<sup>13</sup> m from Earth and still sending and receiving data via radio signals. At this distance, how long did it take signals from Voyager 1 to reach Earth?
- 2. The frequencies of light associated with traffic signals are listed below. For each, calculate the wavelength in nanometers, the energy of a *single* photon in Joules, and the energy of a *mole* of photons in kilojoules per mole. Finally, list the colors associated with each frequency.

```
5.75 × 10<sup>14</sup> Hz 5.15 × 10<sup>14</sup> Hz 4.37 × 10<sup>14</sup> Hz
```

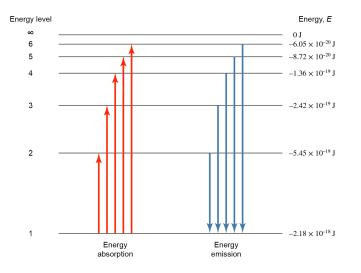
- 3. A laser that emits light energy in pulses of short duration has a frequency of  $4.69 \times 10^{14} \text{ s}^{-1}$  and deposits  $1.3 \times 10^{-2} \text{ J}$  of energy during each pulse. How many photons does each pulse deposit?
- 4. The photoelectric effect refers to the ejection of electrons from a metal by light impinging on the metal. There is a minimum frequency of light needed to cause the ejection of an electron; this frequency is unique to each metal. This frequency is related to an energy called the *work* function ( $\varphi$ ).
  - A. Using <u>this simulation</u>, choose a metal and measure its work function. To do this, determine the *maximum* wavelength that causes ejection of an electron and calculate the energy of the light at this wavelength in electron-Volts (eV).  $hc = 1240 \text{ eV} \cdot \text{nm}$ .
  - B. Using the results of others in your section along with your own, prepare an energy diagram that shows the relative energies of the highest-energy electrons in each metal.

# Quantum Model of the Atom II

- 1. The Bohr model of the atom was an important precursor to the fully quantum model that we use today. Bohr based his model on the observation that atoms only absorb and emit particular wavelengths of light. Draw a picture of the Bohr model of the hydrogen atom and use arrows to show how the electron changes in energy and position when the atom absorbs or emits a photon.
- 2. The Rydberg equation was developed as an empirical model that explains the wavelengths  $\lambda$  of light emitted by excited hydrogen atoms.

$$\frac{1}{\lambda} = R_{\rm H} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

- A. Label each of the variables on the right-hand side of this equation and provide a value for  $R_{\rm H}$  in appropriate units.
- B. The Rydberg equation can be written in an equivalent form with the energy of the emitted photon on the left-hand side instead of its wavelength. Show how this can be done starting from the equation above and use your approach to calculate a value for  $R_{\rm H}$  in units of electron-Volts (eV).
- C. On the diagram below, label the ground state and excited states. Order the emissive transitions from longest to shortest wavelength of light emitted.



3. Atomic electrons are arranged in shells indexed by a positive integer *n* that we will call the *principal quantum number*. Determine the number of electrons that each shell can hold by completing the table below. Start with the second column from the left and fill out the table left to right.

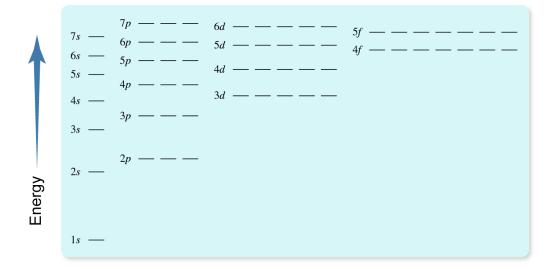
Shell ( <i>n</i> )	Subshells	Orbitals within subshell	Total number of electrons in subshell	Total number of electrons in shell
1				
2				
3				
4				

4. Draw the shapes of the 1s, 2*p*, and 3*d* orbitals in the table below.

1s				
2p	2p	2p		
3d	3d	3d	Зd	3d

#### Quantum Model of the Atom III

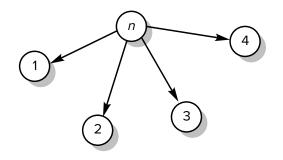
- 1. In the energy level diagram below, label or highlight the following:
  - A. The n = 3 shell
  - B. A subshell that can hold 10 electrons
  - C. An orbital that can hold 2 electrons
  - D. Two or more degenerate orbitals



- 2. Applying the Aufbau principle and Hund's rule, number the first ten orbitals to be filled with electrons based on the diagram above.
- 3. Apply the diagram above to write electron configurations for the following atoms or ions.
  - A. Lithium atom
  - B. Oxygen atom
  - C. Chloride ion (CI-)
  - D. Sulfide ion (S<sup>2-</sup>)
  - E. Calcium ion (Ca<sup>2+</sup>)
- 4. Do you notice anything interesting about the electron configurations of Cl-, S<sup>2-</sup>, and Ca<sup>2+</sup>?
- 5. Compare the electron configurations of neutral carbon, silicon, and germanium atoms, all of which are in group 14. What do you notice about their electron configurations?

# Quantum Model of the Atom IV

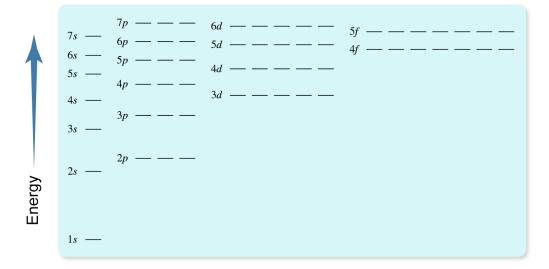
1. One representation of the rules for quantum numbers involves conceiving of them as a kind of tree, with *n* as the "trunk" and the more specific quantum numbers as "branches." Starting from a representation like the one below, depict the shells, subshells, and orbitals as a tree, labeling each node with its associated quantum number (use letters for  $\ell$ ).



- 2. Give the name and number of orbitals for each subshell with the following quantum numbers.
  - A. n = 3,  $\ell = 2$
  - B.  $n = 2, \ell = 0$
  - C.  $n = 4, \ell = 1$
  - D.  $n = 5, \ell = 3$
- 3. List the quantum numbers for each of the following subshells, including the range of possible values for  $m_{\ell}$ .
  - A. 1s
  - B. 2s
  - С. Зр
  - D. 5d

CHEM 1211K Chemical Principles I

4. For the 1s, 2p, and 3d orbitals on the diagram below, indicate the values of n and  $\ell$  for each subshell and list the possible values of  $m_{\ell}$  under each orbital.



# Periodicity and Ionic Bonding I

1. The concept of effective nuclear charge ( $Z_{eff}$ ) explains a great deal of the periodic variation in atomic properties we'll encounter in this chapter. Reasonably accurate values of  $Z_{eff}$  can be calculated using Slater's rules. In the equations below, Z is the total nuclear charge,  $N_{core}$  and  $N_{val}$  are the numbers of core and valence electrons,  $\sigma_{core}$  and  $\sigma_{val}$  are the screening constants of core and valence electrons, and S is the shielding constant. S is a measure of the extent to which other electrons shield a valence electron from the positive charge of the nucleus.

 $Z_{eff} = Z - S$ 

 $S = \sigma_{core} N_{core} + \sigma_{val} N_{val}$ 

 $\sigma_{core} = 0.85, \ \sigma_{val} = 0.35$ 

- A. Using a simple picture of the nucleus, core electrons, and valence electrons, explain why  $\sigma_{core} < \sigma_{val}$ .
- B. Choose an element in the table at <u>this link</u> (make sure to open the sheet for your section and avoid elements that are grayed out). Determine the numbers of core and valence electrons in an atom of the element and calculate the effective nuclear charge for a valence electron. Fill these values into the table. As other students add values, look for patterns in  $Z_{eff}$ .
- 2. Empirical atomic radii based on the work of Slater are listed <u>here</u>. Add the atomic radius of your element in picometers to the table (if your element has "no data," leave the atomic radius cell blank).
  - A. Examine the graph of atomic radius and  $Z_{eff}$  that appears. Within a period, how does atomic radius depend on  $Z_{eff}$ ?
  - B. Compare atomic radii for your element and others in its group. The trend moving down a group appears to be opposite the trend observed in A moving across a period. Why?
- All of the following ions are isoelectronic: they have the same electron configuration. Calculate Z<sub>eff</sub> for a valence electron in each ion and then order them from smallest to largest ionic radius. Explain your ordering.

Se<sup>2-</sup>, Br<sup>-</sup>, Rb<sup>+</sup>, Sr<sup>2+</sup>

# Periodicity and Ionic Bonding II

- 1. Choose an element in the table at <u>this link</u> (make sure to open the sheet for your section and avoid elements that are grayed out). Using the CRC ionization energies listed <u>here</u>, add the *first* ionization energy of your element to the table in units of electron-Volts (eV). If your element has "no data," leave the ionization energy cell blank.
  - A. Examine the graph of ionization energy and  $Z_{eff}$  that appears. Within a period, how does ionization energy depend on  $Z_{eff}$ ?
  - B. Compare ionization energies for your element and others in its group. The trend moving down a group appears to be opposite the trend observed in A moving across a period. Why?
- 2. The table below lists the main-group elements in period 3 in the rows and successive ionization energies (IE1, IE2, IE3, ...) in the columns. In the table, place an "X" where the ionization energy is *much* larger than the one before it for each element. Don't consult a list of ionization energies; consider the number of valence electrons in each atom.

	IE1	IE2	IE3	IE4	IE5	IE6	IE7	IE 8
Na								
Mg								
AI								
Si								
Ρ								
S								
CI								

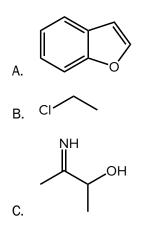
- 3. Write and compare balanced chemical equations corresponding to ionization energy and electron affinity. Is the process for which electron affinity is the measured energy absorbed or released the exact reverse of ionization energy? Explain why or why not.
- 4. Find the electron affinity of the element you worked with in question 1 <u>here</u> in units of electron-Volts (eV). Add it to the table of atomic data at <u>this link</u>. Note that electron affinities here are reported as positive numbers with the understanding that an atom accepting an electron is generally exothermic.
  - A. Examine the graph of electron affinity and *Z* that appears. Within a period, how does electron affinity generally depend on *Z*?
  - B. Find an exception to the trend in A in the same period as your element. Write the electron configuration of this element and explain why its electron affinity is not consistent with the trend.
- 5. Order each series of ionic compounds below from smallest to largest lattice energy. Identify the key structural difference in each series that allows you to make this determination.

Confirm your predictions using the <u>lattice energy calculator</u>.

- A. KF, KCl, KBr, KI
- B. LiCl, NaCl, KCl, RbCl, CsCl
- C. MgO, Li<sub>2</sub>O, NaCl

# **Covalent Bonding I**

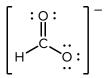
 Organic molecules are often depicted using a shorthand notation that omits unshared pairs (lone pairs), carbon atoms, and C-H bonds. Carbon atoms are understood to be located at the intersection points of lines and it is assumed that carbon atoms bear enough bonds to hydrogens to satisfy the octet rule. Unshared pairs can be identified by assuming that all atoms in the structure are neutral. Using these ideas, add missing unshared pairs and hydrogen atoms to the structures below.



- 2. Draw a valid Lewis structure for each of the following molecules.
  - A. CO
  - B. BF₃
  - C.  $SF_2$
  - $D. \ PH_3$
  - E. CCl<sub>4</sub>
- 3. Examine trends in electronegativity <u>here</u>. On the blank periodic table below, indicate how electronegativity changes moving left to right across a group and down a period. Identify the one main-group element that doesn't fit with this trend and explain why it doesn't.

]									
						_	_		

- 4. The formate ion  $HCO_{2^{-}}$  has two important resonance structures.
  - A. One of these structures is drawn below. Draw the other, which also includes one C=0 bond and one C-0 bond.



B. Considering electronegativity trends, is the negative charge in formate more likely to reside on carbon or oxygen? Explain.

## Covalent Bonding II

- 1. Draw Lewis structures for the following molecules and explain how they violate the octet rule.
  - A. IF<sub>3</sub>
  - B. BeH<sub>2</sub>
  - C. PO<sub>4</sub><sup>3-</sup>
  - D. H<sub>2</sub>SO<sub>4</sub>
- 2. For the molecules in A C in problem 1, indicate the more electronegative atom in each bond and use partial charge indicators ( $\delta$ + and  $\delta$ -) to show the orientation of bond dipoles in each molecule.
- 3. Thiosulfate  $(S_2O_3^{2-})$  reacts with cyanide  $(CN^-)$  to form thiocyanate  $(SCN^-)$  and sulfite  $(SO_3^{2-})$ . A balanced chemical equation for this process is shown below.

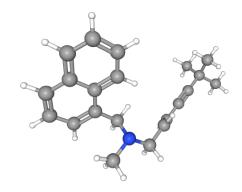
 $S_2O_3^{2-}(aq) + CN^{-}(aq) \rightarrow SO_3^{2-}(aq) + SCN^{-}(aq)$ 

- A. Draw Lewis structures for the reactant and product molecules and determine the bonds made and broken in this reaction.
- B. Use the bonds made and broken along with bond enthalpies to calculate the enthalpy change of this reaction.
- 4. Absorption of a photon by a molecule can promote the cleavage of covalent bonds in a *homolytic* way (meaning each atom in the bond gets one electron). Bond enthalpy can be used as a rough guide for the energy that a photon needs to break a bond. For each bond listed below, calculate the maximum wavelength of a photon that can break the bond based on its bond enthalpy. Which bonds, if any, can be broken by visible light?

0-0, C-0, C-S, C-I, S-S, CI-CI, I-I

## Molecular Shape and Bonding Theories I

1. Examine the three-dimensional structure of the antifungal terbinafine <u>here</u>. Identify atoms in the structure with linear, trigonal planar, and tetrahedral geometry. Identify an atom with tetrahedral electronic geometry but pyramidal molecular geometry.

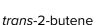


- 2. Determine the electronic and molecular geometries of the central atoms in each of the following ions or molecules. Draw Lewis structures for each, determine the number of electron domains around the central atom, write the electronic geometry, and place unshared pairs to determine the molecular geometry.
  - A. CS<sub>2</sub>
  - B. SiH<sub>2</sub>
  - C. NF₃
  - D. SiF₅⁻
  - E. SF<sub>6</sub>
- 3. So-called "hypervalent iodine" compounds contain iodine linked to three or more atoms or groups. IF<sub>3</sub> is one of the simplest examples of this kind of compound. What are the electronic and molecular geometries of IF<sub>3</sub>?
- 4. Sulfur tetrafluoride (SF<sub>4</sub>) is an important fluorinating reagent. Draw a Lewis structure for this compound and determine its electronic and molecular geometries at sulfur.
- 5. The compound nitramide has the formula H<sub>2</sub>NNO<sub>2</sub>. Draw a Lewis structure for this compound and determine whether it is polar or nonpolar. If the molecule has a permanent dipole moment, draw its direction.
- 6. The following molecules all contain polar covalent bonds. Which are polar molecules and which have no permanent dipole? (a) CCl<sub>4</sub>; (b) CHCl<sub>3</sub>; (c) CO<sub>2</sub>; (d) H<sub>2</sub>S; (e) SO<sub>2</sub>.

## Molecular Shape and Bonding Theories II

- 1. Determine the hybridization at the central atom in each of the molecules below.
  - A. CO<sub>2</sub>
  - B. H<sub>2</sub>CO
  - C. NH₃
  - D. CHCl₃
- 2. Hybrid atomic orbitals are mathematical constructions created by scaling and adding the hydrogenic atomic orbitals (2s, 2p, etc.) on a single atom. Overlap of hybrid orbitals generates localized bonding orbitals, where we can imagine the electrons in bonds live.
  - A. A three-dimensional model of allyl alcohol is <u>here</u>. Determine the hybridizations of the carbon atoms in this molecule.
  - B. Describe the C=C bond in this molecule in terms of valence bond theory. How many sigma and pi bonds are in this bond? What hybrid or atomic orbitals is the sigma bond composed of?
- 3. There are two forms of the compound 2-butene that cannot be interconverted except under harsh conditions: *cis* and *trans*-2-butene. Analogous forms of the related compound butane interconvert extremely rapidly. Use valence bond theory to explain the difference in behavior of butene and butane.

H<sub>3</sub>

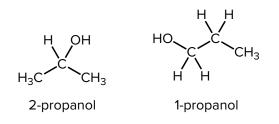


cis-2-butene

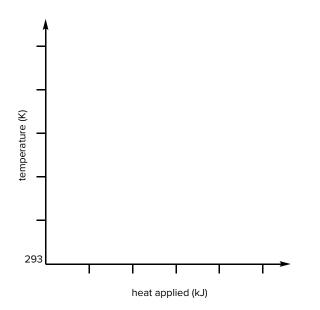
butane

#### Liquids and Solids

- 1. Identify *all* the intermolecular forces in pure samples of each compound below. If more than one force is operating, identify the predominant IMF.
  - A. CH<sub>3</sub>I
  - B. CH<sub>3</sub>CH<sub>2</sub>OH
  - C. Br<sub>2</sub>
  - D. CH<sub>2</sub>Cl<sub>2</sub>
- 2. Explain why, under ordinary conditions, elemental fluorine and chlorine both exist as gases, bromine exists as a liquid, and iodine exists as a solid.
- 3. Suggest a reason why the boiling point of 2-propanol (77 °C) is much lower than the boiling point of 1-propanol (97 °C).



4. Use thermochemical data on the <u>NIST Chemistry WebBook</u> to generate a heating curve for one of the following solvents: (a) ethanol; (b) diethyl ether; (c) tetrahydrofuran; (d) dichloromethane. Make an effort to draw the heating curve to scale. Assume all heating happens at a constant pressure of 1 atmosphere and that 1 mole of substance is being heated; extend the curve at least 40 K above the boiling point. For dichloromethane gas, assume  $c_P = 55$  J/mol-K (a good approximation below 350 K).



- 5. Create a phase diagram for bromine (Br<sub>2</sub>) using the following information. (reference video)
  - A. The critical point occurs at (102 atm, 315 °C).
  - B. The triple point occurs at (0.007 atm, -33 °C).
  - C. The normal boiling point is 59 °C.
  - D. The density of the solid is greater than the density of the liquid at all pressures.
- 6. Examine the unit cells linked below. For each, determine the number of atoms inside each unit cell (*only* inside the bounding box!) and calculate the packing factor as the percentage of space inside the unit cell filled by atoms. Examples of metals that crystallize in each lattice type are listed; using the identity of the metal and its crystal structure, calculate the density of the metal.
  - A. <u>Cubic close packing (ccp) or face-centered cubic (fcc)</u> | silver metal (Ag)
  - B. <u>Simple cubic</u> | polonium metal (Po)
  - C. <u>Body-centered cubic (bcc)</u> | sodium metal (Na)
- 7. Zinc metal crystallizes in the <u>hexagonal close packing (hcp)</u> structure, which has a packing factor equal to that of fcc. Compare and contrast this structure with the fcc structure. How are the structures different despite their equal packing factors?

# Thermodynamics of Solutions

- 1. Describe the process of solution formation in terms of interactions between solute and solvent particles. For each step of the process, indicate whether the step is likely to be endothermic or exothermic and whether the change in entropy ( $\Delta S$ ) is likely to be positive or negative.
- 2. Draw molecular-level depictions of the solute particles and their immediate environment when CaCl<sub>2</sub> is dissolved in water. Pay careful attention to the orientation of the water molecules!
- 3. One approach to thinking about solution thermodynamics for ionic solutes in water involves conceiving of the solution process as ionization followed by hydration:

$MX(s) \rightarrow M^+(g) + X^-(g)$	ionization
$M^+(g) \rightarrow M^+(aq)$	hydration of M+
$X^{-}(g) \rightarrow X^{-}(aq)$	hydration of X-
$MX(s) \rightarrow M^+(aq) + X^-(aq)$	solution formation

Determine the enthalpy of solution for  $MgF_2$  using the following data. Is the formation of an aqueous solution of magnesium fluoride endothermic or exothermic?

Lattice energy of MgF<sub>2</sub>: 2908 kJ/mol Enthalpy of hydration of Mg<sup>2+</sup>: –1926 kJ/mol Enthalpy of hydration of F-: –524 kJ/mol

- 4. Indicate which molecule in each pair is more likely to dissolve in water, drawing Lewis structures where necessary. Explain differences in solubility using intermolecular forces.
  - A. NaNO<sub>3</sub> or  $C_6H_6$
  - B. C<sub>2</sub>H<sub>6</sub> or CH<sub>3</sub>CH<sub>2</sub>OH
  - C.  $C_5H_{12}$  or  $CH_3C(=0)CH_3$