

**CHEM. 253 – Spring, 2015**  
**Exam 3 – May 20, 2015**

Name \_\_\_\_\_

The energy emitted by a black body emitter =  $\sigma T^4$  where  $\sigma = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$   
 Cross-sectional area =  $\pi r^2$  and area of a sphere =  $4\pi r^2$  where r = radius.

**Short Answer and Multiple Choice Section. For multiple choice problems, select the best (only one) answer. 4 points per problem.**

1. As a result of global warming, the poleward (northern in the northern hemisphere) edges of deserts are migrating poleward. This results in forests or shrublands being replaced by sparsely vegetated lands where albedo is higher. This is an example of:

- a) a positive feedback
- b) a negative feedback**
- c) climate sensitivity
- d) the end of the world

2. Which of the following molecules will NOT absorb in the infrared:

- a) CO<sub>2</sub>
- b) HCl
- c) O<sub>2</sub>**
- d) O<sub>3</sub>

3. Which of the following is a so-called “indirect effect” of aerosols on climate?

- a) aerosol particles catalyze the reduction of CO<sub>2</sub> to CH<sub>4</sub> increasing warming
- b) aerosol particles make clouds more reflective, increasing cooling**
- c) aerosol particles absorb solar light, increasing warming
- d) aerosol particles catalyze ozone loss, decreasing warming

4. Both natural gas and coal contain fossil carbon and produce carbon dioxide on combustion. In terms of contributions to global warming, why is natural gas considered a better fuel?

- a) Natural gas provides more heat per mole of CO<sub>2</sub> formed**
- b) Coal contains more sulfur resulting in SO<sub>2</sub> as well as CO<sub>2</sub>
- c) Natural gas releases water when burned which results in cooling
- d) Natural gas burns cleaner producing almost no particulates

5. List one secondary advantage of using biofuels (besides the use of a renewable fuel to reduce overall carbon dioxide emissions).

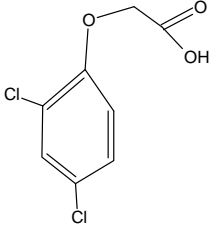
Secondary advantage: oxygenates burn better, can use waste products to create, can improve fuel quality as additive, reduces air pollution

6. What is a “green” advantage of using polylactic acid over polyethylene for bottles?

- a) polylactic acid is easier to recycle
- b) polylactic acid is made from renewable resources**
- c) polylactic acid is a more stable polymer
- d) polylactic acid is better for storing acidic drinks

7. Give one “green” advantage of using an ionic liquid in place of a traditional non-halogenated organic solvent? Green advantage: less volatile, toxic, flammable

8. 2,4-D (see structure below), which is an herbicide is a weak acid ( $pK_a = 2.73$ ) that is weakly polar ( $K_{ow} = 65$ ). During oral exposure, most of the absorption through the GI tract will occur in:  
 a) the mouth                      b) the throat                      **c) the stomach**                      d) the intestines



9. Most toxic compounds have loss processes (transformation or elimination) through one of two organs. List the organ and describe a loss process.

organ: 1) liver 2) kidney                      loss process: 1) transformation 2) elimination

**Problem and Short Essay Question Section (be sure to show work if calculations are needed):**

1. The solar constant (solar light flux) for Venus is  $2620 \text{ W m}^{-2}$  and its albedo is 0.65. What is the expected surface temperature of Venus assuming it behaves as a blackbody emitter and has no greenhouse gases? The average surface temperature on Venus is 753 K. What can be concluded by this? See p. 1 for equations and constants. (12 pts)

$$(1 - A)F_S\pi r^2 = 4\pi r^2 F_V \text{ where } A = \text{albedo, } F = \text{flux (sun or venus), and } r = \text{radius and } F_V = \sigma T^4 \text{ (blackbody emitter)}$$

$$\text{This becomes: } T^4 = (2620 \text{ W m}^{-2})(1 - 0.65)/(4\sigma) \text{ or } T = 252 \text{ K}$$

**Since  $T_{\text{Measured}} > T_{\text{Expected}}$ , there must be greenhouse gas warming on venus.**

2. Chlorofluorocarbons were considered valuable fluids for refrigeration due to being inflammable and non-toxic. However, because of their potential to release Cl into the stratosphere, they have largely been replaced by HCFCs or related compounds (e.g.  $\text{CHF}_2\text{OCHF}_2$ ). Considerations as to replacements also need to

consider if replacement compounds act as greenhouse gases. Describe two factors that would be of interest to know to determine how strong replacement compounds are as greenhouse gases (8 pts).

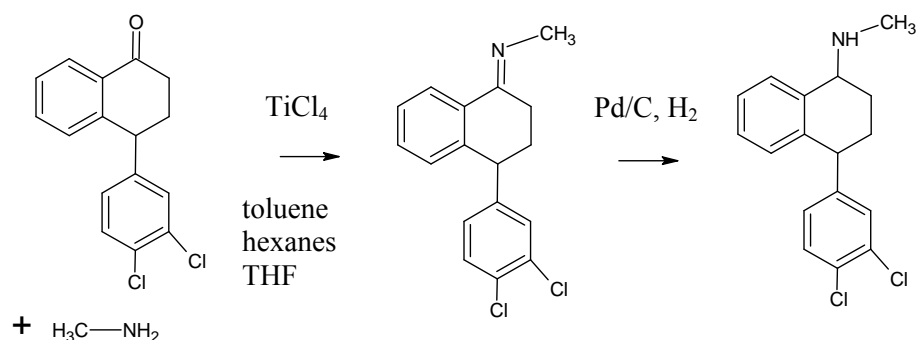
- 1) *If they absorb in window regions in the infrared*
- 2) *There lifetimes*

3. An industrialist is interested in tapping methane clathrates at the bottom of oceans as a fuel source. The methane clathrate ( $\text{CH}_4 \cdot 6\text{H}_2\text{O}$ ) is present as a solid under low temperatures and high pressures, but upon heating or reduction of pressure,  $\text{CH}_4$  can be released as a gas. They are present at moderate concentrations at ocean bottoms. Assume the methane recovered is being used to generate electricity to replace coal combustion sources of electricity. Besides the economical cost to generate electricity, discuss whether this is likely to be beneficial for reduction in greenhouse gases. List one advantage and one potential disadvantage in this switch in resources for generating electricity with regards to greenhouse gas production. (8 pts)

1) *Advantage: Switching from coal to  $\text{CH}_4$  as a fuel is beneficial due to more energy per mole of carbon dioxide released*

2) *Potential Disadvantages: 1) getting fuel from the bottom of the ocean could require a lot of energy, 2) potential methane leaks as it is a strong greenhouse gas*

4. Below is a scheme for the synthesis of setraline.  $\text{TiCl}_4$ , and  $\text{H}_2$  are reactants, while toluene, hexanes, THF, EtOH, and EtOAc are solvents, and Pd/C is a catalyst. (14 pts)



a) Calculate the atom economy for synthesis of the product (don't worry about isomers for this part of the problem). See last page for a periodic table.

product:  $\text{C}_{17}\text{H}_{17}\text{NCl}_2$  MW = 306.2 g/mol

reactants:  $\text{C}_{16}\text{H}_{12}\text{OCl}_2 + \text{CH}_5\text{N} + \text{TiCl}_4 + \text{H}_2$  MW = 514.0 g/mol

% =  $306.2 * 100 / 514 = 59.6\%$

b) Setraline is actually one of the cis isomers of the product shown above, and further workup requires isolation of the correct isomer. If only one of the diastereomers is useful, what does this say about the atom economy calculated in a). Could a synthesis yielding a single enantiomer be greener, even with poorer calculated atom economy?

*The atom economy is overstated because some of the product is waste (unless it can be re-racemized after separation).*

*An enantiomeric synthesis could be greener even if its atom economy was a little lower.*

5. The same glucose containing feedstocks (sugar, starch and cellulose) to produce ethanol, can be used instead to make 1-butanol. The production of 1-butanol, like ethanol, is carried out using microorganisms in water.

fuel	boiling point (°C)	K(octanol – water)	melting point (°C)
ethanol	78.4	0.50	-114
1-butanol	118	6.9	-90

a) Using the stoichiometry of the combustion reaction, determine whether 1-butanol or ethanol, if either, is a more energy dense fuel. (7 pts)

reactions:

ethanol:  $\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 \leftrightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$  ratio  $\text{O}_2/\text{CO}_2 = 3/2$

butanol:  $\text{C}_4\text{H}_9\text{OH} + 6\text{O}_2 \leftrightarrow 4\text{CO}_2 + 5\text{H}_2\text{O}$  ratio  $\text{O}_2/\text{CO}_2 = 3/2$

so energy density should be similar

b) If using the same methods used for ethanol, will isolation of 1-butanol be easier or harder than for ethanol? Explain your answer. (5 pts)

*It will be harder for 1-butanol because it is less volatile so it will require more heat to distill it from water.*

bonus) Is there a potentially less energy consuming method to transfer 1-butanol to fuel as an additive that is not available to ethanol. (3 pts)

*Yes. One could do a direct extraction into fuel because 1-butanol is much less polar.*

6. Given the following hypothetical toxin (below), write two possible reactions showing how the listed compound can be metabolized. Indicate if you expect that the product will be eliminated from the body more or less quickly than the original toxin. (10 pts)

