CHEM 489 Advanced Environmental Chemistry – Spring 2020

WORKSHEET #2 ANSWER KEY

Worksheet #2: Green Chemistry Metrics for Reaction Efficiency.
Due - Tuesday, February 11

(1) "Green chemistry is an approach to chemistry that aims to maximize efficiency and minimize hazardous effects on human health and the environment." Based on the class lectures, you should be able to list six metrics that a chemist can take to design a greener synthesis or process. Identify those that are considered to be reaction efficiency metrics.

- **Minimizing waste**
- **Avoiding the use of hazardous and toxic chemical**
- **Risk assessment: hazards inherent in the reagents, product, and waste; harmful to people or environment.**
- **12 Principles of Green Chemistry?**

Efficiency metrics:

- **%Yield**
- **%Atom Economy**
- **Process Mass Intensity**
- **Chemoselectivity**
- **Regioselectivity**
- **Stereoselectivity**

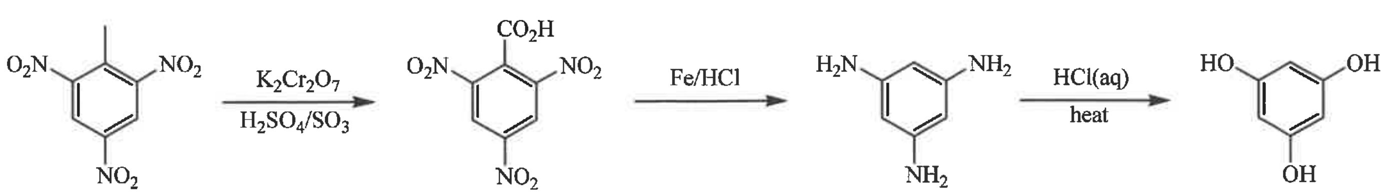
(2) What are the advantages and disadvantages of Atom Economy as a metric?
Atom economy is a useful tool for rapid evaluation of a chemical process that only requires a balanced chemical equation). We get a measure of how efficiently resources are being utilized, and the amount of waste that will be generated. Also a simple approach to compare alternative processes.

The disadvantage of atom economy is that it disregards substances, such as solvents and chemicals used in the work-up of the reaction mixture, which do not appear in the stoichiometric equation.

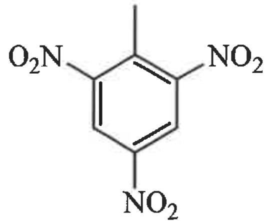
(3) A reaction can have 100% Atom Economy, yet less than 100% yield. How is this possible?
Atom economy is a theoretical number which assumes: (1) exact stoichiometric quantities of starting materials (balanced chemical equation); (2) a chemical yield of 100%; and (3) disregards substances, such as solvents and chemicals used in the work-up of the reaction mixture, which do not appear in the stoichiometric equation. Atom economy is a useful tool for rapid evaluation and prediction, before any experiments are performed, of the resource efficiency, and the amounts of waste that will be generated in the original or alternative processes.

The % yield is determined experimentally, and compares the amount of product formed to the limiting reagent (based on the theoretical yield of product).

(4) The remaining questions require you to **think critically** about the design and outcome of the following chemical process. Phloroglucinol is an important bulk chemical and feedstock for the production of pharmaceuticals. Up to the mid-1980s phloroglucinol was synthesized from trinitrotoluene (TNT). An overview of this process is shown below:



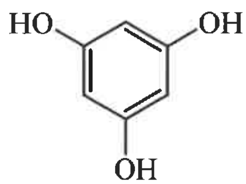
A more detailed synthetic scheme with proper stoichiometry, molecular weights and mass quantities is below:



TNT 224 g/mol
(2.80 Kg)
12.5 mole

+ $K_2Cr_2O_7$ + 5 H_2SO_4 + 9 Fe + 21 HCl ⟶

$K_2Cr_2O_7$	H_2SO_4	Fe	HCl
294.2 g/mol	98.1 g/mol	55.8 g/mol	36.5 g/mol
(3.68 Kg)	(6.13 Kg)	(6.28 Kg)	(9.58 Kg)
12.5 mole	62.5 mole	112.5 mole	262.5 mole



phloroglucinol 126 g/mol
(1.42 Kg)
11.3 mole

+ $Cr_2(SO_4)_3$ + 2 $KHSO_4$ + 9 $FeCl_2$ + 3 NH_4Cl + CO_2 + 8 H_2O

$Cr_2(SO_4)_3$	$KHSO_4$	$FeCl_2$	NH_4Cl	CO_2	H_2O
392 g/mol	138.5 g/mol	127 g/mol	53.3 g/mol	44 g/mol	18 g/mol
(4.90 Kg)	(3.46 Kg)	(14.3 Kg)	(2.00 Kg)	(0.550 Kg)	(1.80 Kg)

PROCESS ASSESSMENT:

(a) Why is the product needed, who needs it, and why? Besides the background given above, you will need to find an additional reference (not Wikipedia), and include this reference in your answer.
Phloroglucinol is an important bulk chemical and feedstock for the production of pharmaceuticals, and an important fine chemical that is used widely for copying process, textile dyeing, crosslinking of polymers, as a stabilizer and anti-corrosive additive, and even in rain cloud seeding.

(b) Conduct a simple **Risk Assessment** by identifying two hazards, and discuss exposure and vulnerability. Again, if you use a resource to answer this question you must cite the reference.
This synthesis is hazardous and wasteful:

Reactants - TNT is a non-renewable feedstock and an explosive; Cr compounds are potential carcinogens; H_2SO_4 and HCl are acids that can cause burns.

Productrs - Waste Cr compounds (potential carcinogen); CO_2 is a greenhouse gas; inorganic salts are difficult to dispose of, will not undergo combustion, and may end up in sludge ponds.

(c) Based on the information given in the balanced equation above, calculate the % yield for this process (note that mass quantities are in units of Kilograms). **Show all work.**

(1) you need to calculate the moles of each reactant to find the limiting reactant. As all reactants are present in stoichiometric amounts (No excess reactants), we can use TNT as "limiting" reactant.

(2) Theoretical yield is based on TNT = 12.5 mole.

(3) $\% \text{ yield} = \frac{\text{exp. yield}}{\text{theoretical yield}} \times 100$

$= \frac{11.3 \text{ mole}}{12.5 \text{ mole}} \times 100$

$= 90.4\ \%$

(d) Based on the information given in the balanced equation above, calculate the % atom economy for this process. Note that you must use the reactant stoichiometry as a multiplier for the molecular mass of H_2SO_4, Fe and HCl. **Show all work.**

$$\%AE = \frac{\text{MW Product}}{\Sigma \text{ MW Reactants (with stoichiometric ratios)}} \times 100$$

$$= \frac{\text{MW phloroglucinol}}{\Sigma \text{ MW}(TNT + K_2Cr_2O_7 + 5H_2SO_4 + 9Fe + 21\,HCl)} \times 100$$

$$= \frac{126 \text{ g/mol}}{[(224)+(294.2)+5(98.1)+9(55.8)+21(36.5)] \text{ g/mol}} \times 100$$

$$= \frac{126 \text{ g/mol}}{(224 + 294.2 + 490.5 + 502.2 + 766.5) \text{ g/mol}} \times 100$$

$$= \frac{126 \text{ g/mol}}{2277 \text{ g/mol}} \times 100$$

$$= 5.53\%$$

(*) suggests that >90% of reactant atoms end up as waste!

(e) Based on the information given in the balanced equation above, calculate the PMI for this process. **Show all work.**

$$PMI = \frac{\text{Total mass used (kg)}}{\text{Mass of P (kg)}}$$

$$= \frac{\text{mass of reactants (kg)}}{\text{mass of phloroglucinol (kg)}}$$

$$= \frac{28.5 \text{ kg}}{1.42 \text{ kg}}$$

$$= 20.1$$

(*) For every kg of product a minimum of 20.1 kg reactants + reagents needed. Note that solvents, etc. are not included!

(f) Based on all information above and Green Chemistry Principles 1-5, write an assessment about the efficiency of this process. Please note that you will be asked to address a similar question on your exam. Please write your assessment on a separate sheet of paper and attach to this worksheet. I am expecting approximately 150-200 words.

I will be looking for a discussion that will include at least several of the following metrics:
1) Prevention
2) Atom Economy
3) Safe Processes
4) Safer Chemicals
5) Safer Solvents

- **% yield**
- **% atom economy**
- **Process mass intensity (PMI)**
- **Selectivity (chemo-, regio-, stereo-)**
- **12 Principles of Green Chemistry**