

## Exercise 9 - Petrochemicals and Climate

- The year of the first U.S. drilled oil well.     *c. 1859*
- Approximately, what percent of the world's remaining oil reserves are in the United States?     *a. 2%*
- Approximately what percent U.S. oil is supplied by U.S. oil companies?     *d. 40%*
- Approximately, what percent of the world's oil is consumed by the United States?     *d. 25%*
- Approximately what percent of the world's population is in the United States (2007)?     *b. 5%*
- When oil is distilled, the boiling range for gasoline is:     *a. 40 - 205 °C*
- The Internet site, [http://tonto.eia.doe.gov/dnav/pet/TblDefs/pet\\_pnp\\_pct\\_tbldef2.asp](http://tonto.eia.doe.gov/dnav/pet/TblDefs/pet_pnp_pct_tbldef2.asp), defines petroleum feedstocks as: "Chemical feedstocks derived from petroleum principally for the manufacture of chemicals, synthetic rubber, and a variety of plastics." Approximately what percentage of the typical barrel of oil is used for petroleum feed stocks?  
*a. 3% - 20%*
- Describe Hubbert's peak: *the point in time when the maximum rate of global petroleum extraction is reached, after which the rate of production enters terminal decline.* [http://en.wikipedia.org/wiki/Peak\\_oil](http://en.wikipedia.org/wiki/Peak_oil)
- Without using a reference, write down what you think are the three most abundant gases in dry (excluding water which varies and is sometimes number 3) air.  
*Most people do not know that nitrogen is the number one gas in the atmosphere and often do not mention nitrogen at all. Most people think carbon dioxide is one of the top three and usually one of the top two presumably because plants need it and we exhale it. It is interesting to ask what gases we do exhale and most will respond carbon dioxide even after they have been told that nitrogen composes 80% of the atmosphere. About 3% of exhaled gas from humans is carbon dioxide.*
- Use the references below to determine the correctness of your answer.  
  
<http://www.physicalgeography.net/fundamentals/7a.html>  
[http://www.kayelaby.npl.co.uk/chemistry/3\\_1/3\\_1\\_4.html](http://www.kayelaby.npl.co.uk/chemistry/3_1/3_1_4.html)  
*Nitrogen N<sub>2</sub> 78.08%   Oxygen O<sub>2</sub> 20.95%   Argon Ar 0.93%   Carbon Dioxide CO<sub>2</sub> 0.039%*  
*\*Water H<sub>2</sub>O 0 to 4%*
- Most people cannot name the predominate gas in the atmosphere and the number of people that can name the top three is extremely small. This is distressing because there is significant evidence the climate of the earth is undergoing change as a result of human action. Because carbon dioxide ranks number 4 and composes only about 0.04% of the atmosphere, fossil fuel burning has over the last couple of decades caused a 39% increase in the carbon dioxide content (from about 280 ppm to 390 ppm). Why do you think many people place carbon dioxide among the three most abundant gases in the atmosphere?  
*See the answer to #9 above.*
- The overwhelming majority of scientists accept human caused climate change as a threat to our quality of life. Explain how the increase in carbon dioxide content of our atmosphere could affect our climate and average global temperatures.  
*Carbon dioxide absorbs some of the infrared that is emitted from the earth's surface. This is part of the so-called Greenhouse effect. Without the "Greenhouse effect", the earth would be a much colder place. However, by increasing the carbon dioxide, it is very likely that we are keeping the amount of energy trapped at a higher than desirable level and many environmental indicators point to a resultant warming that has already started.*
- There are skeptics who do not think an increase in carbon dioxide will cause climate changes. Even if the skeptics are correct, name several other negative effects of fossil fuel combustion.  
*Fossil fuels cause air pollution, water pollution, earth destruction (strip mining as well as deep mine shafts) accidents and fatalities (mining and oil rig, pipeline explosions), wars, diminishing of petroleum feedstock and potentially very destructive acidification of the oceans.*



## Exercise 10 - Solvents

- Although benzene and carbon tetrachloride were commonly used as solvents a few decades ago, their use now is extremely limited and only as solvents of last resort? Why?  
*Both are very hazardous to human health and have tested positive in carcinogenicity tests.*
- Although the use of carbon tetrachloride is strongly discouraged as a general solvent, it is still commonly used as solvent for nmr or ir spectroscopy. Why?  
 *$CCl_4$  and  $CS_2$  are about the only solvents that are good solvents for many organic compounds and do not have hydrogens that cause absorptions in Hnmr and ir spectra.  $CS_2$  has an odor that makes it very undesirable to work with.*
- Select at least three solvents that could be used as solvents for determining ir spectra. Give advantages and disadvantages of each and discuss any possible advantages and disadvantages of using a deuterated form of the solvent.  
 *$CCl_4$  is hazardous but does not interfere in the functional group region of the ir.  $CHCl_3$  is generally a better solvent than  $CCl_4$  due to its mild polarity. Chloroform is not quite as hazardous as  $CCl_4$  but as observable in Exercise 4, does have some interfering absorptions.  $CDCl_3$  is more expensive than  $CHCl_3$  but considering the amounts needed, the price is not prohibitive. The C-D bond absorbs in the triple bond region which usually does not interfere with more common absorptions.*
- Select at least three solvents that could be used as solvents for determining nmr spectra. Give advantages and disadvantages of each and discuss any possible advantages and disadvantages of using a deuterated form of the solvent.  
 *$CCl_4$  is hazardous but does not have absorptions in Hnmr.  $CHCl_3$  is generally a better solvent than  $CCl_4$  due to its mild polarity. Chloroform is not quite as hazardous as  $CCl_4$  but does have an interfering absorption.  $CDCl_3$  is more expensive than  $CHCl_3$  but considering the amounts needed, the price is not prohibitive. The C-D does not absorb in the light hydrogen region of the nmr spectrum*
- Toluene is often used instead of benzene but its relatively high boiling point can be a disadvantage. Why?  
*The higher boiling point means that steam baths will not work to evaporate the toluene and the boiling point of toluene might be close to the boiling point of the desired product.*
- Diethyl ether is still commonly used as a solvent but has several problems associated with its use. Explain these problems.  
*Diethyl ether boils just a few degrees above room temperature and is therefore very volatile and flammable. Once a can of ether has been opened, exposure to oxygen leads to oxidation to peroxides that can be explosive. Thus once a can of ether has been opened, it should be used within a several day period.*
- Dichloromethane (methylene dichloride) is also commonly used but has issues associated with its use. Explain these issues.  
*Generally halogenated compounds are hazardous and dichloromethane is not an exception. It has a low boiling point which makes it easy to evaporate off but also means it has high volatility at room temperature.*
- Water is often used to recrystallize carboxylic acids and other polar organic compounds that have a slight solubility in water. However, water has some disadvantages as a recrystallization solvent. What are the disadvantages?  
*The primary disadvantage is that water evaporates rather slowly compared to most organic solvents thus drying takes substantial time. Any water remaining will cause incorrect melting points and interfere in ir and nmr spectra.*

9. Polar organic compounds often have very low solubility in the most commonly used organic solvents. This can present challenges. Name some of the polar organic solvents that could be considered as possible solvents for polar organic compounds.  
*methanol, DMF, DMSO, acetonitrile*
10. Sometimes, it is desirable for the polar solvent to be aprotic. Suggest reasons for this and list the aprotic polar solvents from question #9.  
*Protonation can interfere with some reactions. DMF, DMSO, acetonitrile*
11. Earlier questions discussed alternative solvents for use in IR and NMR spectroscopy. If a polar organic solvent is needed as a solvent for IR or NMR spectroscopy, what options are available?  
*Deuterated forms of most solvents are available at a cost including DMF, DMSO, acetonitrile.*
12. Solvents like acetone and isopropyl alcohol are not useful for aqueous extractions. Why not?  
*Both acetone and isopropyl alcohol are miscible with water.*
13. In #12 you discussed one of the selection criteria for an extraction solvent. What other properties should be considered when choosing a solvent for the organic phase? Give reasons.  
*The solvent should be reasonably priced, have low toxicity, appropriate solvent properties and be easily separated from the desired compound (usually this means have a low boiling point).*
14. During an aqueous extraction, how do you know which phase is on the bottom?  
*Except for solvents that contain halogens, most organic solvents are less dense than water and form the top layer. When there is doubt as with dichloromethane and saturated aqueous sodium chloride, a few drops of the bottom layer can be added to water to be tested for miscibility.*
15. Select at least five solvents that you would use as possible recrystallization solvents or possibly as elution solvents for column chromatography. Arrange them in terms of increasing polarity.  
*hexanes, diethyl ether, ethyl acetate, acetone, methanol*
16. Is toxicity a special concern for any of the solvents listed in **Appendix B**?  
*Benzene has a low threshold limit and CCl<sub>4</sub> also has a relatively low value.*
- 17.<sup>1</sup> Solvent polarity is an important criteria to use for solvent selection. However, unlike a property such as boiling point, there is no simple method for measuring and reporting polarity. Dipole moments, dielectric constants and spectra shifts (used in **Appendix B**) are commonly used as a measure of polarity. Briefly discuss the issues associated with the ranking of solvent polarity.  
*Polarity is a complex concept and cannot be expressed with a single variable. Very importantly hydrogen bonding needs to be considered. Protic vs aprotic is often just as important as overall polarity. There are also local polarities in molecules with the whole molecule remaining apolar. Spectral shifts involve an attempt to measure practical solvent effects but still are lacking in predictive power.*

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<sup>1</sup>Bonus Question

## Exercise 11 - Energies in Perspective

1. 298°C 0.61% 473°C 3.9%
2. 5.4% 4.6% 2.8% 0.021% *As the size of the alkyl group increases, the unfavorable steric interaction in the axial position also increases.*
3. 42% 30% 27%
4. 0.0093%
5. 7.5
6.  $5.0 \times 10^1\%$  *(half are in each state until calculations are performed to several digits past the decimal)*
7. *A rate factor of  $2 \times 10^9$  means an activation energy difference of 53 kJ/mol. This does fall into the range for resonance effects of 0 - 60 kJ/mol. Resonance structures reveal that the presence of the methoxy enables the intermediate to have an additional resonance structure with the positive charge delocalized onto the oxygen.*
8. *The rate factor of 300 translates into a 14 kJ/mol difference in activation energies. This value falls within the range for inductive effects of 0 - 25 kJ/mol. The methyl helps to decrease the positive charge density on the resonance structure that has a positive charge on the para carbon.*
9. 0.028% 0.57%
10. 0.97 sec.  $1.6 \times 10^7$  yrs. *The lifetime for di-t-butyl peroxide is over 10 million years. This should be regarded as very stable.*
11. 28.5 kJ/mol
12. 103 kJ/mol. *Compounds with  $E^*$  values below or even a little above this value will have to be stored at low temperature to prevent rapid decomposition.*
13. *The half life is  $5.4 \times 10^{-6}$  seconds. In other words, the conformational change occurs rapidly at room temperature. As the temperature increases, the change will go even faster.*
14. *Bond energies are comparable in magnitude to the energy of ultraviolet light. Absorption of uv can and sometimes does result in bond cleavage and other forms of reaction.*
15. 32 kJ/mol
16. 10.4 kJ/mol *In water the ketone is stabilized by hydrogen bonding to the water. The enol has intramolecular hydrogen bonding and water does not contribute much to stabilizing the enol. Hexane cannot hydrogen bond thus the ketone is at a higher relative energy in hexane which in this case is enough to make the enol more stable than the ketone.*
17. 7.5
18.  $k = 7.9 \times 10^{10} \text{ sec}^{-1}$  *assuming an A value of  $1 \times 10^{13}$ . This rapid rate will increase with temperature.*

