CHEM 230
Exam 1 – Key

Short Answer/Multiple Choice Section:
Each Question worth 3 points

1. and 2. An insect pheromone (a chemical) is being extracted from beetles by shaking a flask containing 1.00 g of coarsely ground beetles with 10 mL of ethyl acetate. This solvent is filtered and saved, and then a second 10 mL of ethyl acetate is added to the filtered beetle solids for a second extract. What is a purpose of the second batch of ethyl acetate?
Purpose = _To determine if the first 10 mL of ethyl acetate effectively extracted the pheromone_
List a method to improve the percent of pheromone extracted.
Method = _1) use Soxhlet extraction equipment, 2) use ultra sound bath, 3) heat flask, 4) grind insects more finely, 5) use a greater ratio of solvent to insect mass_

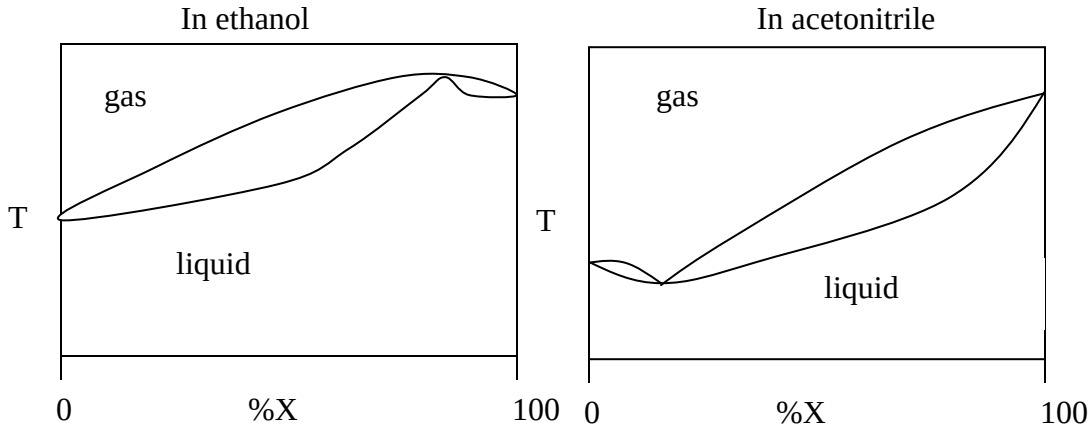
3. Which of the following additives can be used to extract an anion such as perchlorate from an aqueous phase to an organic phase:
a) no additive is needed b) use of a crown ether c) use of an anionic ligand
d) use of an ion pair reagent (e.g. tetrabutyl ammonium chloride)

4. Synthetic diesel consist mainly of linear alkanes from 8 to 26 carbons. All of the molecules are very non-polar. Fuel samples with higher percentages of longest chain alkanes are observed to cloud (precipitate) at low temperatures (not desired). Which of the following treatments should improve the fuel against clouding?
a) Liquid-liquid extraction with water
b) Distillation to remove "lightest" fraction (keeping original minus first fraction to distill out)
c) low temperature precipitation and filtration removing low temperature solids
d) solid phase extraction with polar solid phase

5. Which type of compounds in water are most suitable for trapping at low concentrations using solid phase extraction (SPE) with large water volumes if using non-polar (e.g. C18) stationary phase.
a) ionic compounds b) highly polar compounds
c) moderately polar compounds **d) weakly polar compounds**

6. An advantage of solid phase microextraction (SPME) over most other extraction methods when coupled with GC is:
a) no solvent is required between trapping on fiber and injection
b) essentially all analytes are moved to the solid phase
c) SPME equipment is very low cost and long lasting
d) all of the above

Longer Answer Questions:
1. Compound X can be synthesized in ethanol or in acetylnitrile. The following phase diagram shows its behavior in distillations of those two solvents. (12 points)



Answer the following questions (and give brief explanations):
In which solvent systems are azeotropes formed?
Both. Ethanol shows a maximum and acetonitrile shows a minimum.

If the reaction produces product X at a mole fraction of 40%, for which system is it possible to isolate pure compound X?
In acetonitrile only. In ethanol, distillation will cause the mixture to move from 40% to the azeotrope maximum (that will be left in the flask following distillation). In acetonitrile, moving to the right eventually leads to pure X.

In which phase (liquid or gas) will compound X be enriched following distillation (true for either distillation)?
In both cases, X is the higher boiling point liquid and will be enriched in the liquid phase (the solvent will be enriched in the gas phase).

2. An industrial electroplating bath has ions Ag^{+} and Cd^{2+} present in an aqueous solution. Give two possible methods for separating these two ions. What constants would be useful in determining if each method would work? (6 pts)
1) Precipitate out using an anion. One would need the K_{sp} values.
2) Use crown ether or ligand and separate through extraction to organic solvent. One would want the ligand formation constants and partitioning coefficients.
3) Use solid phase extraction (trap one but not the other or trap both and selectively elute one. One would want to know the relative binding strength of each cation.

3. (14 points) A research scientist isolates a compound (compound X) from a plant and conducts the tests using liquid – liquid extraction to optimize its extraction. Using water and 1-octanol, the following distribution coefficients, K_D (= $[X]_{octanol}/[X]_{water}$) are calculated as a function of pH (with water being the extractant phase):

pH	2	4	6	8	10	12
K_D	0.008	0.8	39	76	75	76

a) Does compound X appear to have acidic functional groups, basic functional groups or both types of groups? Explain your answer.
Basic groups. *A basic group undergoes the following reaction:* $BH^+ \leftrightarrow B + H^+$
Through Le Chatelier's principle, low pH (high $[H^+]$*) shifts the reaction to the left leading to most compound X in the aqueous phase (giving a low* K_D *value) as observed.*

b) If 50 mL of an aqueous plant extract buffered to a pH of 8.0 is extracted with octanol (**now octanol is the extractant phase**), calculate the volume of octanol needed to extract 98.0% of compound X to the octanol phase.
$K_D = [X]_{rafinate}/[X]_{extractant} = [X]_{water}/[X]_{octanol} = 1/76 = 0.0132$
$Q = 0.98 = 1/(1 + k)$ *or* $0.98 + 0.98k = 1$ *or* $k = 0.02/0.98 = 0.0204$
$k = K_D(V_{water}/V_{octanol})$ *or* $0.0204 = 0.0132(50\ mL/V_{octanol})$
$V_{octanol} = 0.0132(50/0.0204 =$ ***32 mL***

4. A 500.0 mL water sample is analyzed for pesticide X using solid phase extraction and LC-MS analysis. The entire water sample is passed through a non-polar solid phase extraction cartridge, which is then rinsed with 20.0 mL of water. The pesticide-containing fraction is removed with 20.0 mL of methanol, evaporated, and then transferred to a 2.00 mL volumetric flask using methanol (filled to line). A 20 μL aliquot (from the final 2.00 mL extract) is injected into the LC-MS and the concentration of pesticide X in this extract is found to be 27.1 ng/mL.
a) determine the concentration of pesticide X in ng/L in the water sample assuming 100% transfer efficiency. (10 pts)
mass isolated in pesticide extract = (27.1 ng/mL)(2.00 mL) = 54.2 ng
(2.00 mL = final extract volume)
initial water volume = (500.0 mL)(1 L/1000 mL) = 0.500 L
initial water conc. = mass isolated/water volume = 54.2 ng/0.500 L = **108 ng/L**

bonus) If use of a recovery standard showed that the extraction method was 63% efficient, what would the true concentration be? (2 pts)
63% = (conc. recovered/true conc.)100 so true conc. = conc. recovered/0.63 = **170 ng**