Chemistry 210 Final Exam
January 20, 1996
Prof. D. L. Naud

Name_____

I.D. No._____Section_____

1. (6 points, no partial credit) Successful crystallization depends upon proper solvent choice. Order the following solvents in decreasing polarity.

A. acetone B. toluene C. water D. methanol
E. ethyl acetate F. cyclohexane G. diethyl ether H. acetic acid

Polar ----------→ Non-polar

2. (8 points) Give a BRIEF step by step procedure how one could separate a mixture of p-methylphenol, benzoic acid, cyclohexylamine, and cyclohexanone by extraction only. (pKa of phenols is approx. 10; pKa of carboxylic acids is approx. 5)

3. (5 points) The purity of a compound by melting point can be established by two ~~ways~~ observations. What are they?

4. (8 points) A student needs to purify 6-chloro-4-hexen-2-one by distillation, however, the compound decomposes at its normal boiling point. He believes that he has two options to succeed in purifying the compound. In the first, he could co-distill the compound with water (the compound is barely soluble in water at room temperature) or distill the compound under reduced pressure (i.e. vacuum distillation). Which is better and state your reasoning.

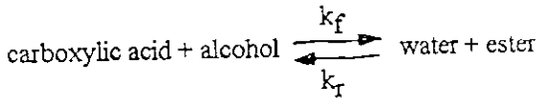
5. (6 points) Calculate the mole fraction of compound A in the vapor phase (at 80°C) for the following solution:
$X_A = 0.40$ (mol fraction in liquid phase), $P_A^o = 760$ torr at 80°C (vapor pressure of pure A)
$X_B = 0.60$, $P_B^o = 180$ torr at 80°C.
Assume the solution behaves ideally.

$P_T = P_A X$

6. (6 points) A student attempts to purify an organic product by recrystallizing it from water. After his first recrystallization, the student filters his product from the mother liquor and immediately takes a melting point to determine purity. Unfortunately, his sample melts at 73°C, ten degrees below the substrate's literature melting point. He repeats the recrystallization and obtains a new melting point (using identical procedure) and finds the melting point didn't change; the substrate still melts at 73°C. The students finally hits upon a bright idea and carries out a procedure. After the procedure, he finds the material melts at 83°C. What procedure did the student perform?

7. a. (4 points) What's the structure of isoamyl acetate?

b. (12 points) Given the following equilibrium:



i) Upon addition of acid catalyst, how will k_f be affected? How will k_r be affected?

ii) How will the ratio k_f/k_r compare before and after addition of acid?

iii) How will k_r change when water is added to the above mixture initially at equilibrium?

8. (12 points) Briefly give an efficient method for separating a 50/50 mixture of:

a) cyclohexene and benzene
b) aniline and cyclohexene
c) 2-aminophenol and 4-aminophenol

9. (6 points) A good protecting group should meet three basic requirements. What are they?

10. (3 points) What is the electrophile in the reaction of acetanilide and mixed acids?

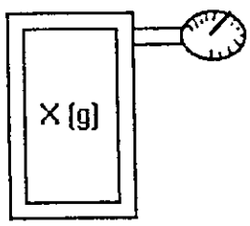
11. (9 points) Compound **A** decomposes to compound **C** via **B** according to the following scheme:

$$\mathbf{A} \xrightarrow{k_1} \mathbf{B} \xrightarrow{k_2} \mathbf{C}$$

All reactions are first order in substrates. A solution of compound **A** was made (initial concentration is unknown) and the progress of reaction was followed. Four measurements were made 1500 seconds into the reaction. The concentration of **A** is 0.1396 M; concentration of **B** is 0.2651 M; the rate of formation of **B** is 25.9 μM per second; and the rate of formation of **C** is 92.81 μM per second.
Calculate the rate constants, k_1 and k_2 and the initial concentration of the solution.

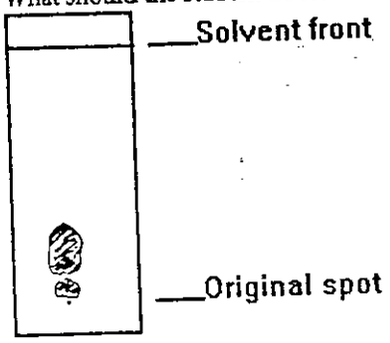
12. (9 points) Compound **X** decomposes to compound **Y** and **Z** following first order kinetics. All three compounds are gases. The rate of reaction was determined by following the pressure of the gaseous mixture as a function of time. An initial pressure of pure **X** was measured at 35.15 torr. After 540 seconds, the pressure of the vessel measured 58.85 torr. Calculate for the rate constant, k_{rxt}. Assume ideal gas behavior.

$$\mathbf{X}(gas) \xrightarrow{k_{rxt}} \mathbf{Y}(gas) + \mathbf{Z}(gas)$$



t = 0, P = 35.15 torr

13. (8 points) A student has in his laboratory silica gel TLC plates, cyclopentane, and ethyl acetate solvents only. The student prepares a solution made up of 50/50 (v/v) cyclopentane and ethyl acetate and uses it to elute a sample mixture containing three compounds of different polarities. The result of the TLC is shown in the figure below. What should the student do next in order to better resolve the mixture?

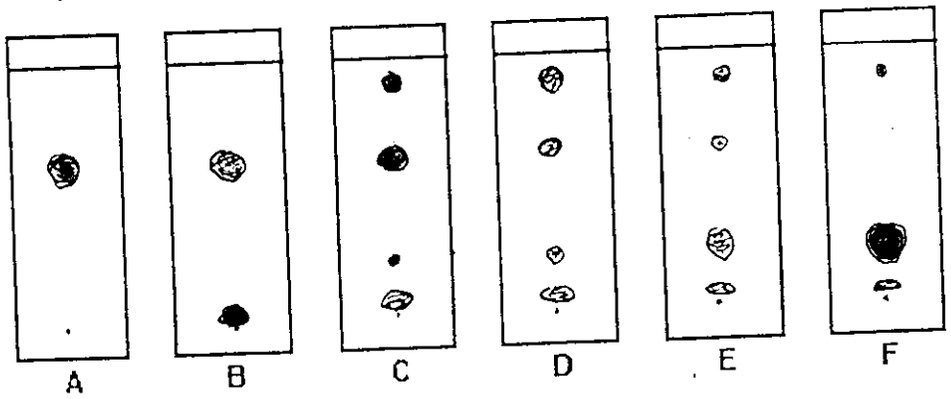


14. (8 points) A researcher was studying the oxidizing ability of a new reagent on benzyl alcohol. Overall, the reaction is known to oxidize the alcohol to benzoic acid:

$$PhCH_2OH \xrightarrow{\text{reagent}} PhCOOH$$

In order to understand the oxidation mechanism a little better, the researcher followed the oxidation of benzyl alcohol at different stages of the reaction by TLC. These are the results:

TLC plate A is the analysis of benzyl alcohol dissolved in ether.
TLC plate B is the above ether solution with the oxidizing agent at reaction time equal to zero.
TLC plate C is the same solution after one hour.
TLC plates, D, E, and F are the analyses at reaction times of 2, 3, and 4 hours respectively.



From the TLC data, speculate as to what reactions are occurring in this oxidation reaction.