13 July 2010

MINISTRY OF SCIENCE, RESEARCH AND TECHNOLOGY
NATIONAL ORGANIZATION
FOR
EDVCATIONAL TESTING

3th International Olympiad summer 2010

15th National and the 3nd International Chemistry Olympiad
Summer: 2010

Physical Chemistry I and II

Time: 90 minutes

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Question No.	Points for each question	Signature	total score (out of 100)
1	15		
2	10		
3	20		
4	25		
5	15		
6	15		

Name:

Surname:

Subject title:

Date of Exam:

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NO 1: Under what conditions, for a certain transition between two incompressible solid phases, ΔG is independent of the pressure.

NO 2: Determine the number of independent components to be considered, for the application of the Gibbs phase rule, for each of the following systems:

a) KCl, NaCl, H_2O

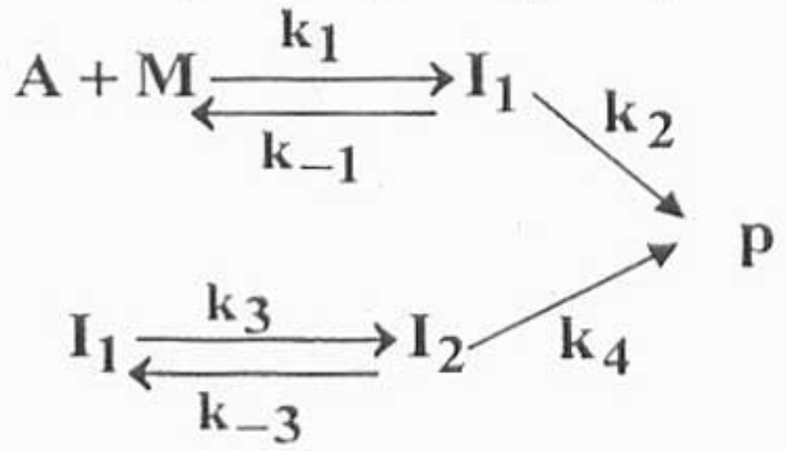
b) KCl, NaBr, H_2O

NO 3: Osmotic coefficient (ϕ) is defined as $\phi = -\left(\frac{x_A}{x_B}\right) \ln a_A$.

By writing $r = \frac{x_B}{x_A}$ and using Gibbs-Duhem equation, show that we can calculate the activity of B from the activity of A over a composition range by using the formula:

$$\ln\left(\frac{a_B}{r}\right) = \phi - \phi(0) + \int\left(\frac{\phi - 1}{\gamma}\right) dr$$

NO 4: Consider a reaction with two intermediates I_1 and I_2 which both decompose to the same product *P* by competing steps.



a) Find an expression for $\frac{dp}{dt}$ by applying the steady state approximation with $[I_1]_{ss} = [I_2]_{ss} = o$

b) Find an expression for $\frac{dp}{dt}$ by applying the steady state approximation with $[A]_t = [A]_\circ - [I_1] - [I_2] - [p]$

c) How you can obtain The activation energy for this reaction.

NO 5: The following information are given at 298 K

$$Cr(s) + SO_4^{=}(aq) \rightarrow CrSO_4(s) + 2e \qquad E° = 0.4 \quad V$$

$$Cr(s) \rightarrow cr^{3+} + 3e \qquad E° = 0.5 \quad V$$

solubility product constant, K_{sp}, for $CrSO_4$ is 10^{-4}

a) write the cell reaction for the cell:

$Cr \,|\, CrSO_4\ (s)|\ 0.001\ m\ H_2SO_4 |\ H_{2_{p=1\ atm}}\ |pt$

b) Calculate the emf for this cell at = 98 K regarding only the concentrations.

c) Calculate the emf at 323 K, if $\Delta H° = -5\ kJmol^{-1}$.

$R = 1.98 \quad calmole^{-1}\ k^{-1} = 8.314\ Jmole^{-1}K^{-1}$

NO 6: A second-order phase transition is defined as one where $\Delta H = T\Delta S = 0$, $\Delta V = 0$, and C_p does not become infinite at the transition temperature but does change by a finite amount. Henceforth, the clapeyron equation $\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$ becomes meaningless $\left(\frac{0}{0}\right)$ for the second-order phase transitions. So, deduce the appropriate alternative for the clapeyron equation in this regard.

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15th National and the 3rd international Chemistry Olympiad
Summer: 2010
Tehran, Iran

Inorganic Chemistry I and II

Time: 90 minutes

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3rd International Olympiad Summer 2010

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1. Draw a Born-Haber cycle for the formation of GaBr(s) and specify each step. Consider Ga as a solid in this experiment.

2. The table below shows the rate constants for the hydrolysis (k_H) and anation (k_A) reactions of some complexes (M is a transition metal), what do these values suggest about the mechanism (associative or dissociative) for these reactions?

$$M^{III}(NH_3)_5X^{n+} + H_2O \underset{k_A}{\overset{k_H}{\rightleftharpoons}} M^{III}(NH_3)_5H_2O^{3+} + X^{n-}$$

X	k_A	k_H
SO_4^{2-}	2.4×10^{-5}	9.9×10^{-7}
Cl^-	2.1×10^{-5}	1.8×10^{-6}
NCS^-	1.6×10^{-5}	3.7×10^{-10}
NO_3^-	2.2×10^{-5}	2.4×10^{-5}

3. Possible structures for coordination number 6 are: hexagonal, trigonal prism and octahedral.

a) for each of the above structures, write the number of predicted geometrical isomers of MA_3B_3 and $MA_2(en)_2$. "A" and "B" are monodentate ligands and "en" is a symmetrical bidentate ligand.

Complex	Hexagonal	Trigonal prism	Octahedral
MA_3B_3			
$MA_2(en)_2$			

4. 4(a) How does Crystal Field theory account for the following observations? In each part where it is relevant, show the relative positions of the e_g and the t_{2g} orbitals and the number of d- electrons in each.

1) The color of a solution of $[Cr(CN)_6]^{4-}$ ions appears orange whereas a solution of $[Cr(H_2O)_6]^{2+}$ appears violet.

2) $[MnF_6]^{4-}$ is found to be paramagnetic whereas $[Co(NH_3)_6]^{3+}$ is found to be diamagnetic.

b) Which complex is most likely to be a low spin complex?

$[Co(en)_3]^{3+}$ or $[Co(en)_2Br_2]^{+}$

5. a) Arrange the following compounds is order of anticipated decrease of thei molar conductivities in aqueous solution:

$Pt(NH_3)_6Cl_4$, $Pt(NH_3)_3Cl_4$, K_2PtCl_6 , $Co(NH_3)_5NO_2Cl_2$, $Co(NH_3)_3(NO_2)_3$

b) Match the following complex molecules with the proper ground state symbal:

1) $[Cr(NH_3)_6]^{3+}$ $^3T_{1g}$

2) $[Ti(H_2O)_6]^{3+}$ $^5T_{2g}$

3) $[Mn(CN)_6]^{3-}$ $^4A_{2g}$

4) $[CoF_6]^{3-}$ $^2T_{2g}$

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15th National and the 3nd International Chemistry Olympiad
Summer: 2010
Tehran, Iran

Organic Chemistry
I, II and III

Time: 90 minutes

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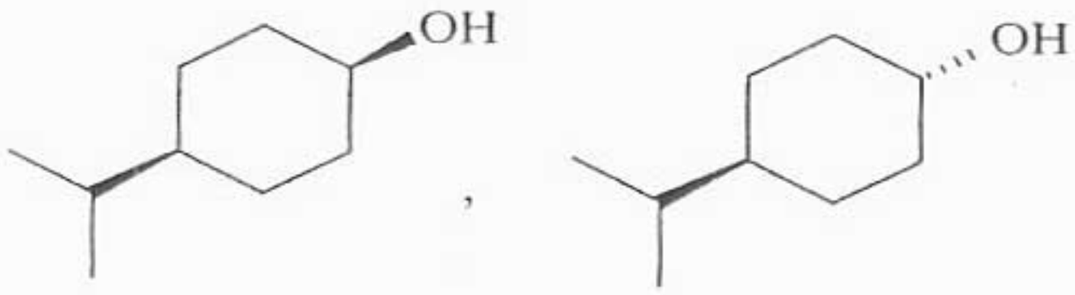
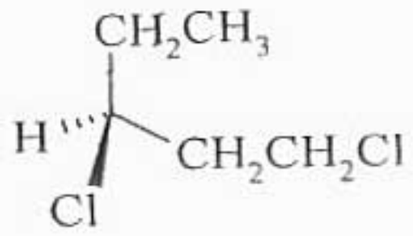
1. what is the relationship between these compounds?

a) 

b) 

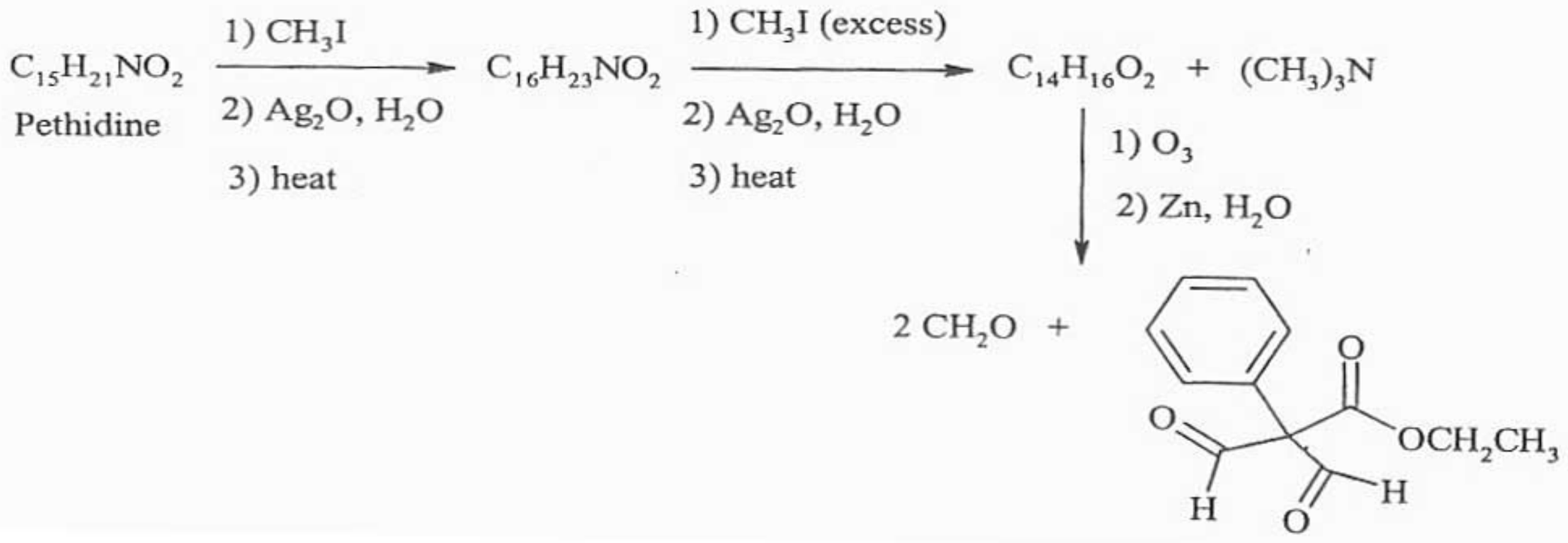
2. Monochlorination of the following compound at C3 and C4, in the presence of light, produces several isomers of formula $C_5H_9Cl_3$.



For each part, give the following information:

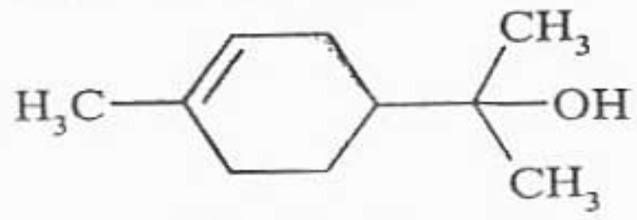
a) **How many stereoisomers are formed?**
b) **If more than one is formed, are they generated in equal or unequal amounts?**
c) **Designate every stereo center, including the stating material, as R of S.**

3) Pethidine ($C_{15}H_{21}NO_2$), the active ingredient in the narcotic analgestic Demerol was subject to the following reactions. Propose a structure for Pethidine base on these information.



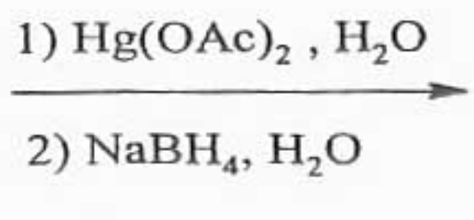
4) Treatment of α-Terpineol (A, $C_{10}H_{18}O$) with the following reagents gave compound B as a major product, which is an isomer of A. Propose a structure for the B base on these information.

IR spectrum of B shows no peaks between 1600 - 1800 cm^{-1} and no peaks between 3200 - 3700 cm^{-1}.



α-Terpineol

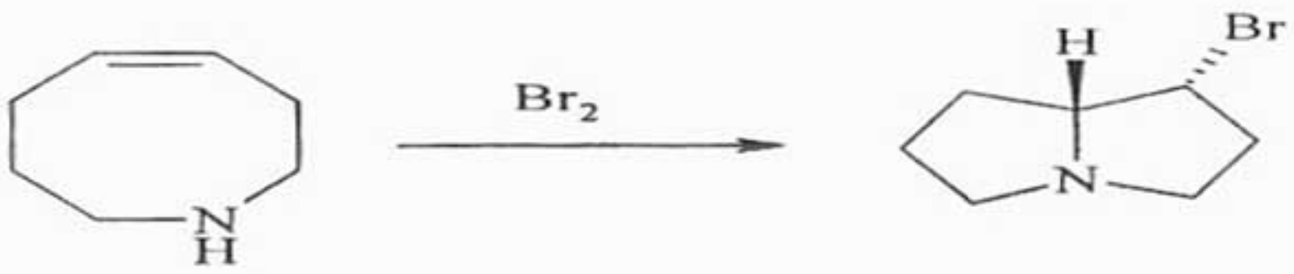
A ($C_{10}H_{18}O$)



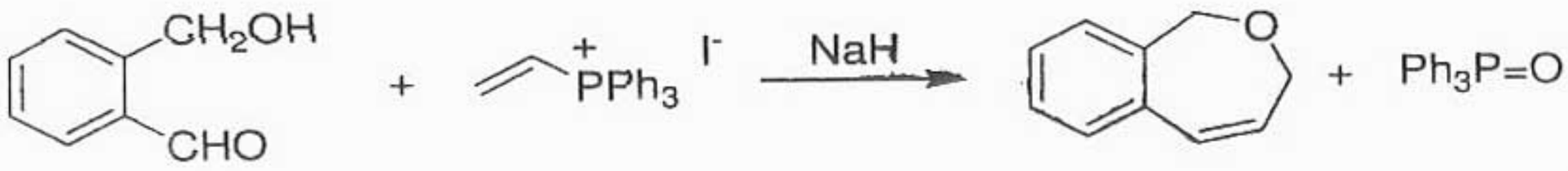
B ($C_{10}H_{18}O$)

Ac = $CH_3C{=}O$

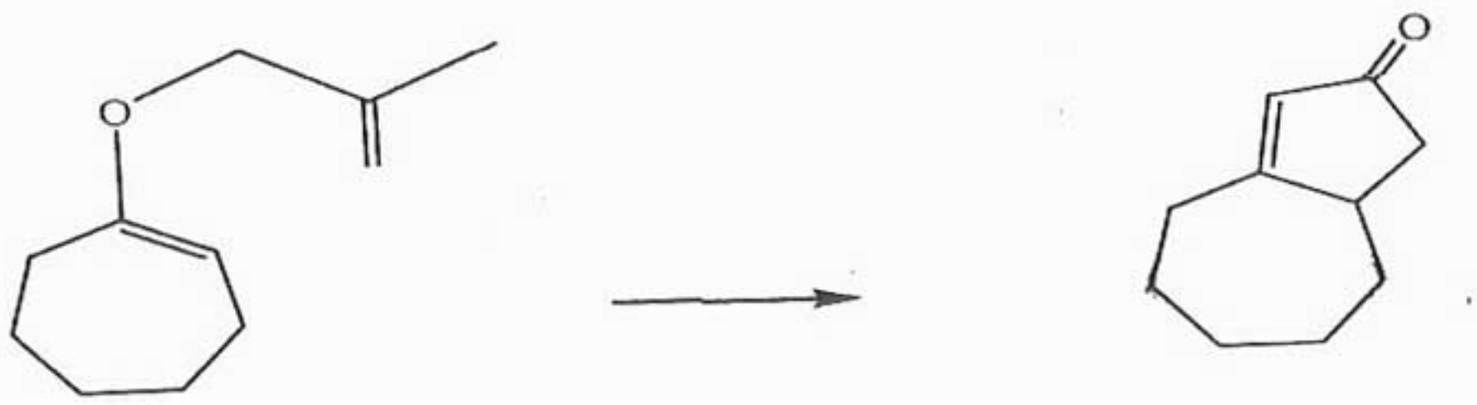
5. Give mechanism for the following conversion.



6. Write out a detailed mechanism which accounts for the illustrated transformation.

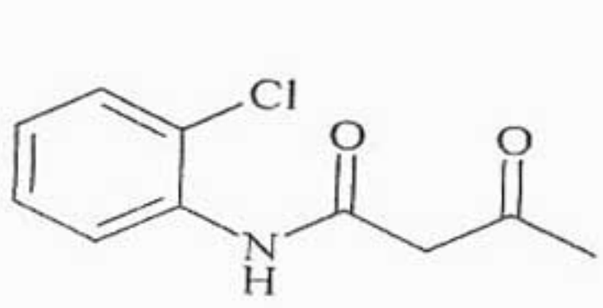


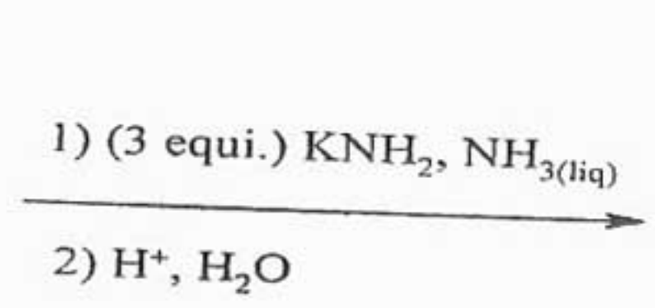
7. Suggest reagents and reaction conditions that would be suitable for the following conversion.

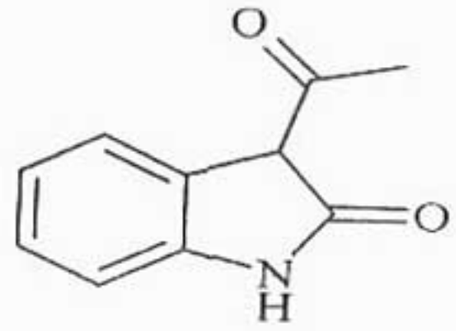


8. Analyze the following reactions by mechanism.

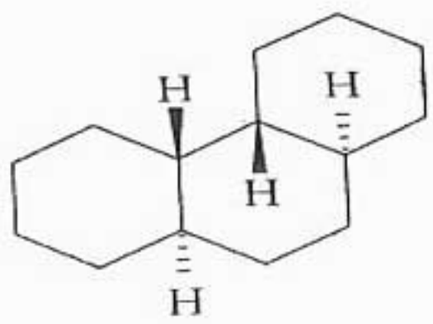
a)



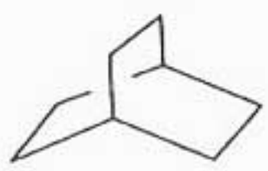




9. How many peaks would you expect in the proton decoupled ^{13}C NMR spectra of the following compounds?

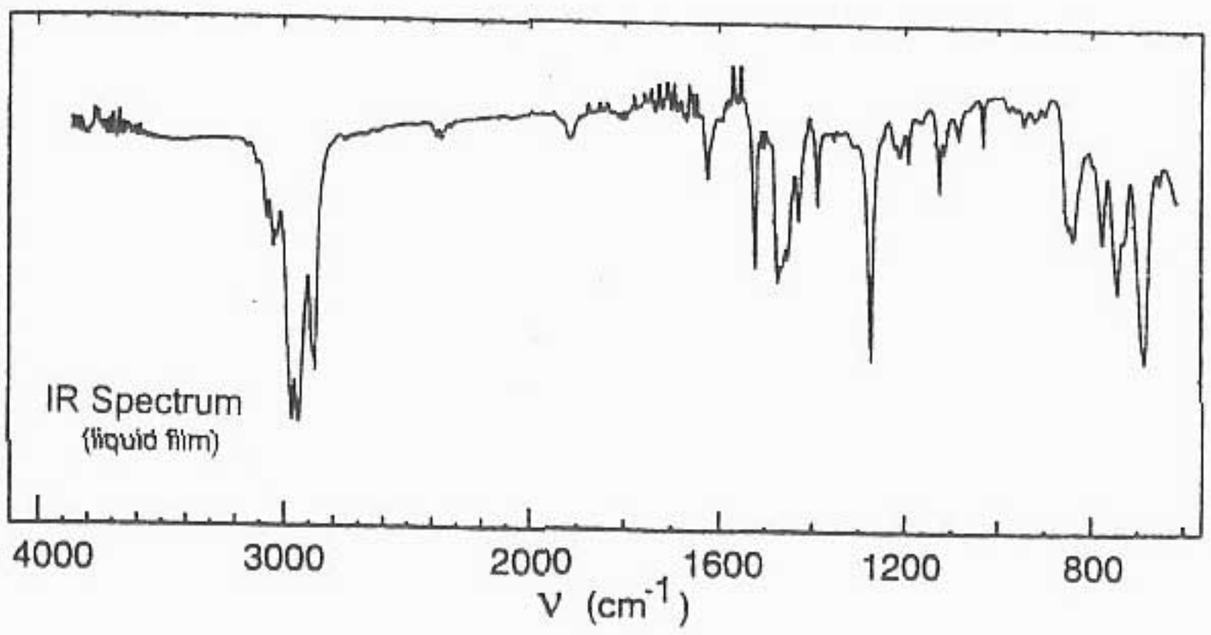


a

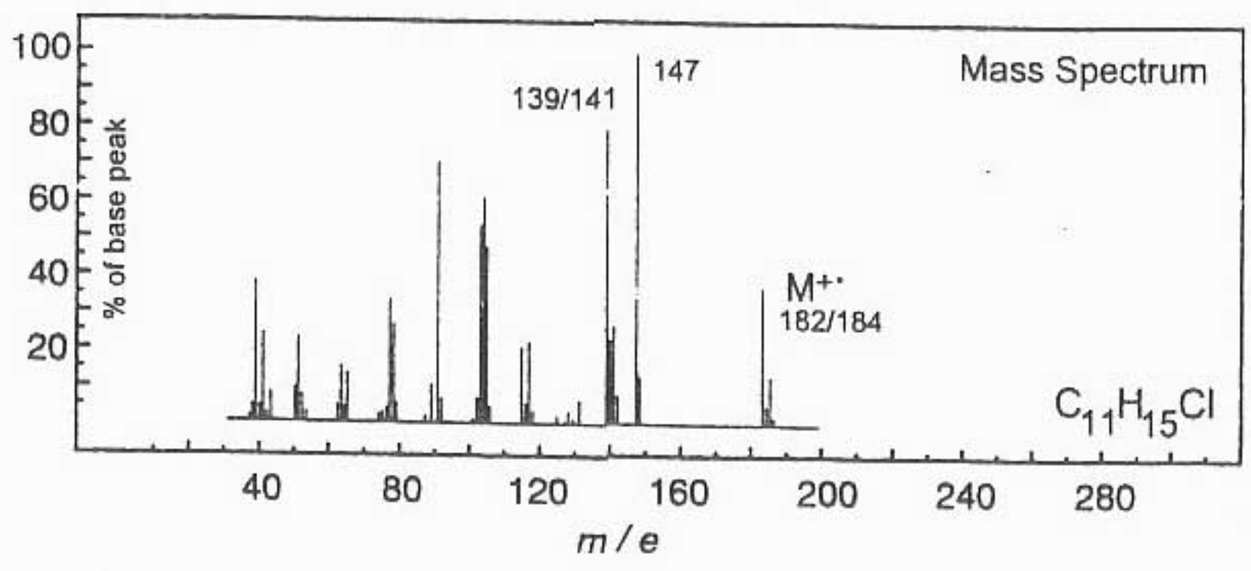


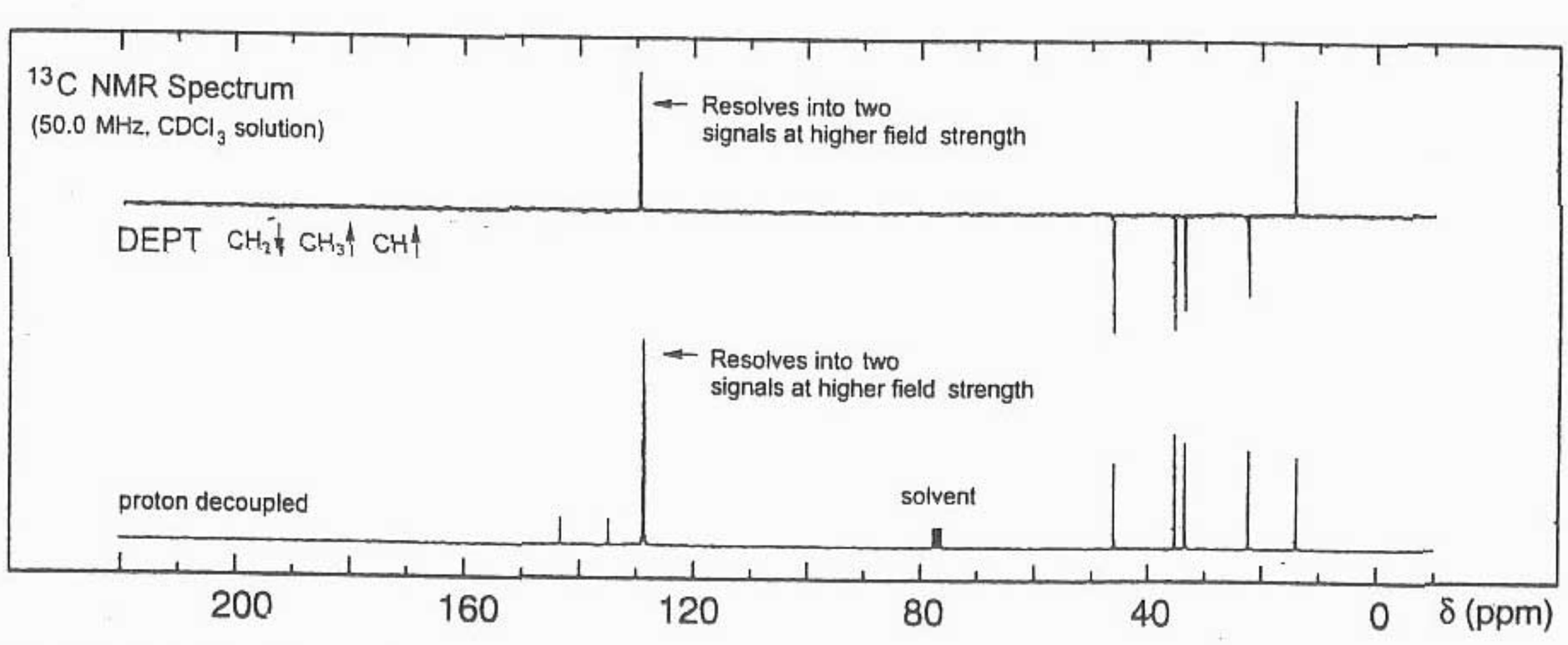
b

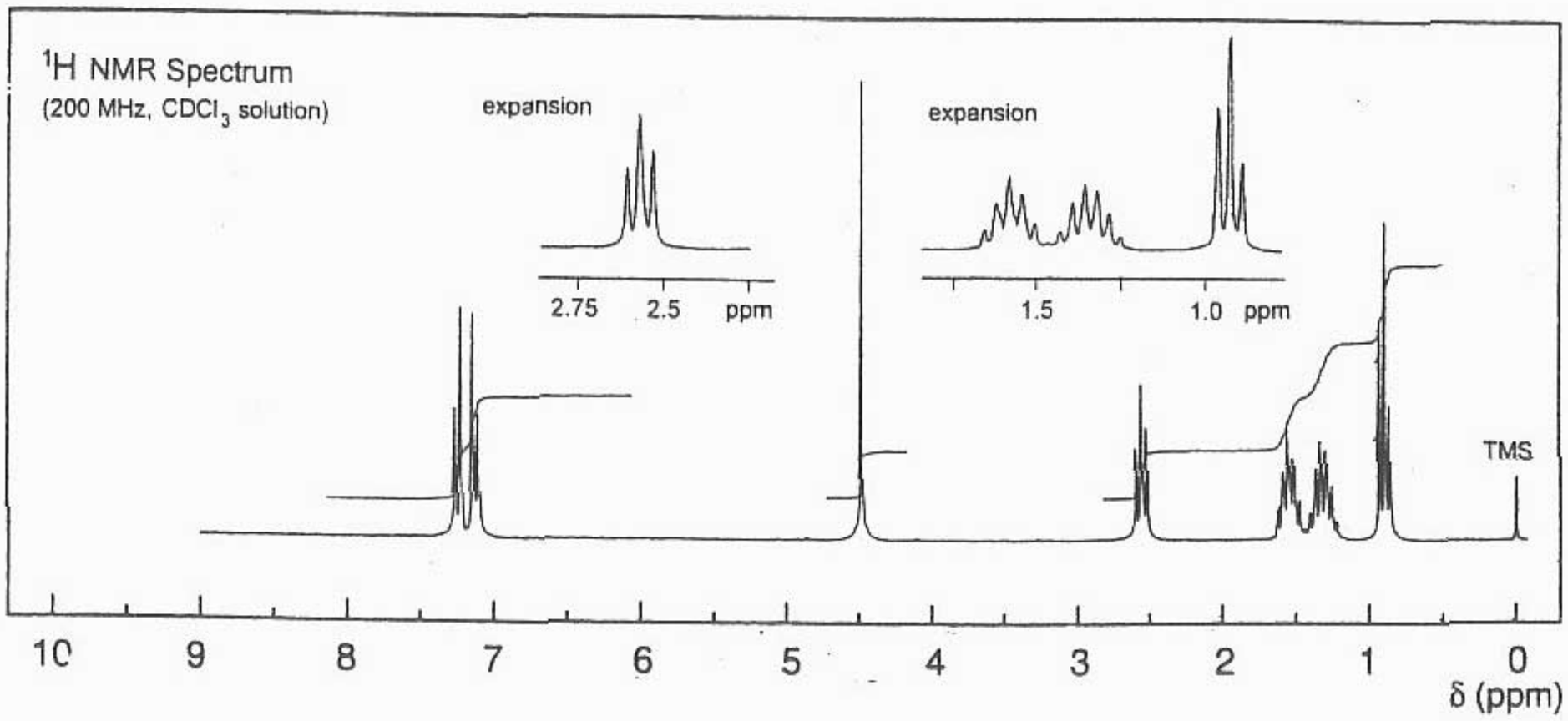
10) All spectra of compound C are given below. Propose a structure for this compound, and show how you have reached to your proposed structure.



Compound C







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15th National and the 3nd International Chemistry Olympiad
Summer 2010
Tehran, Iran

Analytical Chemistry and Instrumental Analysis

Time: 90 minutes

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3nd International Olympiad Summer 2010

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1. **A sample of ammonium phosphate is received to laboratory. In order to determine the percentage of its components as $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$, the following titrations were performed on it.**

   1) **0.10 gram of the sample was dissolved in 20 ml of distilled water and titrated with 0.10 M solution of HCl. 2.27 ml of acid is consumed up to methyl red indicator color change from yellow to red.**
   2) **Another 0.10 gram of the sample was dissolved in 20 ml of distilled water and 5 ml of a neutralized formaldehyde solution was added to it. Neutralization of this solution was done with 0.10 M solution of NaOH and in presence of phenolphthalein as indicator. 16.71 ml of titrant was consumed up to the appearance of pink-red color in solution.**

Based on to the following data:

- $H_3PO_4 : pK_{a1} = 2.1 \qquad pK_{a2} = 7.2 \qquad pK_{a3} = 12.4$
- $NH_4^+ : pK_a = 9.2$
- **In the presence of formaldehyde:**

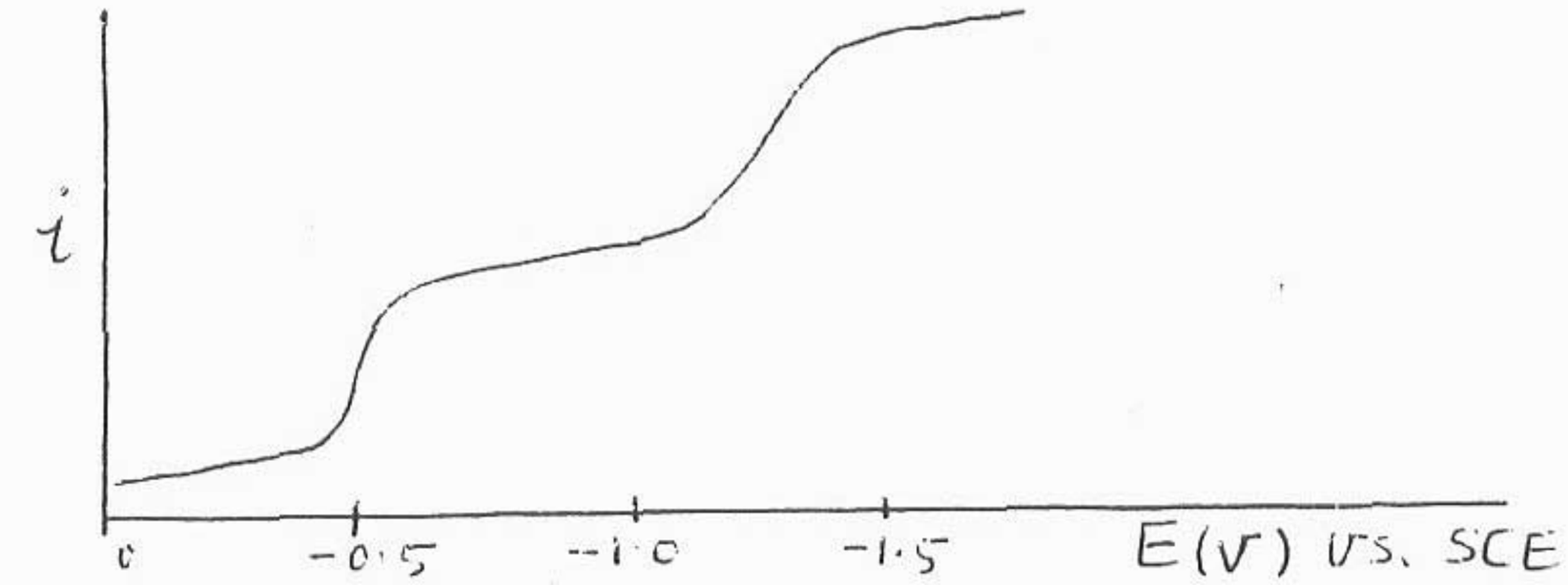
$$4NH_4^+ + 6HCHO \leftrightarrow H(CH_2)_6N_4^+ + 3H^+ + 6H_2O$$

$$H(CH_2)_6N_4^+ \leftrightarrow (CH_2)_6N_4^+ + H^+ \quad Pk_a = 5.0$$

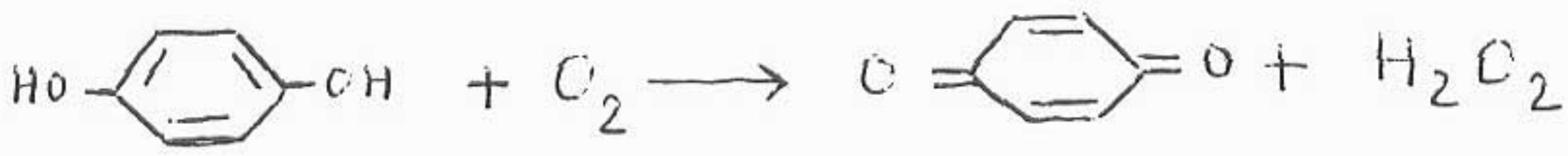
- **Molecular weight of $NH_4H_2PO_4 = 115$**
- **Molecular weight of $(NH_4)_2HPO_4 = 132$**
- **Methyl red: (red) $4.2 > pH > 6.2$(yellow)**
- **Phenolphthalein: (colorless) $8.3 > pH > 9.9$(pink − red)**

   1) **Write the neutralization reaction occurred during the neutralization by 0.10 M HCl. Calculate the percent of ammonium salts involved in neutralization reaction in the sample**
   2) **What will be the composition of solution after addition of an excess of formaldehyde.**
   3) **Write the neutralization reactions occurred during the addition of 0.10 M NaOH on formaldehyde containing solution. Calculate the percent of other ammonium salt that remains intact during neutralization by HCl, in the sample.**

2. **Contents of H_2O_2 and O_2 in an aqueous solution is determined by the tast-polarography. Following figure shows a typical polarogram for a mixture solution of both compounds.**

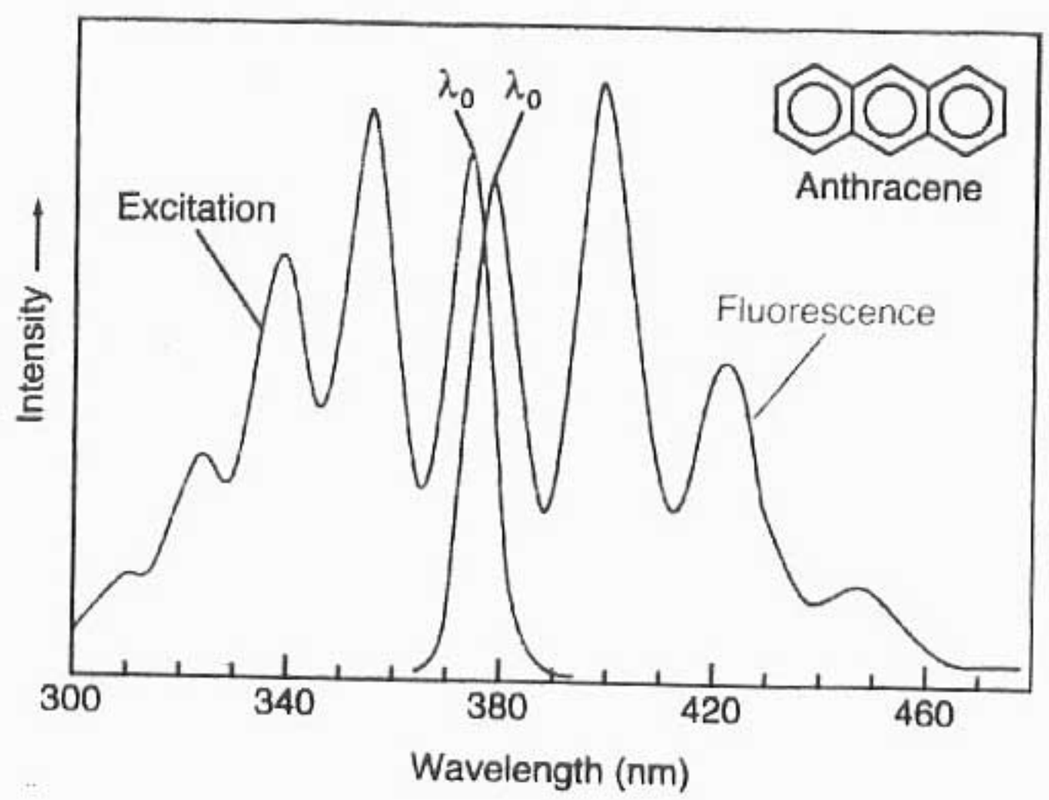


Polarogram of 25.00 ml solution containing KNO_3 (0.1 M, as supporting electrolyte) shows diffusion currents of 24 μA and 44 μA at potentials of -0.6 and -1.5 volt, respectively. In another determination, 0.25 milimole of hydroquinone was added to the solution (which caused to the reduction of H_2O_2 to O_2) and the polarogram was recorded.



The diffusion current in the region of -0.6 V was decreaed to 12 μA. Calculate the ppm of each O_2 and H_2O_2 in the aqueous solution (O=16.00, H=1.00).

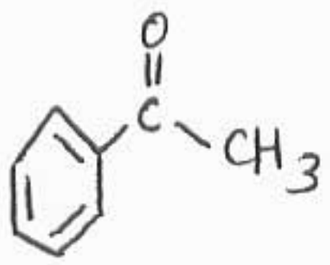
3. **Here are the absorption and emission spectra of anthracene.**



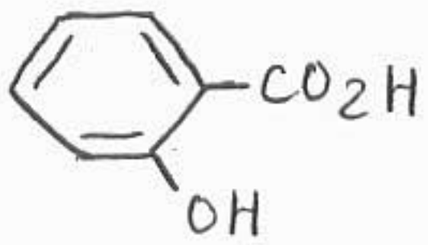
(a) Why does the absorbance spectrum show a set of peaks?
(b) Why does the emission spectrum show a set of peaks?
(c) Why is the spacing between the peaks different for the absorbance and emission spectra?
(d) The emission spectrum was generated with an excitation wavelength of 355 nm. What would the emission spectrum look like if the excitation wavelength was 340 nm? Why?

4. **Capacity factors for three solutes separated on a Cs nonpolar stationary phase are shown below. Eluent was a 70:30 (vol/vol) mixture of 50 mM citrate buffer (adjusted to pH with NH_3) plus methanol. Draw the dominant species of each compound at each pH in the table and explain the behavior of the capacity factors.**

Analyte	pH 3	pH 5	pH 7
Acetophenone	4.21	4.28	4.37
Salicylic acid	2.97	0.65	0.62
Nicotine	0.00	0.13	3.11



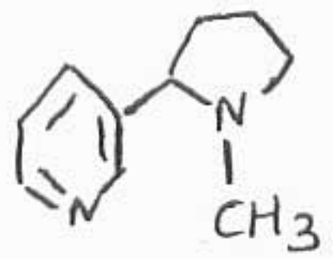
Acetophenone,



salicylic acid

$pKa = 2.97$

,



Nicotine

$pKa_1 = 3.15$

$pKa_2 = 7.85$

5. **What is the reason for the superior detectability provided by the electrothermal atomic absorption relative to the flame atomic absorption?**