مجلس الخدمة المدنية
اللجنة الفاحصة

مباراة 2008/4/5 المفتوحة لقبول طلاب في شهادة الكفاءة في كلية التربية في الجامعة اللبنانية
للتعيين بوظيفة أستاذ تعليم ثانوي

الاختصاص: كيمياء باللغة الانكليزية. الوقت: أربع ساعات

مسابقة في الاختصاص المطلوب.

I. 1) Calculate the pH of the following solution:
0.1 M HF + 0.2 M NaCN

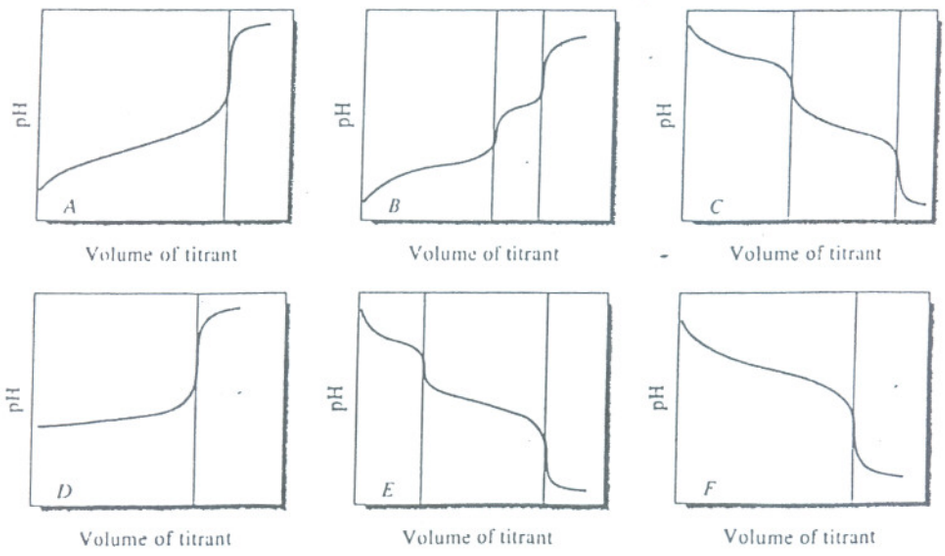
Given: pKa for: $HF/F^- = 3.2$ $HCN/CN^- = 9.4$

2) Calculate the pH of the solution that results upon mixing 20.0 mL of 0.2000 M HCl with 25.0 mL of:

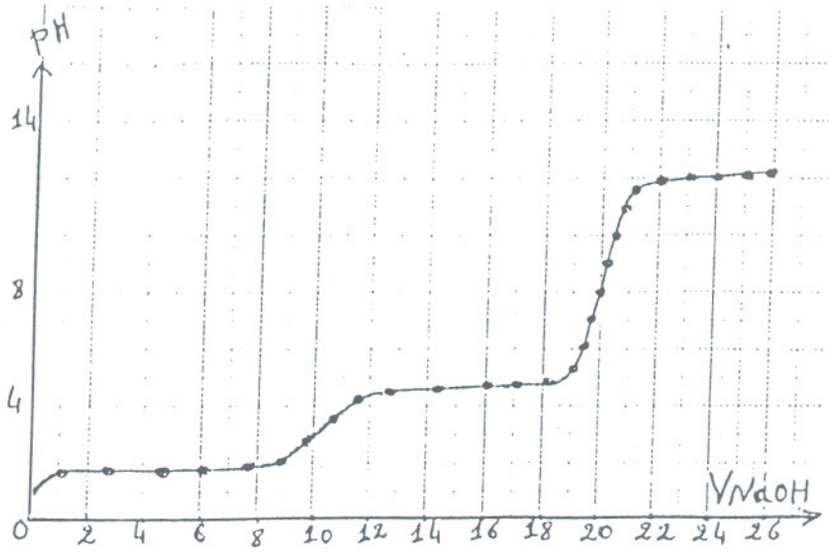
a) distilled water
b) 0.13 M $AgNO_3$
c) 0.13 M NaOH
d) 0.13 M NH_3
e) 0.23 M NaOH

II. Given the figure below, identify by letter the curve you would expect in the titration of a solution containing:

a) A weak acid, HA, with standard base.
b) Sodium carbonate, Na_2CO_3, with standard acid.
c) A mixture of NaOH + NaCN with standard acid.



III. The curve below represents the titration of a carboxylic acid solution of unknown concentration with NaOH.



a) Does the curve indicate the presence of a weak acid or strong acid? Justify your answer.

b) Determine from the curve the pK_a value of the acid being titrated and identify the acid utilizing the following data:

- Formic acid $K_1 = 1.8 \times 10^{-4}$
- Oxalic acid $K_1 = 5.60 \times 10^{-2}$ $K_2 = 5.40 \times 10^{-5}$
- Phthalic acid $K_1 = 1.12 \times 10^{-3}$ $K_2 = 3.9 \times 10^{-6}$
- Malonic acid $K_1 = 1.42 \times 10^{-3}$ $K_2 = 2.0 \times 10^{-6}$

c) What are the different species present in the initial solution (V = 0)? Knowing that the pH of this solution is 1.1, calculate the molar concentration of each of the species present and deduce the initial molar concentration (C_0) of the acid solution.

IV). 30 mL of 0.1 M K_2HPO_4 were added to 20 mL of 0.10 M formic acid (HCOOH).

a) Write a balanced equation for the chemical reaction and calculate the pH of the obtained mixture.

b) The obtained mixture was titrated with 0.08 M solution MnO_4^-. Write the equation of the reaction and trace the general shape of the titration curve E as a function of the volume of MnO_4^- added.

c) Calculate the mass of $KMnO_4$ required to totally oxidize the formic acid.

Given: For H_3PO_4 $pK_1=2.3$; $pK_2=7.2$; $pK_3=12.3$. HCOOH/$HCOO^-$ pKa =3.8.

$HCOO^- / CO_2$ $E^0 = 0.40$ V
$MnO_4^- / MnO_2 \downarrow$ $E^0 = 1.68$ V
} at pH = 0

Atomic Masses for Mn = 55 K = 39 O = 16

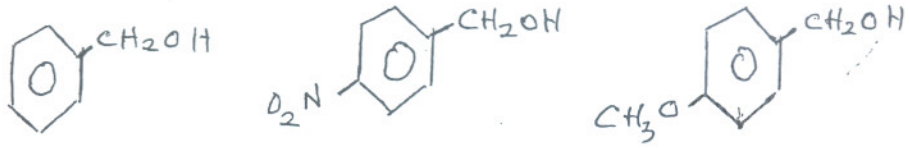
V- Benzyl acetate $CH_3COOCH_2C_6H_5$ is one of the constituents of the jasmine scent.

1) Write down the equation of the esterification reaction leading to the formation of the above ester starting with the required acid **A** and alcohol **B**.
   Write down the detailed mechanism of esterification. Suggest a catalyst. What is the role of a catalyst?
2) In the synthesis of the above ester **E**, 30.0 mL of **A** and 20.0 mL of **B** were used. 12 grams of **E** were obtained. Calculate the percentage yield of **E**.

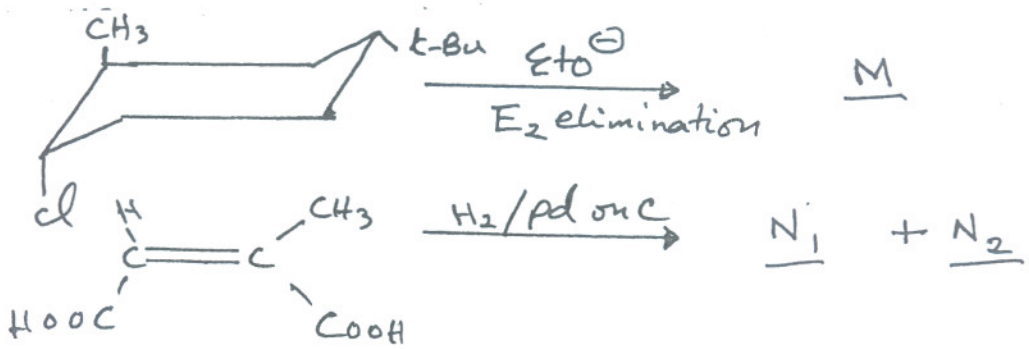
Compound	A	B	E
Density (g. cm^{-3})	1.049	1.042	1.056

Element	H	C	O
Atomic mass	1	12	16

3) When the reaction reaches completion, a quantity of acid **A** remains in solution. Why? How can you remove the remaining acid from the organic phase? Give an equation showing the necessary reaction.
4) Alcohol **B** is treated with HBr. Predict the product(s). Show the mechanism of its formation and indicate the type of the mechanism.
5) List the following alcohols in the order of reactivity with HBr (slowest, medium and fastest).



VI-A. Consider the following reactions:



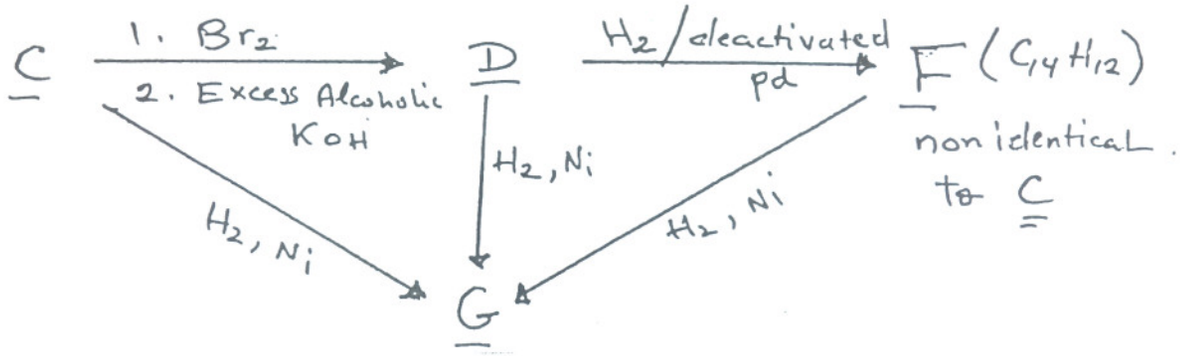
1) Show the product **M** and the mechanism of its formation.

2) Show N_1 and N_2 with the proper stereochemistry. Give the absolute configuration of N_1 and N_2. Is the mixture optically active? Why?

B. Compound **C** of molecular formula $C_{14}H_{12}$, decolorizes a Br_2/CCl_4 solution rapidly, and reacts with a dilute solution of $KMnO_4$. On catalytic hydrogenation it reacts with hydrogen in equimolar ratio (1:1). The product of oxidation with concentrated $KMnO_4$ is only benzoic acid.

1) What do you conclude from each of the above reactions?

What is the structure of **C**? To prove its structure unequivocally, it was reacted with the following reagents as shown:



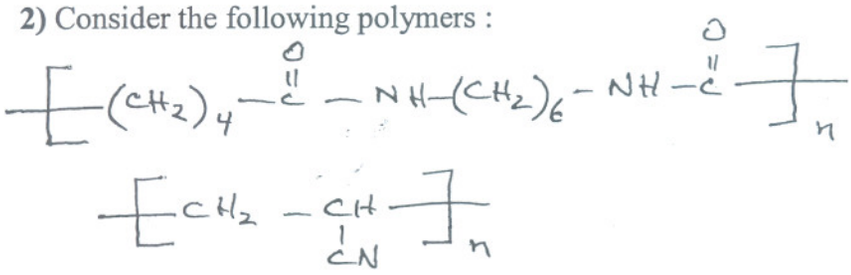
2) Give the structures of **D**, **F** and **G**.

VII – 1) Give the structures of the following peptides:

a) Ala-Phe.

b) Asp-Lys.

2) Consider the following polymers :



a) Give the formulas of the monomer(s) of each.

b) Which of the above is a polyaddition polymer and which is a polycondensation polymer.

1) Which of the following species can be used for the removal of oily spots and soil from cloth? Justify your answer.

a) methanoate anion: $HCOO^-$.

b) palmitate ion : $C_{15}H_{31}COO^-$.

c) Nonane

VIII- Potassium fluoride (KF) possesses the NaCl crystalline structure. In this case the K^+ ions possess a face centered cubic lattice (f.c.c) (The F^- ions possess the same lattice type).

a) State which are the F^- sites in a K^+ cell.
b) Give the coordination number of F^- ions in the cell?
c) How many K^+ ions and F^- ions of KF are present in a unit cell.
d) Given that the volumic mass of KF is 2.481 $g.cm^{-3}$ at 20°C :
   1- Calculate the edge of the unit cell.
   2- Calculate the minimal distances between
      - two cations K^+ - K^+
      - two anions F^- - F^-
      - one cation K^+ and one anion F^-.
e) The compound KF is used for storage of hydrogen H_2. Hydrogen having a small atomic radius, the hydrogen molecule H_2 can be inserted in the KF lattice and occupy the vacant sites. What is the type of these sites? What is their number and where are they located?

Given: $N_A = 6.023 \times 10^{23}$ M (K) = 39.1 g M (F) = 19.0 g

IX- The compactness of a cell is defined by the ratio of the volume occupied by the matter and the total volume of the cell.
Classify the following cells in an increasing order of compactness: simple cubic, centered cubic and face centered cubic.

X- a) What are the property that differentiate the three classes of solids: conductors, semi-conductors and insulators? Explain.
b) How would each class of the above solids behave when heated, according to the property that differentiates them?
c) Metals, which are conductors, are crystalline solids at normal state. Describe briefly the type of the bond between the atoms in the metal crystal.

XI- a) The complex $[CoCl_4]^{2-}$ is tetrahedral.
   1- Represent this complex using the valence bond theory showing all the steps involved.
   2- Name the hybridization type of the central atom.
b) Repeat questions 1 and 2 for the complex $[Pt(NH_3)_4]^{2+}$ which is square planar. **Given:** Z (Co) = 27 and Z (Pt) = 78.

XII. A hydrogen atom in the ground state is excited to a level n by absorbing a photon of wavelength $\lambda = 102.5$ nm. $R_H = 109677.5\ cm^{-1}$.

a. Show that $n = 3$.
b. Draw the emission diagram of this excited atom and calculate the wavelengths of the emitted radiations.

XIII. An iron container having a 3.7L volume contains air at atmospheric pressure and constant temperature. Assuming that air composition by volume is 78.1% N_2, 20.9% O_2 and 1% other gases. Oxygen reacts completely with the iron walls of the container to form solid iron oxide of negligible volume.

a. Determine the initial partial pressure of each constituent in the container.
b. Determine the final pressure of the mixture in the container and the final mole fraction of each of its constituents.
c. What would the volume of the mixture of gases be if the initial conditions of temperature and pressure were restored?

XIV. The complete combustion of a certain quantity of ethylene at constant pressure and 25°C liberates 3010 calories.

a. Calculate the volume of CO_2 produced at STP.
b. The quantity of heat produced by the combustion of 1 m^3 of ethylene measured at STP is used to convert a certain quantity of water at 20 °C to vapor at 365 °C at atmospheric pressure. Calculate this mass of water.

Given:
Enthalpy of formation at 25 °C of ethylene is 12.42 kcal/mole, that of CO_2 is – 94.05 kcal/mole, and that of liquid water is – 68.3 kcal/mol.
Heat of vaporization of water is 540 cal/g at 100 °C and 1 atm.
Specific heat of liquid water is 1 cal/g °C, and that of water vapor is 0.5 cal/g °C.
Consider the change of the specific heats by temperature is negligible.
Molar volume is 22.4 L.

XV. Buta-1,3diene undergoes dimerization according to the equation:

$$2\ C_4H_{6(g)} \rightarrow C_8H_{12(g)}$$

At 326 °C the pressure of butadiene in the reaction vessel is 632 mm of Hg at time t = 0. In order to follow up the reaction, one records the values of the total pressure in the vessel as a function of time t. These values are shown in the following table:

t (min)	P (mm of Hg)
0	632
10	591
20	557
50	497
75	466
100	446

a. Calculate the partial pressure p_B of butadiene in the gaseous mixture for each time indicated in the table. Draw the graph $p_B = f(t)$. Deduce the half-time of the reaction.
b. Is this reaction first or second order? Explain.
c. Using the previous results, calculate the rate constant of the reaction.
d. Calculate the activation energy of the reaction knowing that the rate constant at 370 °C is 1.1×10^{-4} $min^{-1}.(mm\ of\ Hg)^{-1}$

اللجنة الفاحصة بيروت ٢٠٠٨/٤/٥