Mansoura University
Faculty of Science
Chemistry Department
Course: Physical Chemistry
Date: 2/ 01/ 2016

First term Examination
Subject: Chemistry (441)
Fourth level, Chemistry students
Full Mark: 60 Marks
Time Allowed : 2hours

Answer the Following Questions:

I-1-Comment on the following rate equations and what is the effect of heat of adsorption of different species on the true activation energy for each case (A, B, C and I are reactants, product and poising)? **(10 marks)**

a) rate $= k_r b_A P_A$ b) rate $= k_r b_A P_A / b_I P_I$ c) rate $= k_r b_A b_B P_A P_B$

d) rate $= k_r b_A P_A / b_B P_B$ e) rate $= k_r b_A b_B P_A P_B / (b_C P_C)^2$

2-The dissociation of general acids and general base is reflected in a dependence of rate on pH and must be taken into account in the kinetic model. Explain. **(6 marks)**

3- At high pressure and 400°C the specific rate constant for the catalytic decomposition of HI on Pd-surface is 500 mm Hg Sec^{-1} and at low pressure, the specific rate constant becomes 60 Sec^{-1}. Calculate the P_{HI} at which the value of dP_{HI}/dt should be 300 mm Hg Sec^{-1}.**(4marks)**

II-A- Which of the following statements are FALSE? **(6marks)**

1- Catalysis can speed up reactions as much as a million-fold.

2- Catalysts play no chemical role in the reactions they catalyst.

3- Catalysts increase the value of the equilibrium constant for a reversible reaction.

4- Catalysts reduce the value of ΔH for reactions.

5- In catalytic to reactions the reaction follows an alternative pathway of higher activation energy.

6- An enzyme is a catalyst that only binds certain substrate.

B) The velocity constants k_{OH} for certain catalytic reaction were 0.15 and 0.85 hr^{-1} at 140° and 200°C respectively in a solution of pH = 9. Calculate the true and the observed activation energies for this reaction. Comment on the results.**(5 marks)**

C) An enzyme having a K_m of 3.9×10^{-5}M is studied at 50g of certain substrate (Mwt= 2500g) in 250 ml of certain solvent. After one minute, it is found that 10.5 μmol L^{-1} of product has been produced. Calculate V_m and the substrate concentration when the initial rate = $V_m/2$. **(5 marks)**

D) The catalyst cannot affect the equilibrium point in reversible reactions. Explain? **(4 marks)**

III-1- Catalytic activity of a solid catalyst depends on the strength of chemisorption. Give reasons and Examples.**(5marks)**

2-Indicate why in heterogeneous catalysis, desorption of products should be slower than adsorption of reactants in some cases. **(3marks)**

3-Indicate why the heterogeneous catalysis is the backbone of industrial processes.**(3marks)**

4-Fxplain why the selectivity is an important factor for the performance of the catalyst? **(5marks)**

5-What is the role of diffusion in heterogeneous catalysis? **(4marks)**

GOOD LUCK

Examiner: Prof. Sohier A. Hakam

Mansoura University
Faculty of Science
Chemistry Department
Subject: Chem. (421)
f-Block Elements and Organo-Metallic Chemistry

First term
B.Sc. Students
Date: 9/01/2016
Time Allowed: 2 hrs
Total Marks: 80

Answer the following Questions:-

A- Put (√) or (x) and correct the following statements:- (30 Marks)

1- Ce^{3+} and Yb^{3+} are colored .
2- The tendency to form complexes decrease with increasing metallic character of ligands.
3- Ce^{3+} ion is less active than Lu^{3+}.
4- The greater positive charge on the carbonyl complexes the higher should be the C-O bond order.
5- μ-bond is formed, between M → L, and used to explain olefinic complexes.
6- Eu^{2+} ion is the most stable divalent between lanthanides.
7- The ability of lanthaides ions (M^{3+}) to form complexes is small.
8- $[Co(CO)_4]$ is stable and has tetrahedral structure.
9- Carbonylate ion is obtained by lossing an electron.
10- Butadiene complexes are types of of 2 donor atoms.
11- Ce^{3+} salts are more stable than Ce^{4+}.
12- Ce reacts with H forming CeH_4.
13- Magnetic properties of lanthanides are more affected by the type of ligand.
14- Nd^{3+} has the electronic configuration $[Xe\}4f^4$.
15- The 4f electrons in the lanthanides are taking part in bonding.
16- Ce_2O_3 is less more stable than CeO_2.
17- $Gd(OH)_3$ is less basic than $Al(OH)_3$.
18- $[Mn(CO)_5]$ is less stable than $K[Mn(CO)_5]$.
19- $HMn(CO)_5$ behaves as a weak base in aqueous solution.
20- Bridged halides in metal carbonyl halides are easily dected by NH_3.

B- Write short notes on the following: (40 Marks)

1- Extraction of lanthanides from Monazite.
2- Explain the methods of synthesis of carbonyls using indirect metal halides.
3- The differences of color between lanthanides and d-block elements.
4- Molecular orbital describtion of CO molecule.
5- The resembles and differences between Eu^{2+} and Ca^{2+}.
6- Explain using VBT theory the complex $[HRe_2Mn(CO)_{14}]$.
7- Magnetic moment of Gd^{3+} ion .

P.T.O

8- Bonding in Zeise's salt.

C- Comments on the following: (10 Marks)

1- Pt perfers to form square-planar complexes.
2- Lanthanides and d-block elemnts give bands in the visible region.
3- Allylic complexes.
4- Lanthanides are more active than d-block elements.

Good Luck

Prof. Dr. Mohsen M. Mostafa

Mansoura University Faculty Of Science Chemistry Department Code: Chem. 442 Subject: Advanced Electrochemistry		First term Fourth level Program: Chemistry Date: Jan. 2016 Time Allowed: 2 Hours Full Mark: 80 Marks

Answer All Questions الأسئلة على الوجهين

First Question: **(20 Mark)**

[A] Complete: **(6 Mark)**

(1) The common intermediate mixed potential is called .....

(2) The presence of H^+ ions in electroplating path cause.....

(3) The presence of active ions such as $Cl^-, Br^-.I^-$ during passivation of electroactive passive metal cause .....

(4) A metal characterized by higher exchange current density its electrodeposit is characterized by .....

[B] Discuss briefly the electrodeposition on plastic. **(8 Mark)**

[C] Write short notes on the following: **(6 Mark)**

(i) Errosion corrosion (ii) Anodizing (iii) Adhesion

Second Question: **(20 Mark)**

[A] Tick (√) for the correct answer: **(12 Mark)**

(1) When coupling a metal M its $E_{M/M^{+n}}$ = +0.345 with a metal N its E_{N/N^+} = -0.75 the corrosion rate of metal M is:

(i) Increase (ii) Decrease (iii) Not change

(2) Rubber is added to some electroplating path to:

(i) Stabilize the PH

(ii) Increase conductivity

(iii) Stabilize the solution

(iv) Give smooth deposit

(3) The presence of precipitating ions such as OH^- or SO_4^{-2} ions during passivation of electroactive passive metal:

(i) Decrease the limiting passivating current

(ii) Increase the passive potential

(iii) Not change the passive potential

(4) Increasing the deposition potential the electrodeposit change to:

(i) Coarse crystalline

(ii) Smooth deposit

(iii) Dense crystalline

[B] Show how to modify an electrdeposit in the form of needle or trees like crystal. **(8 Mark)**

Third Question: **(20 Mark)**

[A] Give reason: **(12Mark)**

(1) When coupling an active metal with an inert metal, the corrosion rate of the active metal increases vigorously.

(2) The presence of indifferent cations increase the deposition potential.

(3) Copper is deposited rapidly on Zn rode placed in copper sulpahte, while Zn dissolved.

(4) A pit is formed in some electroplationg metal.

[B] Write briefly on the following:

(i) The disadvantage of the E/PH diagram. **(6 Mark)**

(ii) The role of complex ions on the electrodeposited metal. **(2 Mark)**

Fourth Question: **(20 Mark)**

[A] (i) Illustrate the growth of electrodeposited metal.

(ii) From the point of view of mixed potential theory show how to protect the metal against corrosion.

(iii) What is meant by current efficiency 90%?

(iv) Show how to modify a coarse crystalline electrodeposited metal?

With best wishes

Prof. Dr. H. Abd El-Rasoul

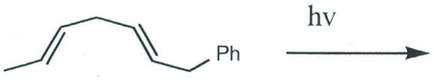
كيمياء - كيمياء وبنات - كيمياء وحيوان

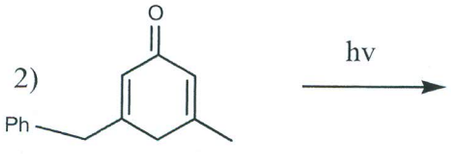
Mansoura University **Faculty of Science** **Chemistry Department** Total Marks: 60		**First term** **4th Year, Students.** **Photochemistry& Organic spectroscopy (Chem431)**

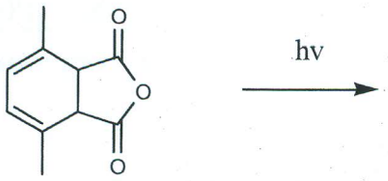
Answer the following questions as stated **(7 pages)** **Time allowed: 2 hours**

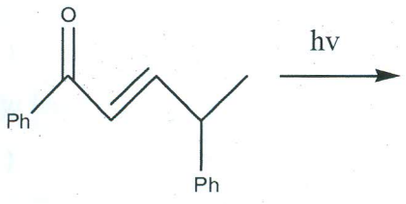
Photochemistry Section A: [30 Marks]

Q1 - Complete the following reactions and suggest their mechanisms: [15 Marks]

1) 

2) 

3) 

4) 

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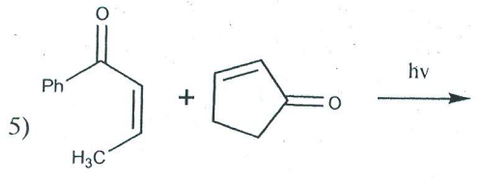

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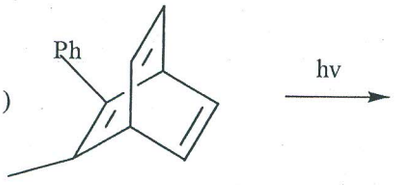


Q2 - Put true or false (+ or -) on the following sentences: [15 Marks]

1) The excitation occur by absorption of energy to transfer electron from S_1 to S_0 ( )
2) Electron transfer from singlet ground to singlet excited states with loss of energy with the same multiplicity is called fluorescence ( )
3) Intersystem crossing is the process, which transition from one state to another with different multiplicity via loss of energy ( )
4) Singlet excited state has shorter life time than triplet excited state ( )
5) Energy is inversely proportional with frequency ( )
6) Sensitizer is a substrate which can increase the energy for activation ( )
7) Norrish type I occurred only on saturated cyclic carbonyl compounds ( )
8) Norrish type II is a photochemical reaction and gives cyclobutanol and aldehyde ( )
9) Photochemistry of α,β-unsaturated cyclic ketone afforded cyclopropane ring fused with the same ring size ( )
10) Photochemistry of β,γ-unsaturated ketone produce α,β-unsaturated ketone ( )

Organic Spectroscopy Section B: [30 Marks]

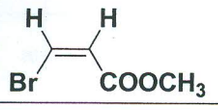
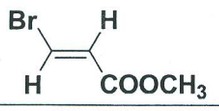
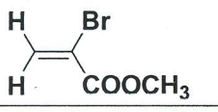
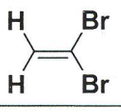
Question #1: [15 Marks]

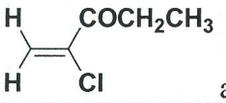
(A) Choose the correct answer for each of the following statements. [12 Marks]

(i). Which of the following nuclei has the property of nuclear spin.

a) $^{12}C_6$	b) $^{13}C_6$	c) $^{16}O_8$	d) $^{32}S_{16}$

(ii). In ^{1}H NMR, for which of the following structures you expect coupling constant J = 8 Hz for the doublet signal.

a) 	b) 	c) 	d) 

(iii). In ^{1}H NMR, the expected signals for compound  are :

a) 2 signals	b) 3 signals	c) 4 signals	d) 5 signals

(iv). In ^{1}H NMR, which of the following compounds gives two signals "one signal as a doublet and the other one as a septet".

a) $(CH_3)_2CHCl$	b) $CH_3CH_2CH_2Cl$	c) $(CH_3)_3CCl$

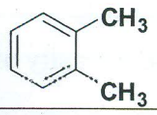
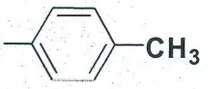
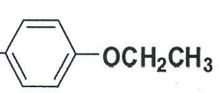
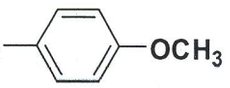
(v). In ^{1}H NMR spectrum, the expected splitting pattern of the structural formula CH_3CHCl_2 is:

a) singlet, singlet b) doublet, triplet
c) singlet, quartet d) doublet, quartet

(vi). In ^{1}H NMR, which of the following compounds has the highest chemical shift (δ ppm) for $-CH_2-$.

a) CH_3CH_2F	b) CH_3CH_2I	c) CH_3CH_2Br	d) CH_3CH_2Cl

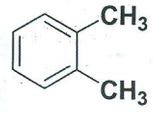
(vii). Which of the following compounds gives four signals in ^{1}H NMR spectrum .

a) 	b) 	c) 	d) 

(viii). In ^{1}H NMR, which of the following compounds has a proton disappear in D_2O.

a) $CH_3CH_2CH_2CH_3$	b) $CH_3CH_2CH_2OCH_3$	c) $CH_3CH_2CH_2CH_2OH$

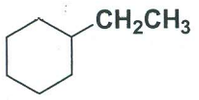
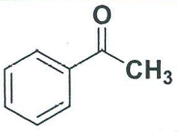
(B). How many carbon lines for each of the following compounds in ^{13}C NMR. [3 Marks]

a) 	b) $CH_3CH_2CH_2NO_2$

Answer only one question from Questions #2 & #3:

Question #2: [15 Marks]

A) [6 Marks] **(i)** According to the fragmentation rules, give the expected fragmentations for each of the following compounds. **"show the bond of cleavage"**

Compound	Fragmentations "In mass spectrometer"
	
	

(ii). The mass spectrum of benzyl chloride ($PhCH_2Cl$) showed a base peak at m/e 91. Explain the reason? In ionization chamber (Electron impact), what type of species is initially produced radical cation **or** radical anion. [Mass C = 12, H = 1, Cl = 35].

B) Choose the correct answer for each of the following statements. [5 Marks]

(i). The expected electronic transitions when compound  is irradiated with UV light :

a) $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$

b) $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$

c) $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$

d) $\sigma \rightarrow \sigma^*$

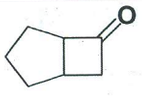
(ii). In UV, increasing congujation leads to a blue-shift.

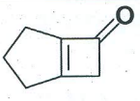
a) True b) False

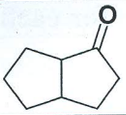
(iii). An auxochrome is a substituent in a chromophore that alters the λ_{max} and the intensity of the absorption. for example –OH, $-OCH_3$, $-NH_2$ are auxochromes.

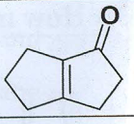
a) True b) False

(iv). In IR, for which of the following compounds you expect the lowest wave number (ν') for the carbonyl group.

a) 

b) 

c) 

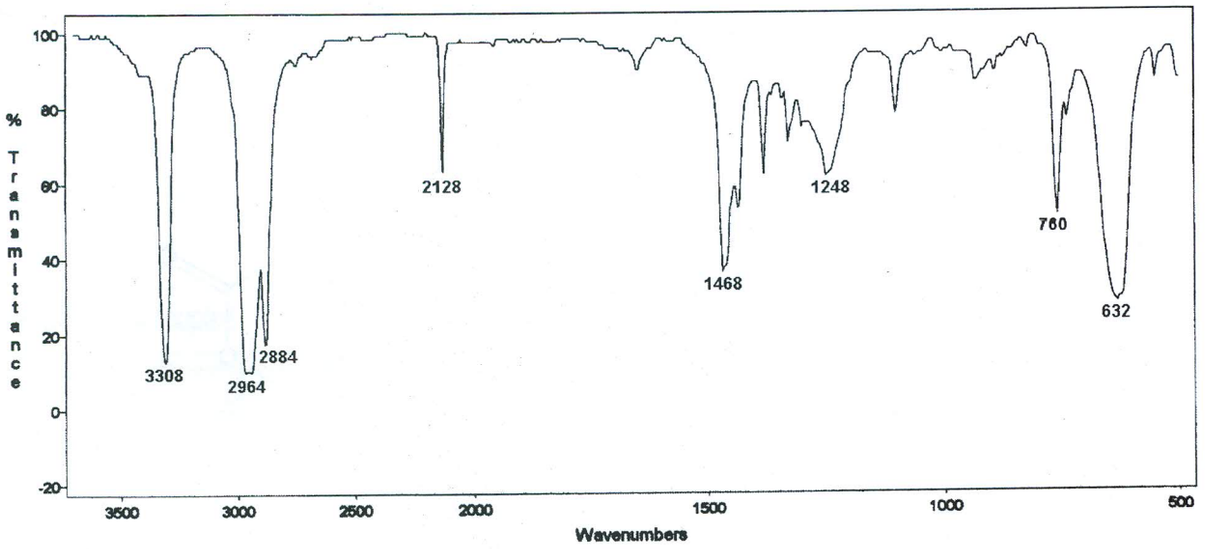
d) 

(v). In IR, for which of the following groups you expect the wave number (ν') value of 2250 cm^{-1}.

a) NH_2 b) CO c) CN d) OH

C) In a laboratory trial to carry out the following reaction, and by monitoring the reaction using IR. The recorded spectrum below confirm which structure **A <u>or</u> B**. Explain the reasons. [4 Marks]

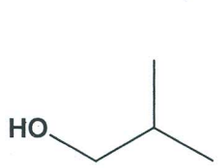
A B



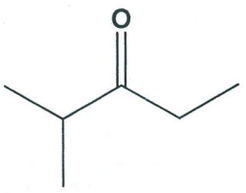
<u>Question #3:</u> [15 Marks]

a) A compound with molecular formula $C_{12}H_{24}$ exhibits a <u>^{1}H NMR spectrum with only one signal</u> and a <u>^{13}C NMR spectrum with two signals</u>. Deduce the structure of this compound. **[5 Marks]**

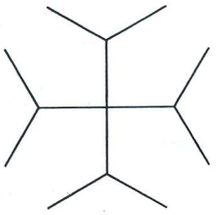
b) Consider the following compounds, **A** – **F**: [10 Marks]



A



B



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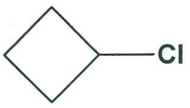

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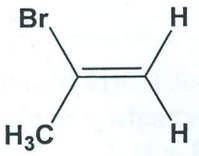
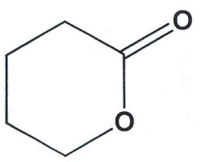


E



F

More than one answer may be correct. GIVE ALL CORRECT ANSWERS

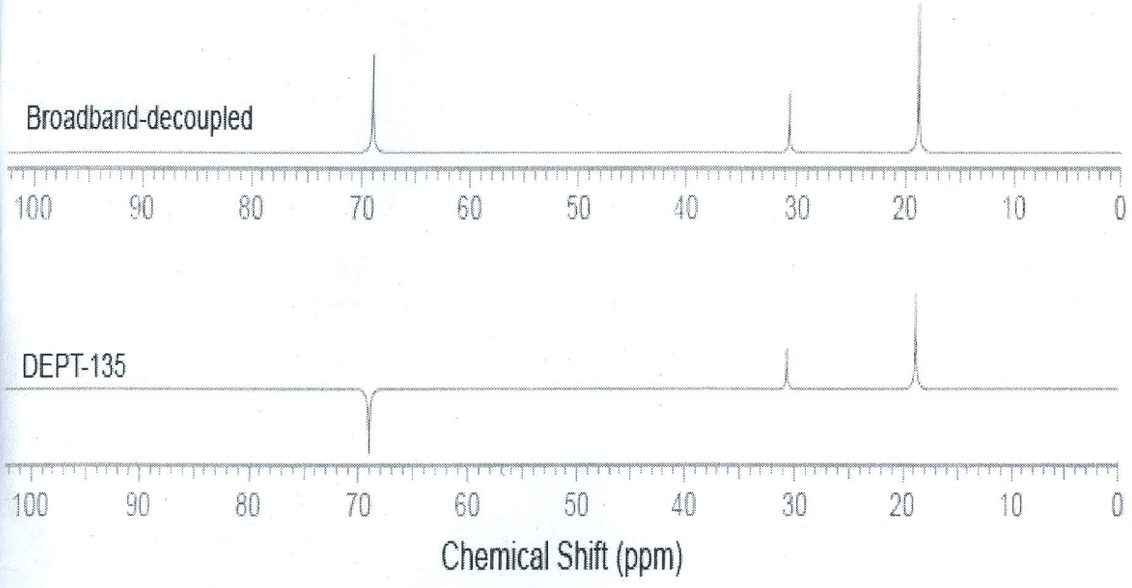
1) Which of the compounds would give three signals in ^{13}C NMR spectrum?

2) Which of the compounds would give four signals in the ^{1}H NMR and five signals in ^{13}C NMR spectrum?

3) How many triplet signals would be observed in the ^{1}H NMR spectrum of compounds **B**, **D** and **F**?

4). Outline the change(s) that will happen in the ^{1}H NMR and ^{13}C NMR spectra of compounds **A** and **F** when they are treated with D_2O?

5) Examine the ^{13}C NMR spectrum below. To which of the compounds does it belong?



Besst wishes

Prof. Dr. Mohamed Abou El-Zahab & Prof. Dr. Mohamed Ismail

Dr. Saad Shaban & Dr. Iman Hellmy

Faculty of science
Dept of chemistry
Course Title &Code
Analytical Chemistry
412.

First Semester (Jan.2016)
Exam
B.Sc. students
Time allowed: 2 hours
Full Mark: 80 Marks

Notes: Express your answer by formula& equations & figures wherever possible.

1- Define 5 only of the following express your answer by equation, diagram: (15 Marks)

1-D l (AAS& AES. 2-Heavymetals Specificaton (cpds , elements). 3- $K_{d,\&}$ α & R % -1 4- D , capacity of resin , Doerner-Hoskens law. 5- F%,R_e % flotation . 6- F-, t-, Q-, X^2 – tests.

7-Renolles- Soveck & Bragg' s , Scheibe, Lomakin-Kaiser equations.

2- A) *Complete 10 only from the following: (15 Marks)*

1-Preconcentration methods should be done two overcome on difficulties …….and…….
2-The most important of these effects of heavy metal ions human body are1-….., 2-….,3.,
3-Flotation is define as……. the classification of the methods based on …. ,…. and….
4-Using the Flotation method for separation of 1…2….3…..4……5…..6….and …..
5 -Advantages of solid phase extraction are ……., ……. and…….
6- Applications of ions exchanger in analytical chemistry 1…,.2….,3…..,4……, 5…..and6-…..
7- Factors affecting up on Flotation 1….2……3…..4…5…..6….7- … and 8…..
8-- Give 10 methods for determination of multi trace heavy or single element 1…to 10…
9- Ions exchanger techniques are 1-……. and 2-……
10- Factors affecting up on ions exchanger separation are 1…..,2…,.3…,.4…,.5…,.and.6…
11-Applications of Electrophoresis in 1-…,2-….,3-… and .4…..
12- Three methods for pre-concentration and determination in the same time 1…, 2…. & 3…..
13 the methods of dissolution solid samples are…,……, ….., ,…., …, …..,,…., ….., ….and….

B)-Hg (II) ion 20 ppm in solution after pre-concentration on modified silica 20 mg was 2 ppm . If the log K_d = 2.3 for Zn (II), calculate α .
& R%,If the volume of solution 100 ml. ***(10 Marks)***

P.O.
انظر الخلف

Good Luck : prof. Dr. prof. Dr. I.Kenawy

1) Draw a block diagram of flame atomic absorption instrument, indicating the source and sample introduction system. (4marks)

2) Define the following: (5marks)

a)atomization b) sputtering c) derivative spectra d) plasma e) Group frequency

3) Compare between: (8marks)

a) Resonance and non-resonance fluorescence b) Arc and spark AES
c) AAS and AE d) Advantages and disadvantages of graphite furnace technique.

4) Circle the correct answer: (8marks)

1) The fundamental frequency expected in the infrared absorption spectrum for the C - O stretching wavenumber is (K=5.0 X 10^5, C=12, O= 16, Avogadro's no=6.02x10^{23}, C=3x10^{10})
.. .a)1112 b) 1200 c) 1650 d) 2200

2) If the transmittance is 50.8% in a 2.00 cm cell, the absorbance in a 5.00 cm cell will be
.. a) 0.355 b) 1.471 c) 0.735 d) 0.934

3) A solution with a known concentration equal to 3.4 mmol L-1 gave an absorbance of 0.820 What absorbance would be obtained for a solution with a concentration 2.6 mmol L^{-1}?
... .. a)0.432 b)0.627 c)0.512 d).0.315

4) 4x10^{-5}M Fe(III) complex ion is transferred in 1cm cell, on passing light of particular wave length, it was noticed that the transmitted light was 10% of the incident light, the molar extinction coefficient is

a) 1.3x10^4 b) 2.5x10^4 c)5x10^4 d) 7.5x10^4

5) Give reason for the following: (6marks)

i) Graphite is common used in atomic spectroscopy
ii) IR spectra is used to differentiate between inter and intra molecular hydrogen bonding
iii)Any sample which can run by either the flame or the graphite furnace is best run on the flame

6) Complete the following: (5marks)

ii)There are several methods for introduction; an analyte solution into the plasma such as, ..., ..., ...
iii)Examples of organic chromophores are, ..., ..., ..., ...
iv)Inorganic groups containing ..... bonds absorb in the ..... region. The most transitions are a result of ..... transitions, while the colourc of solutions of some transition metals is due to ..... transitions
v) Charge transfer complexes are of special interest as their molar absorptivities are .....; allowing ..... determinations.

7) Draw a curve for photometric titration of (Bi^{3+} + Cu^{2+}) mixture with EDTA indicting how can you determine the end point of each constituent? (2marks)

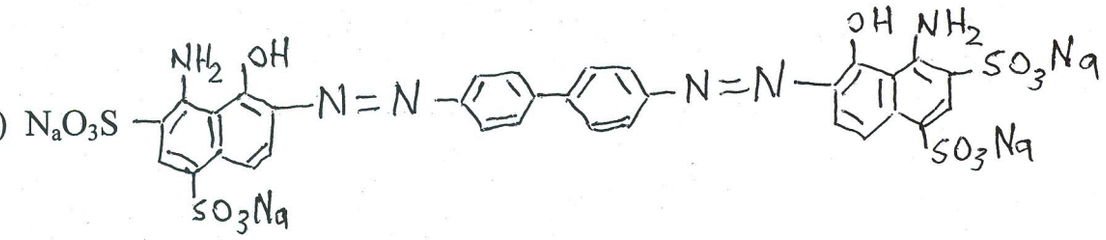
8) How can a chemist control the analytical interference in the flame process? (2marks)

With best wishes Prof. Dr Ibrahim Kenawy , Prof. Dr. Magdi E. khalifa

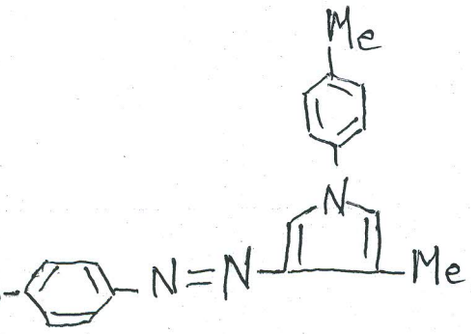
Mansoura University **Faculty of Science** **Chemistry Department** **Subject: Clinical Chemistry** **Course(s) : Org. Chem.(432)**		**First Term** **4th Level Students** **Date : Jan., 2016** **Time Allowed : 2 hours** **Full Mark : 80 Marks**

Answer the Following Questions

I. Illustrate with equations the synthesis of each of the following compounds : (27Mark

a) 

b) Crystal violet

c) 

II. Write an essay to illustrate each of the following : (27 Marks)

a) Reactive dyes
b) Anthraqunone dyes.
c) Indigoid and thioindigoid dyes.

III. Illustrate with example each of the following : (26Marks)

a) Metal-azo dyes complexes
b) Azoic dyes

مع اطيب الامنيات بالتوفيق

د/ محمد محمد يوسف