



Answer the following questions

Section A:-

Answer the following questions:-

1- (A)- Put (✓) or (x) for the following and correct the statements (30 Marks):-

- i- Cl⁻ ions act as a bridging ligands.
- ii- Mn²⁺ complexes prefer octahedral structures.
- iii- The term letter of L = 2 is F term.
- iv- Primery valence is directed towards fixed position and represented by dotted line.
- v- [AuCl₄]⁻ has a tetrahedral structure.
- vi- L = 1 and S = 1 the ground term is ³D.
- vii- Double salts are easily dissolved in H₂O and dissociate to its constituents.
- viii- Tetrahedral Cr³⁺ complexes are more stable than octahedral complexes.
- ix- I ligands prefer to form tetrahedral complexes due to the weak effect of π-bonding.
- x- Low-spin complexes are spin-paired complexes or inner-orbital complexes.
- xi- The ground term of [Mn(H₂O)₄Cl₂]Br is ⁴F.
- xii- EAN of Li₂[Ti(dipy)₃] equals 34.
- xiii- [CoCl₄]²⁻ has a deep blue color due to the allowance of both spin and orbital.
- xiv Square-pyramidal and trigonal-pyramidal are examples of 5-coordinated complexes.
- xv- Zeeman effect equals 2J+2.
- xvi- He₂ molecule is very stable compound.
- xvii- In heavy metals the orbit-orbit coupling becomes the most important and effective.
- xviii- The energy of CO is less electronegative than metal ions.
- xix- σ-Bond is formed between t_{2g} orbitals of metal ions and P_z of the ligand.
- xx- [FeO₄]²⁻ has a square-planar structure.

2- Comments on the following:-

(15 Marks)

- i- Fe³⁺ complexes are pale yellow in color. (3 Marks)
- ii- Log k₂ for Ag(NH₃)₂⁺ is greater than log k₁ while log k₃ for [Hg(CN₄)]²⁻ is smaller than log k₂. (4 Marks)
- iii- Six water molecules are replaced by EDTA in metal complexes cause a large value of entropy. (3 Marks)

- iv- In high-spin Mn^{2+} complexes the hydration energy of the theoretical and the experimental values are equal. (3 Marks)
- v- Bidentate ligands form complexes which are more stable than monodentate ones. (2 Marks)

3- Write short notes on the following:- (15 Marks)

- i- Labile and inert complexes. (2 Marks)
- ii- The second postulation of Werner's theory. (2 Marks)
- iii- Preparation of complexes by thermal decomposition with reference to $CuSO_4 \cdot 5H_2O$. (1.5 Marks)
- iv- Charge-transfer of the type $M \rightarrow L$. (1.5 Marks)
- v- Limitations of CFT. (1.5 Marks)
- vi- State two methods to detect complex compounds (2 Marks)
- vii- Stability of complexes (1.5 Marks)
- viii- Spin multiplicity (1 Marks)
- ix- Hydrated isomerism (1 Marks)
- x- Synthesis of complexes using substitution reaction (1 Marks)

4- Compare between the following two complexes using VBT, CFT and MOT and answer the following questions: (20 Marks)

- i- $[Ni(CO)_4]$ (At. No. = 28) ii- $[CuCl_2(OH)_2]^{2-}$ (At. No. = 29). (7.5 Marks)
- ii- Determine the EAN and U_{eff} for each complex. (3 Marks)
- iii- Name and state the types of isomerism in each complex. (3 Marks)
- iv- State the type of complex. (1.5 Marks)
- v- Determine the ground term for each complex. (3 Marks)
- vi- Which of the two complexes have a regular structure? (2 Marks)

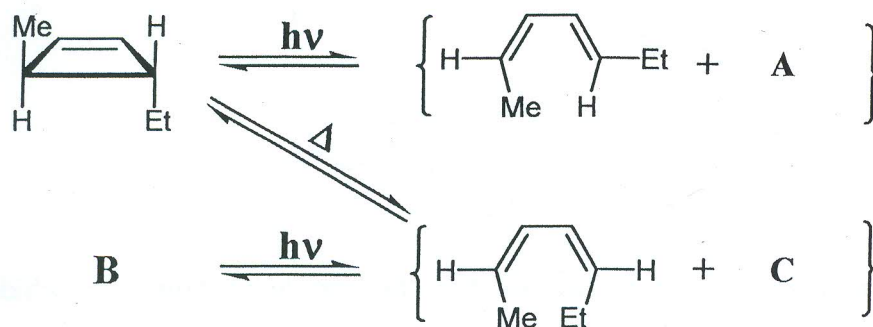
Good Luck and Best Wishes

Prof. Mohsen Mostafa

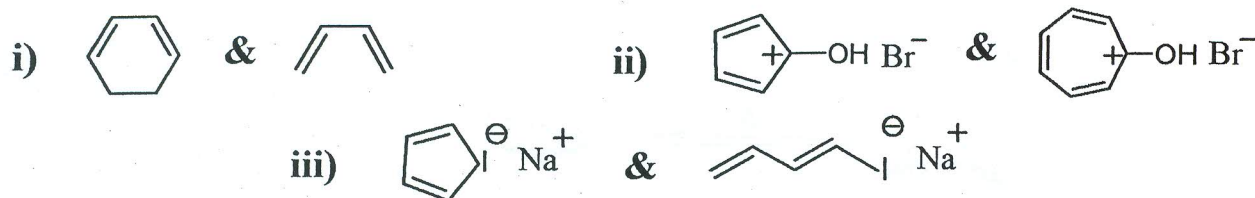


ANSWER ALL QUESTIONS AS DESIRED

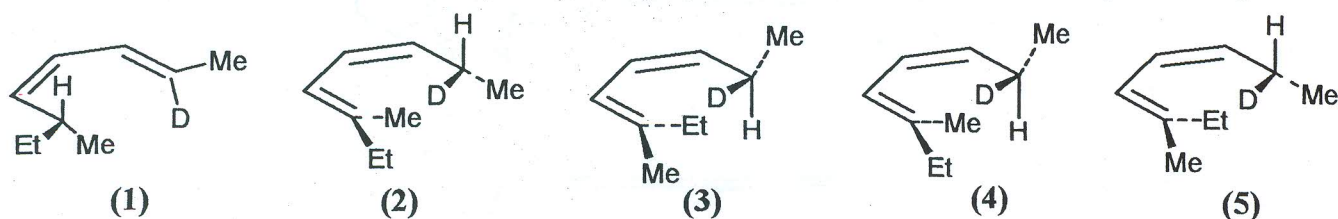
1-a) What is the structure of A, B and C in the following reaction? **EXPLAIN!** Use an energy correlation diagram to account for the stereo chemical course of the reaction. [12 marks]



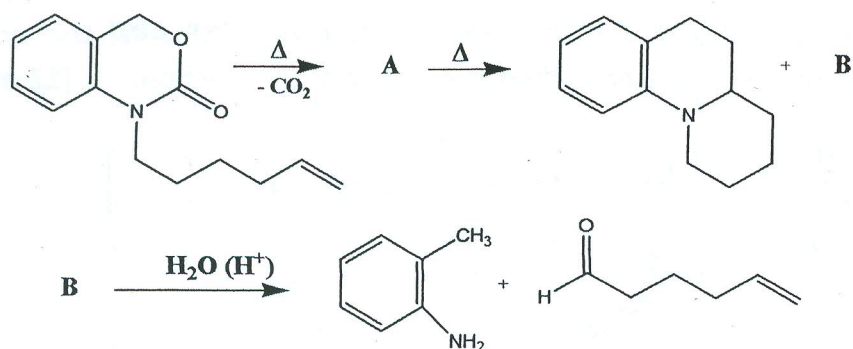
b) Compare the stability of **only two pairs** of the following compounds on the basis of the resonance concept, the molecular orbital theory and the HÜCKEL-[4n+2]-Rule. [2 x 4 = 8 marks]



2-a) When compound 1 is heated, predict the resulting product(s) among the stereo isomers 2, 3, 4 and 5 by classifying them as **symmetry allowed** or **symmetry forbidden**. Suggest a **pericyclic concerted mechanism**, which may explain your predictions and account for your answer on the basis of only one theoretical approach of your choice. [10 marks]

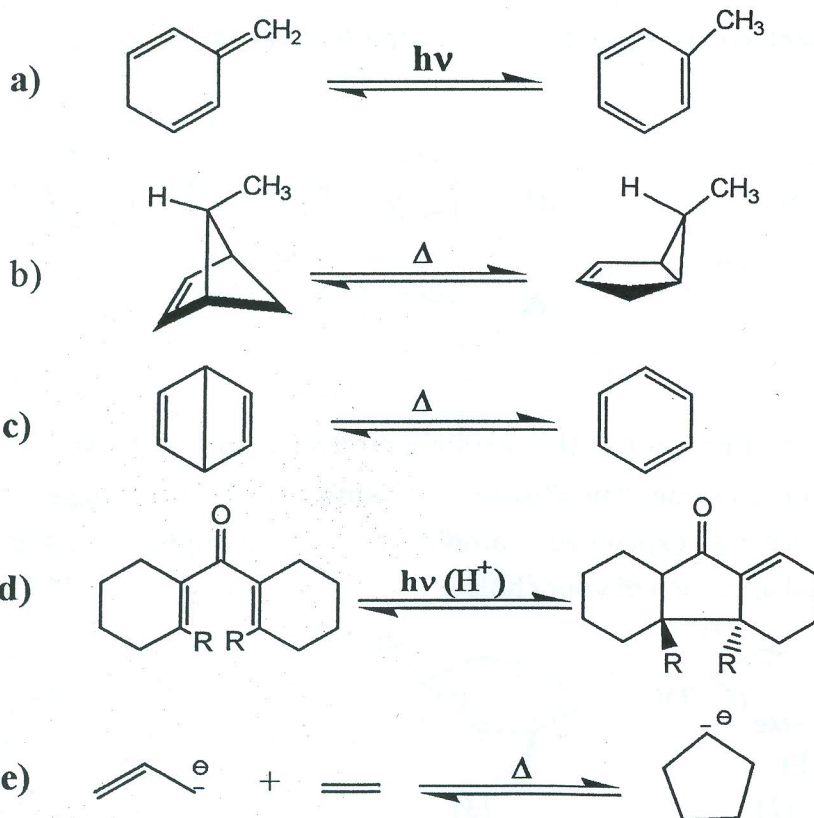


b) Suggest Structure for compounds A and B and discuss mechanism, which may account for all the steps in the following reaction sequence. (Hint: there are three different types of pericyclic concerted steps and one non-concerted step that should be recognized and exactly classified). [10 marks]



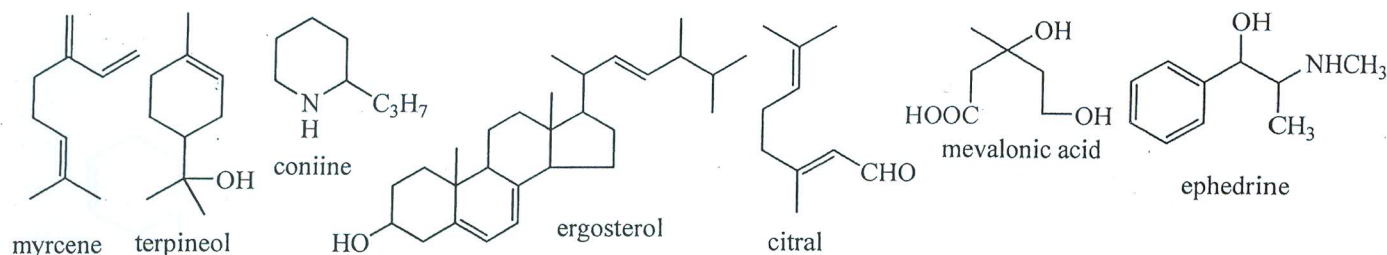
3- Classify each of the following reactions and indicate whether they would be allowed or forbidden under the given conditions. Suggest alternative allowed routes for the forbidden reactions and account for your answer:

[5 x 4 = 20 marks]





ANSWER THE FOLLOWING QUESTIONS



Question (I):

- (A) In your answer notebook write the letter representing the right statement for the following (24 marks).
- Phenylalanine [$\text{PhCH}_2\text{CH}(\text{NH}_2)\text{COOH}$] can be produced from:
 - Shikimic acid pathway
 - Mevalonic acid pathway
 - Polyketide pathway
 - All of them
 - Shikimic acid pathway starts by Aldol-like reaction between phosphoenol pyrovate and:
 - phosphorylated isoprene unit
 - acetyl CoA
 - malonyl CoA
 - erythrose-4-phosphate
 - The precursor of diterpenes is:
 - geraniol
 - farnesol
 - geranylgeraniol
 - squalene
 - Myrcene reacts with maleic anhydride to give a Diels-Alder adduct.
 - True
 - False
 - The number of isoprene units in sesquiterpenes is:
 - 1
 - 2
 - 3
 - 4
 - Treatment of α -terpineol ($\text{C}_{10}\text{H}_{18}\text{O}$) with Br_2/CCl_4 gives a compound of the formula:
 - $\text{C}_{10}\text{H}_{18}\text{BrO}$
 - $\text{C}_{10}\text{H}_{18}\text{Br}_2\text{O}$
 - $\text{C}_{10}\text{H}_{18}\text{Br}_3\text{O}$
 - $\text{C}_{10}\text{H}_{18}\text{Br}_4\text{O}$
 - Nerol cyclizes in dil. H_2SO_4 to form α -terpineol 9 times faster than Geraniol, this indicates that:
 - Nerol is the trans-isomer
 - Nerol is the cis-isomer
 - Geraniol is the cis-isomer
 - Both (a) and (c)
 - Distillation of a steroid with selenium gives:
 - Naphthalene
 - Anthracene
 - Phenanthrene
 - Diel's hydrocarbon
 - Ozonolysis of Ergosterol indicated the presence of one double bond in the side chain between:
 - C-20 & C-21
 - C-20 & C-22
 - C-22 & C-23
 - C-23 & C-24

10- Pregn-4-en-3,20-dione (Progesterone) belongs to:

- (a) Sex hormones (b) Bile acids (c) Sterols (d) Cardenolides

11- Heating of coniine with hydroiodic acid at 300°C under pressure gives:

- a) Isooctane (b) 2-Methyloctane (c) n-Octane (d) Cycloocatne

12- Cholesterol has a hydroxyl group (OH) at:

- (a) C-2 (b) C-3 (c) C-4 (d) C-6

(B) Sesquiterpene **A**, $C_{15}H_{26}$, when hydrogenated gave **B**, $C_{15}H_{28}$.

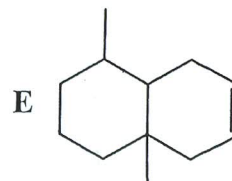
Treatment of **A** with hot acidic permanganate gave acetone and **C**, $C_{12}H_{20}O$.

Treatment of **C** with $LiAlH_4$ gave **D**, $C_{12}H_{22}O$.

Treatment of **D** with hot conc. H_2SO_4 gave **E**.

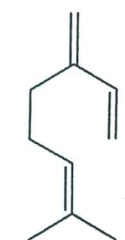
Give the structure of **A**.

(6 marks).

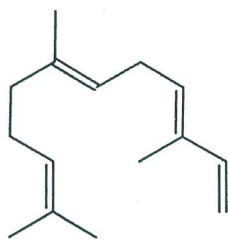


Question (II):

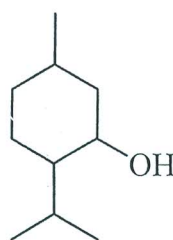
1. Locate the isoprene units in the following terpenes, use the sign - - - - to indicate "head to tail" joint and the sign $\sim\sim\sim$ to indicate the ring closure. (9 Marks)



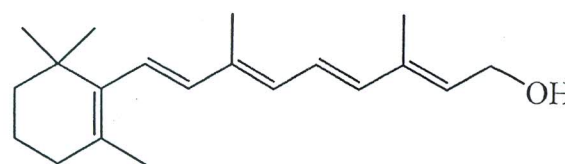
Myrcene



α -Farnesene



Menthol



Vitamin A

2. How can you prove that nicotine ($C_{10}H_{14}N_2$) contains a pyridine ring substituted at the 3-position by a group $C_5H_{10}N$? Write the complete structure of nicotine. (6 Marks)

Question (III): Illustrate by chemical equations the following conversions: (15 Marks, 3 for each)

1. Mevalonic acid into α -terpineol.
2. Citral into a mixture of α -ionone and β -ionone.
3. Ergosterol into vitamin D₂.
4. Benzyl chloride into β -phenyl ethyl amine.
5. 1-Phenyl-1,2-propandione into ephedrine.

Best Wishes: Prof. Mamdouh Abdel-Mogib, Prof. Dr. Ehab Abdel-Latif and Dr. Mona Elsayed



Answer the Following Questions:

1- اكتب الاجابة الصحيحة في ورقة الاجابة 2 - وضح حل المسائل في ورقة الاجابة 3 - الامتحان في صفتين

Question 1

(A) Choose the response answer: (11marks)

- 1- For tap water and clean glass, the angle of contact is
(a) 0° (b) 90° (c) 140° (d) 8°
 - 2- When the angle of contact between a solid and a liquid is 90° , then
(a) Cohesive force > Adhesive force (b) Cohesive force < Adhesive force
(c) Cohesive force = Adhesive force (d) Cohesive force \gg Adhesive force
 - 3- A sheet can be made water proof by coating it with a substance that changes the angle of contact
(a) To $\pi/2$ (b) To zero (c) From acute to obtuse (d) From obtuse to acute
 - 4- The height of a liquid in a fine capillary tube
(a) Increases with an increase in the density of a liquid
(b) Decreases with a decrease in the diameter of the tube
(c) Decreases with an increase in the surface tension
(d) Increases as the effective value of acceleration due to gravity is decreased
 - 5- Potential energy of a molecule on the surface of a liquid is as compare to another molecule inside of the liquid is
(a) More (b) Less (c) Both a and b (d) None of these
 - 6- Which of the following characteristics is not correct for physical adsorption?
(a) Adsorption on solid is reversible. (b) Both enthalpy and entropy of adsorption are negative.
(c) Adsorption is spontaneous. (d) Adsorption increases with increase in temperature.
 - 7- The BET adsorption isotherm can be used to model:
(a) Multilayer adsorption (b) Monolayer adsorption (c) Both (d) None of the above
 - 8- Which of the following does not have an effect on adsorption from solution onto a solid adsorbent?
(a) Solubility level of solute (b) Adsorption capacity
(c) Temperature of adsorption medium (d) Surface area of adsorbent
 - 9- At the boiling point of water, its surface tension
(a) Is infinite (b) Is zero (c) Is the same as that at room temperature (d) Is maximum
 - 10- Which one of the following is a property of chemical adsorption?
(a) Nonspecific nature (b) low heat of adsorption (c) irreversibility (d) none
 - 11- If common salt is dissolved in water, then the surface tension of salt water is
(a) Increased (b) Decreased (c) not changed (d) First decreases and then increases
- (B) The isosteric enthalpy of adsorption of ammonia, NH_3 on a nickel surface is -155 kJ mol^{-1} . Calculate the Relative change in the value of the equilibrium constant for adsorption when the temperature is increased from 25 to 50°C . (3marks)**

P.T.O.

- (C) As a result of a capillary action, the water rose inside the tube to a height of 11.4 cm. Determine the diameter of the tube given $\gamma = 72.75 \text{ dyne cm}^{-1}$ and $\rho = 0.998 \text{ g.cm}^{-3}$ for water. (3marks)
- (D) In the Du Nouy tensiometer, if the diameter of the ring is 1.0 cm and the force needed to pull the ring up (with the liquid attached to the outer and inner periphery of the ring) is 6.77 mN, what is the surface tension of the liquid. (3marks)
-

Question 2

(A) Write True or False and correct the false one(one mark for each one)

- 1- The surface tension of homologous series tends to decrease with increasing molecular weight
- 2- An increase in the pressure of the adsorbate gas decreases the extent of adsorption.
- 3- In general, easily liquefiable gases are adsorbed to a greater extent than the elemental gases.
- 4- Porous and finely powdered solid adsorb less as compared to the hard non-porous materials.
- 5- The coloring matter which gets adsorbed on activated charcoal is the adsorbent
- 6- Langmuir's theory of unimolecular adsorption is valid only at low pressures and high temperatures.
- 7- Ampholytic surfactants are soap and detergents adsorbed on the interface and thus reduce the surface tension between dirt and cloth.
- 8- Foaming agents are break foams and reduce frothing that may cause problems as in foaming of solubilized liquid preparations. in pharmacy they are useful in aerobic fermentations, steam boilers.
- 9- Anionic surfactants are the surface active part is anion.
- 10- Surface tension may be defined as the work done per unit area in increasing the surface area of a liquid under adiabatic condition.

(B) Derive the relation between surface tension and vapor pressure.(5marks)

(C) If the density and the surface tension of polyethylene oxid are equal 1.12 g/cm^3 and 41.6 mj/m^2 . Determine the parachor of O when the parachor of C=9.0 and H=15.5.(5marks)

Question 3

(A) Derive the Gibbs adsorption equation. (6marks)

(B) Give an account on the types of adsorption isotherms. (6marks)

(C) An unknown liquid forms a convex meniscus when poured into a test tube. Does the liquid wet the test tube? (2marks)

(D) The Langmuir adsorption isotherm of the adsorption of CO_2 onto charcoal gives a slope of 0.00904 cm^{-3} and intercept of 8.99 atm cm^{-3} at STP. Calculate the Langmuir constant and the surface area of one gram charcoal if the cross sectional area of CO_2 is 22.1 \AA^2 . (6marks)

Good luck

Prof. S. A. El-Hakam, Prof. A. I. Ahmed

d- Consider the following frequency table

(8 Marks)

X	0	2	3	4
frequency	15	10	20	5

- Find 1) The sample mean 2) The sample variance
3) The sample median 4) The sample mode

[Q3] Choose the correct answer:

(20 Marks)

1- The set of all possible outcomes of an experiment is said to be

- a) Population b) Sample c) Sample space

2- If A and B are independent with $P(A) = 0.4$, $P(B) = 0.5$ then $P(A \cap B) =$

- a) 0.2 b) 0.5 c) 0.9

3- The qualitative variables is the variable which has valued are

- a) word descriptions b) numbers c) non is correct

4- A die is tossed 2 times, then the total number of outcomes is...

- a) 64 b) 36 c) 12

5- The sum of relative frequencies of any frequency table is equal to

- a) 100 % b) sample size c) 1

6- If $P(A) = 0.2$, $P(B) = 0.5$ and $P(A \cap B) = 0.1$ then, $P(A/B) =$

- a) 0.5 b) 0.1 c) 0.2

7- If $P(A) = 0.2$, $P(B) = 0.5$, A and B are mutually exclusive, then $P(A \cap B) =$

- a) 0 b) 0.5 c) 1

8- The range of the data: 3 , 5 , 6 , 10 , 3 is equal to

- a) 3 b) 7 c) 5

9- The Correlation Coefficient r satisfy

- a) $r \geq 1$ b) $-1 \leq r \leq 1$ c) $r \leq -1$

10-Any subset of the population is said to be

- a) Sample space b) Event c) Sample

$$Z_{0.025} = 1.96 , \Phi(-2) = 0.0228 , \varphi(1) = 0.8413 , \Phi(2) = 0.9772 , \varphi(-1) = 0.1587$$

مع أطيب التمنيات بالنجاح د. فائق شبيحه - د. محمد عبدالرحمن



Answer The Following Questions

Section (A)

1. A) Complete [10 Marks]

- i) A dispersion of solid in solid is And of solid in an alcohol is
- ii) The pH at which the particles have neither a positive nor a negative charge is
- iii) The colour of a colloidal solution is due to

B) Give reasons : [10 Marks]

- i) Tyndal effect of a colloidal solution .
- ii) Addition of an emulsifying agent to an emulsion.
- iii) Addition of protecting colloids to a colloidal solution.

2. A) Chose the correct answer : [10 Marks]

- i) The dispersion of protein in water is :
 - a) an emulsion
 - b) Hydrophilic sol.
 - c) Solid aerosol .
- ii) The dispersion of Ag Cl in water is :
 - a) Solid sol
 - b) Hydrophobic sol.
 - c) Solid foam.
- iii) Gel is :
 - a) A dispersion of solid particles in air
 - b) A semi solid precipitate retaining an appreciable quantity of the liquid.
 - c) A very fine droplets of liquids in air.

B) Write on the following : [10 Marks]

- a) The critical Z-potential
- b) Sedementation equilibrium.

SECTION (B) PTOTOCHEMISTRY

- A) Explain the excited – state processes in molecules. (10 Marks)
- B) Discuss the concept of quantum efficiency (10 Marks)
- C) Write on photoluminescence and chemiluminscence . (10 Marks)
- D) Irradiation of propionaldehyde with light of wavelength = 3020 A

The quantum efficiency was 0. 54 calculate the rate of the reaction if
the intensity of the incident light is 15 kj/sec (10 Marks)

$$N = 6.02 \times 10^{23}$$

$$h = 6.62 \times 10^{-34} \text{ j}$$

Best Wishes :

Prof. Dr. Hamrd Abu Elnader
Prof. Dr. Hanem Abd Elrasol

Mansoura University
Faculty of Science
Chemistry Department
Subject: Chromatography &
Electro analysis
Course(s) : Chem. (312)



Second Term
Third Year Chem. Students
Date : May, 2015
Time Allowed: 2 hours
Full Mark : 100 Marks

Answer the Following Questions

Section (A) [30 Marks]

- a)** The width of two consecutive peaks is 15 and 30 sec. at a retention time of 10 and 11 min. in a 0.25 meter column. Calculate n , H , R . Interrelate your results to the high efficiency of chromatographic separations.
- b)** Give clear diagrams for gas and HPLC and compare between them.
- c)** Show how paper and thin layer chromatography could be used in qualitative analysis. Compare between planar and column Chromatography .
- d)** Give a short account on : i) Tswett Experiment,; ii) Ion exchangers and its application.
- e)** Effect of pH on Chromatographic separations.
- f)** Interpretation of experimental results.
- g)** Programme controlled temperature .
- h)** Silica gel is a distinct phase .

II.a) Define with examples the following:

(6marks)

- I) Platinum gauze
- iv) Current maxima

- ii) Polarogram
- v) Selectivity of membrane

- iii) Fast linear polarography
- iv) The errors in pH measurements

II.b) Compare between:

(10marks)

- i) Differential pulse and normal pulse polarography
- ii) Coulometric titration and conventional titration both in instrumental and application
- iii) Diffusion current (i_d) in classical polarography and (i_p) in cyclic voltametry
- iv) Advantages and limitations of ion selective electrodes.

II.c) Calculate the solubility product of AgI if the standard potential of Ag/AgI electrode is -0.151V and the iodide ion activity is exactly 1.00 ($E^0_{Ag^+/Ag} = 0.799V$)

(2marks)

III.a) Give an account on

- i) The steps used in stripping analysis explaining in detail examples of cathodic and anodic stripping analysis
- ii) Applications of potentiometric measurements

(6marks)

III.b) Discuss the effect of:

(6marks)

- i) pH on the determination of fluoride using LaF_3 single crystal electrode
- ii) Complex formation on the polarographic waves indicating its application
- iii) Dissolved oxygen on the polarographic measurements

III.c) A 650-mg of brass sample is dissolved and diluted to 50ml. 10ml of this sample is analysed polarographically for Zn(II) by adjusting the pH and diluting to 100ml. The diffusion current was found to be $5.13 \mu A$ (corrected for residual current). When 10 ml of $1.6 \times 10^{-2} M ZnSO_4$ solution was added to another 10ml of sample, buffered and diluted to 100ml, the wave height increased to $18.2 \mu A$. Find the %Zn in brass sample (Zn=65.4)

(5marks)

With best wishes Prof, Dr, Magdi Khalifa