

Photochemistry and Reactive Intermediates (313C)

Final Examination For Third Level Students

Answer on the following Two sections: (50 Marks)

Section A : Photochemistry : (25 Marks)

Answer the Following Questions:

I]- Answer **Only Four** of the Following : (2 X 4 = 8 Marks)

- 1- What is the theory of Photochemistry ?.
- 2- Discuss the application Franck–Condon Principle in photocatalytic Cleavage.
- 3- Explain the role of Chemical Actinometers in Photochemistry?, give an example.
- 4- Discuss the possible Norrish **type II** cleavage of 2-pentanone.
- 5- Describe the chemical changes of Rhodopsin during the process of vision.

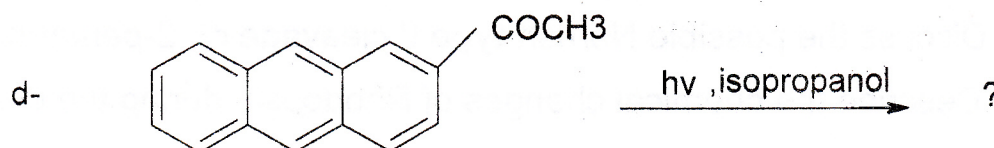
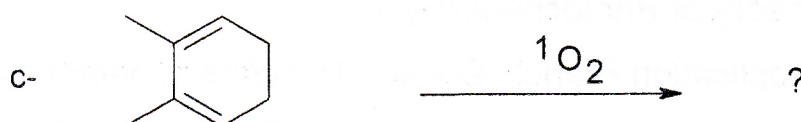
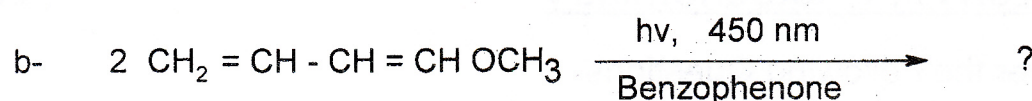
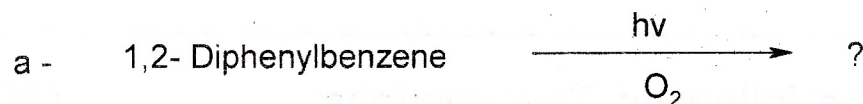
II] – Mark right ($\sqrt{}$) or wrong (X) on **Only Four** of the following statements, and **explain** your answer : (2 X 4 = 8 Marks)

- 1- Light filters absorbing ≥ 220 nm radiations can be used for UV photolysis of organic compounds. ()
- 2- Microwaves heating is due to molecular vibrations. ()
- 3- Gerade \rightarrow Gerade transition is a spin allowed transition. ()
- 4- **Z/E**-Thermal and photoisomerization are similar. ()
- 5 - Photosensitization is very effective when the triplet energy of the photosensitizer is much higher than that of the acceptor. ()

ملحوظة هامة : الأسئلة ٣ صفحات

123

III] - Complete **Only Three** of the following reactions and **discuss** the reaction mechanism: (3 X 3 = 9 Marks)



Section (B) Reactive Intermediates :

(25 Marks)

Answer the Following Questions:

1) Write on the following (use equations):

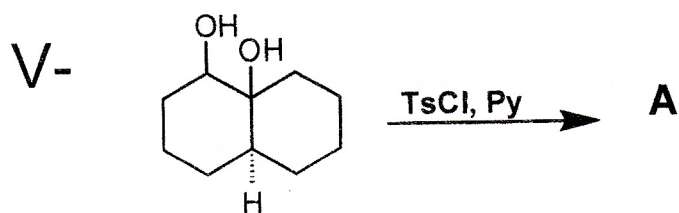
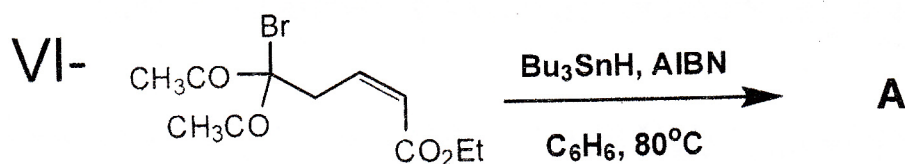
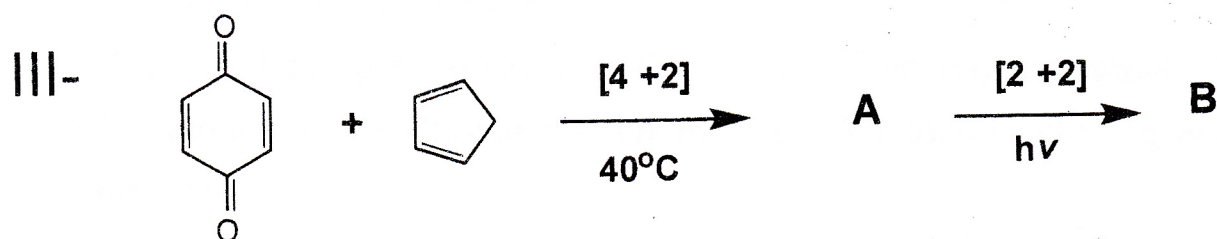
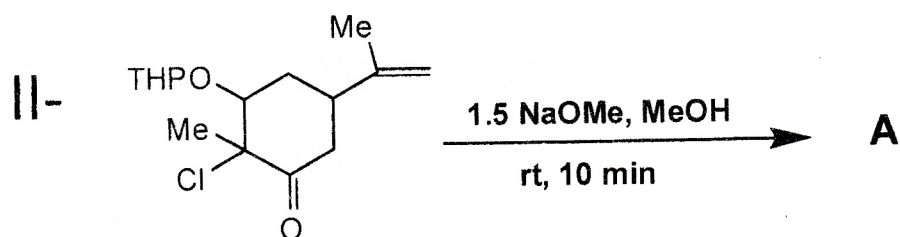
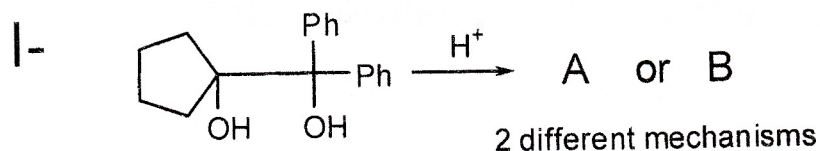
(3x3 = 9 Marks)

- Difference between singlet and triplet carbenes.
- Generation of nitrene compound from phthalic acid.
- Benzyl carbocation is more stable than methyl carbocation, (explain this statement).

(3)

2) Complete Only Four of the following reactions. Suggest the suitable mechanism, and give the name of this mechanism:

(4x4=16 Marks)



Good Luck Prof. A.A.Abdel-Wahab & Dr. M. A. Abdel-Rahman

Organic Chemistry Examination for 3rd Chemistry Students
311C (Spectroscopy and Stereo Chemistry)

Section A: Spectroscopy

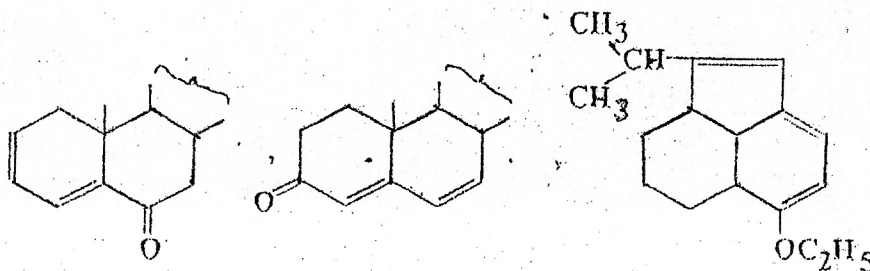
(34 Marks)

Answer the following questions:

1) Write what is meant by:

Chromophore , Auxochrome , Bathochromic shift , Hypochromic effect
(3.5 Marks)

2) Using the provided tables show if the following compounds are coloured or not:
(3.5 Marks)



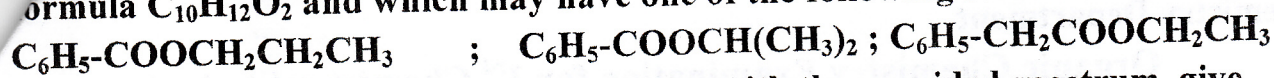
3) Substitution of alkyl group on benzene ring produces a bathochromic shift of B-band, and the addition of a second alkyl group is most effective in red shift if it is in para position (not ortho), explain this statement.
(3.5 Marks)

4) Interpret the following table and show what can you deduce from these readings:
(3.5 Marks)

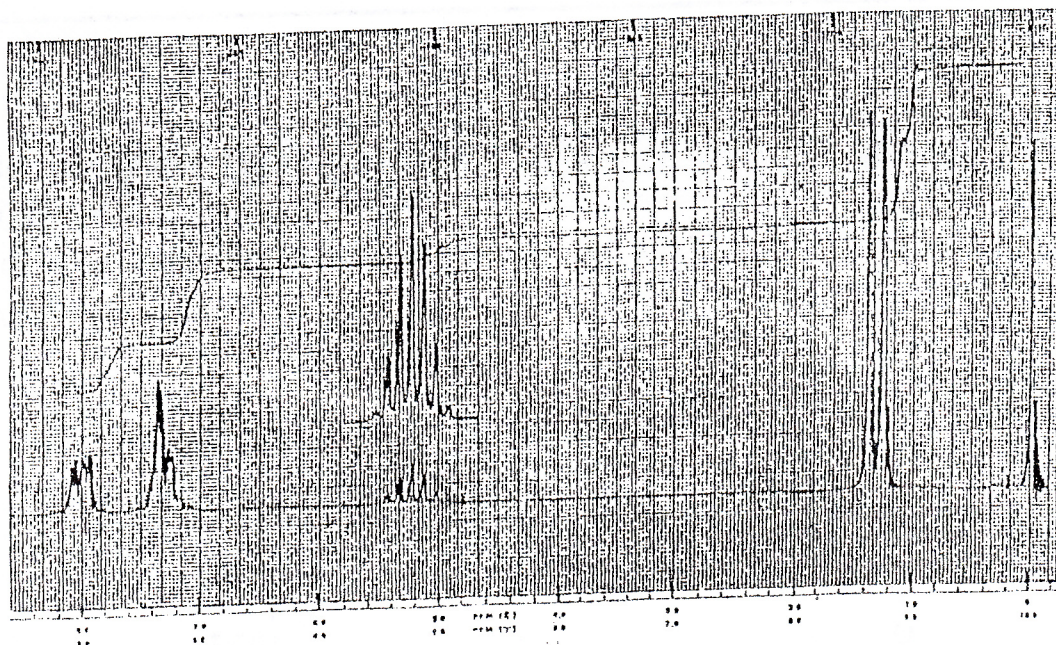
	λ_{\max}	ϵ_{\max}
Benzene	204	7.000
Phenol	210.5	6.200
Phenolate anion	235	9.400
Aniline	230	8.600
Anilinium cation	203	7.500
N,N-Dimethylaniline	251	15.500
2-Methly-N,N-dimethylaniline	248	6.300

12

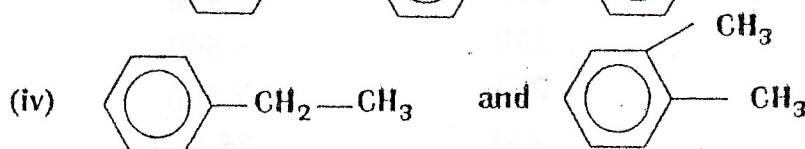
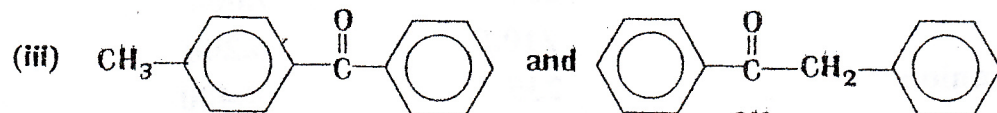
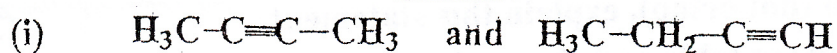
are provided with the NMR spectrum of a compound having the molecular formula $C_{10}H_{12}O_2$ and which may have one of the following structures:



Assign the suitable structures which agrees with the provided spectrum, give reasons for your assignment and show the NMR peaks which confirm your answer. (3.5 Marks)

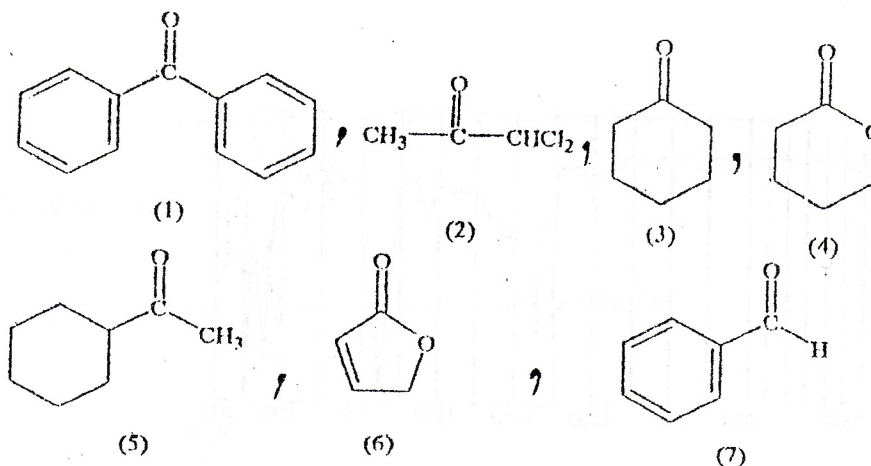


6) Explain how can you differentiate between the following pairs of isomers by the Use of I.R. spectra. (3.5 Marks)



(3)

- 7) Assign the most appropriate carbonyl frequencies in cm^{-1} for the following compounds, try to explain the reason. (3.5 Marks)



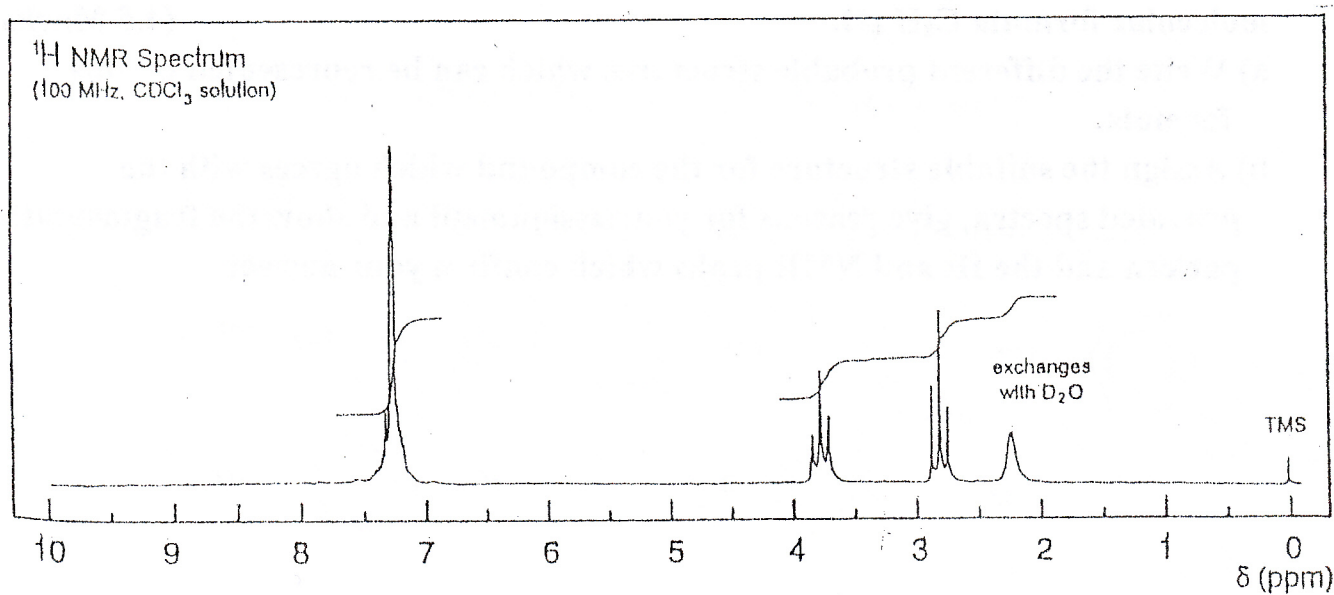
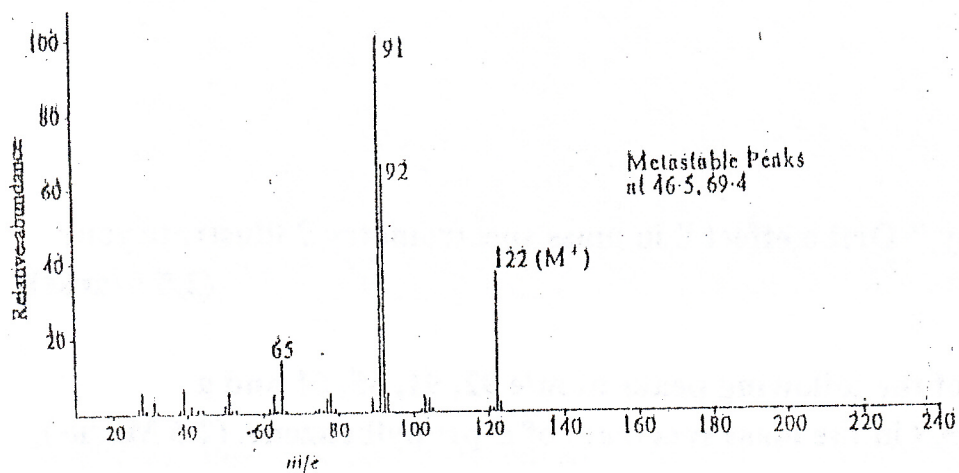
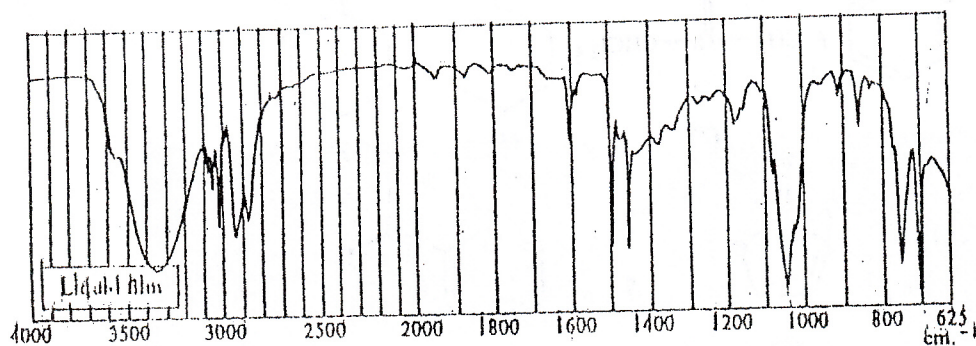
- 8) Explain what is meant by "Ortho effect" in mass spectrometry? illustrate your answer by an example. (2.5 Marks)

- 9) Explain the appearance of the following peaks at m/e 92, 91, 65, 51 and a metastable ion peak at 33.8 in the mass spectrum of *n*-propylbenzene. (2.5 Marks)

- 10) You are provided with the IR, MS and NMR spectra of a compound having the molecular formula $\text{C}_8\text{H}_{10}\text{O}$. (4.5 Marks)

- Write the different probable structures which can be represented by this formula.
- Assign the suitable structure for the compound which agrees with the provided spectra, give reasons for your assignment and show the fragmentation pattern and the IR and NMR peaks which confirm your answer.

(4)



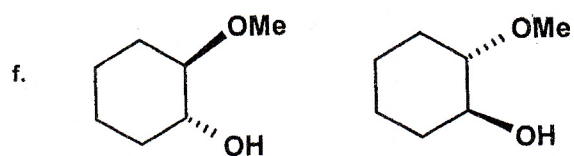
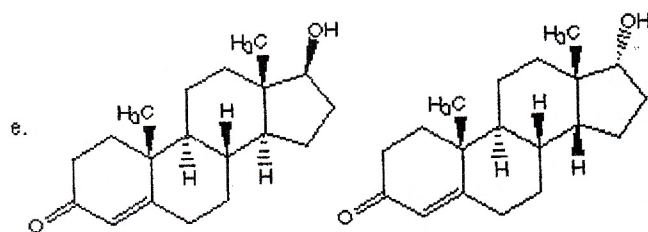
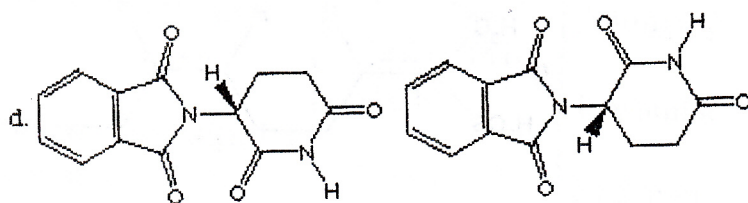
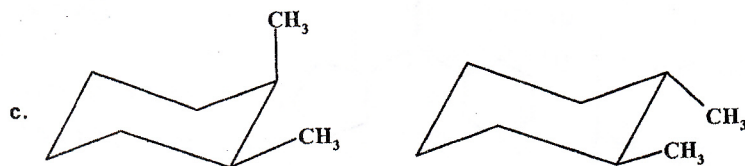
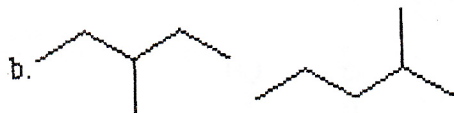
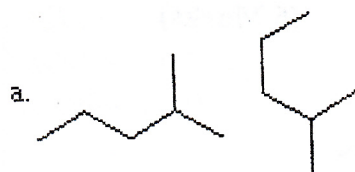
(Stereochemistry)

Answer the following questions:

Section A: Stereochemistry:

Question 1: State how the following structures in each pair are related:

(6 Marks)



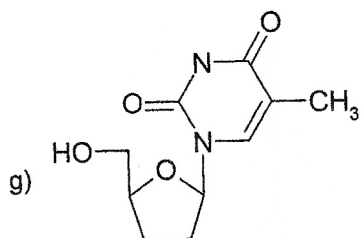
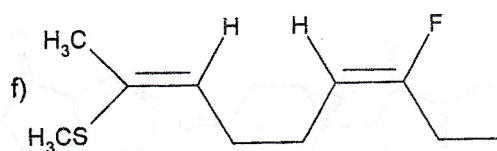
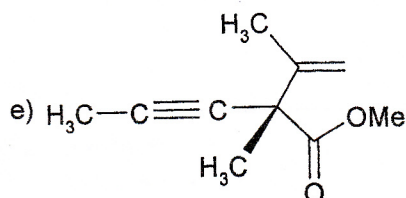
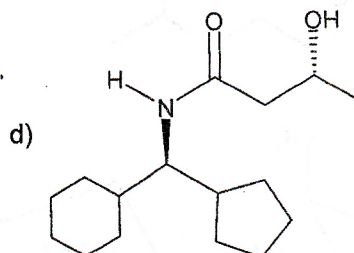
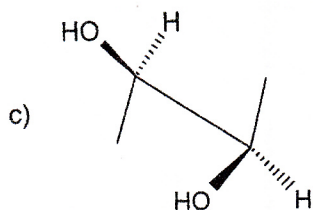
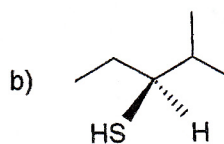
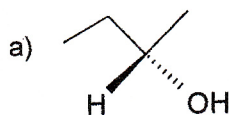
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Question 2:

(4 Marks)

- a) Given that (R)-2-bromobutane has a specific rotation of -23.1° , what is the specific rotation of (S)-2-bromobutane?
- b) Using the data from the previous point, what is the optical purity and % composition of a mixture of (R)- and (S)-2-bromobutane whose specific rotation was found to be $+18.4^\circ$?
- c) What about a mixture whose specific rotation was found to be -9.2° ?

Question 3: Designate the RS configurations for **ONLY SIX** of each chiral center in the structures shown below: (6 Marks)

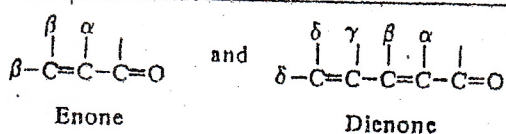


(7)

Characteristic Infrared absorption of functional groups

<u>C - H Stretching</u>		<u>C \equiv C Stretching</u>	
Alkane	2962 - 2853		2100 - 2260
Alkene monosubst. (vinyl)	3040 - 3070	Aromatic skeleton	1600
Alkene disubstit. (cis, trans)	3040 - 3010		1580
Alkene disubstit. (gem)	3095 - 3070		1500
Alkyne	~ 3333		1450
Aromatic	3030 - 3100	<u>Carbonyl Stretching</u>	
Aldehyde	2720, 2820	Saturated ketone acyclic	1720
		6 - memb. saturated ketone	
<u>C - H Bending</u>		Amides } I	~ 1696
Alkane	~ 1340	1 ry } II	~ 1656
Alkane - CH ₂ -	1485 - 1445	<u>Alcohols</u>	
Alkane - CH ₃	1470 - 1430	O - H str. Free	6350 - 3590
	1380 - 1370	O - H str. associated	3400 - 3200
Alkane gem. Dimethyl	1385 - 1380	<u>Carboxylic Acids</u>	
	1370 - 1365	O - H str associated	2700 - 2500
Alkane tert-butyl	1395 - 1385	<u>Coupled - OH bending and C - O str.</u>	
	~ 1365	1 ry alcohol	~ 1050
Alkene, monosubst. (vinyl)	995 - 985		1350 - 1260
	915 - 905	2 nd alcohol	~ 1100
	1420 - 1410		1350 - 1260
Alkene, disubst. cis	~ 690	3 ry alcohol	~ 1150
Alkene, disubst. trans	970 - 960		1410 - 1300
	1310 - 1295	Phenols	~ 1200
Alkene, disubst. gem	895 - 885		1410 - 1316
	1420 - 1410	<u>Amines N - H str</u>	
	~ 636	1 ry amine	~ 3506
<u>Aromatic Substitution</u>			~ 3400
Monosubst.	~ 750	2 nd amine	~ 3500 - 3310
	~ 700	<u>Amine salt</u>	
Disubstit. ortho	~ 750		3136 - 3036
Disubstit. meta	~ 780	<u>Amines N - H bending</u>	
Disubstit. Para	~ 820	1 ry amine	1656 - 1590
<u>C = C Stretching</u>		2 nd amine	1650 - 1550
Non conjugated	1680 - 1620	amine salt	1600 - 1575
Monosubstituted (vinyl)	~ 1645		~ 1500
Disubstit., cis	~ 1658	C \equiv N stretching	2260 - 2240
Disubstit., trans	~ 1675		
Disubstit., gem	~ 1653		
Trisubstit.,	~ 1669		
Tetrasubst. (weak)	~ 1669		

Rules of Enone and Dienone Absorption (α,β -Unsaturated Carbonyls of Ketones)



Base values:

Acyclic α,β -unsaturated ketones	215
Six-membered cyclic α,β -unsaturated ketones	215
Five-membered cyclic α,β -unsaturated ketones	202
α,β -Unsaturated aldehydes	210
α,β -Unsaturated carboxylic acids and esters	195

Increments for

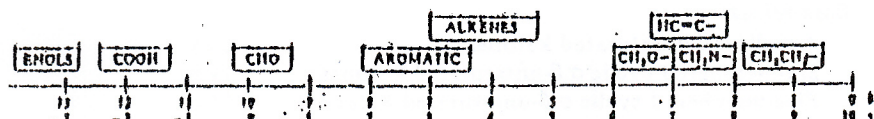
Double bond extending conjugation	+30
Alkyl group, ring residue α	+10
β	+12
γ and higher	+18
Polar groupings: $-\text{OH}$ α	+35
β	+30
δ	+50
$-\text{OAc}$ α,β,δ	+6
$-\text{OMe}$ α	+35
β	+30
γ	+17
δ	+31
$-\text{SAlk}$ β	+85
$-\text{Cl}$ α	+15
β	+12
$-\text{Br}$ α	+25
β	+30
$-\text{NR}_2$ β	+95
Exocyclic double bond	+5
Homodiene component ^a	+39
Solvent correction (see table below)	variable
$\lambda_{\text{calc}} = \text{Total}^b$	

Solvent Corrections*

Solvent	Correction (nm)
Ethanol	0
Methanol	0
Dioxane	+5
Chloroform	+1
Ether	+7
Water	-8
Hexane	+11
Cyclohexane	+11

Rules of Diene Absorption

Base value for heteroannular diene	214
Base value for homoannular diene	253
Increments for	
Double bond extending conjugation	+30
Alkyl substituent or ring residue	+5
Exocyclic double bond	+5
Polar groupings: OAc	+0
OAlk	+6
SAlk	+30
Cl, Br	+5
N(Alk)_2	+50
Solvent correction*	+0
$\lambda_{\text{calc}} = \text{Total}$	



Approximate chemical shift positions for protons in organic molecules.

Chemical Shifts of Representative Types of Protons

Type of proton	Chemical shift (δ), ppm*	Type of proton	Chemical shift (δ), ppm*
$\text{H}-\text{C}-\text{H}$	0.9-1.0	$\text{H}-\text{C}-\text{NH}$	2.2-2.8
$\text{H}-\text{C}-\text{C}=\text{O}$	1.6-2.6	$\text{H}-\text{C}-\text{Cl}$	3.1-4.1
$\text{H}-\text{C}-\text{C}(=\text{O})-\text{H}$	2.1-2.5	$\text{H}-\text{C}-\text{Br}$	2.7-4.1
$\text{H}-\text{C}\equiv\text{C}-$	2.5	$\text{H}-\text{C}-\text{O}$	3.3-5.7
$\text{H}-\text{C}-\text{Ar}$	2.3-2.8	$\text{H}-\text{NH}$	1-3†
$\text{H}-\text{C}=\text{C}-$	4.5-6.5	$\text{H}-\text{OH}$	0.5-5†
$\text{H}-\text{Ar}$	6.5-8.5	$\text{H}-\text{OAr}$	0-8†
$\text{H}-\text{C}(=\text{O})-\text{H}$	9-10	$\text{H}-\text{OC}-$	10-13†

* Approximate values relative to tetramethylsilane; other groups within the molecule can cause a proton signal to appear outside of the range cited.

† The chemical shifts of protons bonded to nitrogen and oxygen are temperature- and concentration-dependent.

Assiut University

Faculty of science

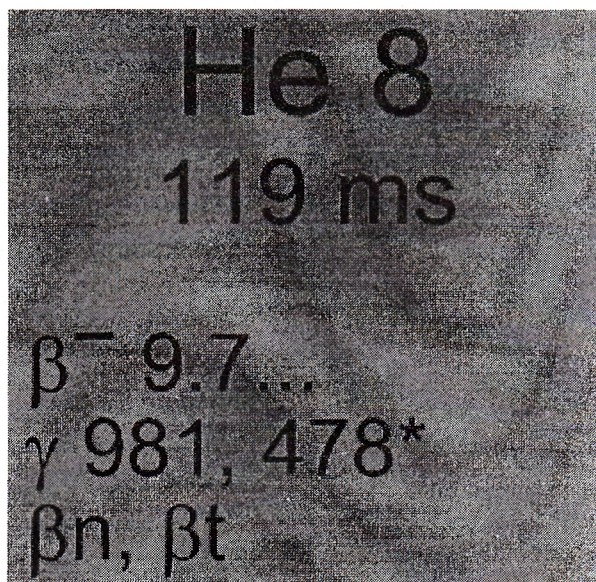
Chemistry department

Final Exam. For course no.333 (nuclear and radiochemistry) , academic year 2014/2015

Time allowed (3 hours)

Answer the following question (18 marks)

Given the following nuclear data for He-8.



1) Sketch the decay scheme of He-8

2) Write the complete decay equations (β⁻ , βn , βt).

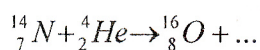
3) Insert spin and parity of both parent and daughter nuclei

4) The reaction $^{33}_{16}\text{S}(n,p)^{33}_{15}\text{P}$ is exoergic by 0.533 MeV. The mass of $^{33}_{16}\text{S}$ is 32.971458 u

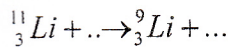
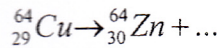
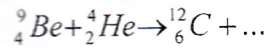
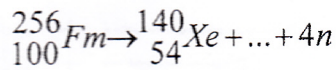
What is the mass of $^{33}_{15}\text{P}$.

5) What is the time intervals during which Ga-67 ($T_{1/2} = 3.2$ d) decay to 40% of the original activity

6) Complete the following nuclear equations



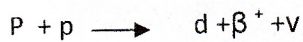
(2)



7) Consider the odd-odd nuclei ${}^{38}\text{Cl}$, ${}^{26}\text{Al}$ and ${}^{56}\text{Co}$. predict the ground and excited states spins **only** for the nuclei.

8) write short notes on the interaction of neutrons with matter

9) for the fusion reaction



Balance the nuclear equation of the reaction

Calculate the Q-value of the reaction

Is this reaction exothermic or endothermic

Answer two

(32 marks)

only of the following questions

1) Given the SEMF below

$$EB = 16 A - 20 A^{2/3} - 0.75 Z^2/A^{1/3} - 21 (N-Z)^2/A + 11.2/A^{1/2}$$

A) Calculate the binding energy per nucleon for $\text{Fe} = 52$

B) Consider the nuclei ${}^{15}\text{C}$, ${}^{15}\text{N}$, and ${}^{15}\text{O}$. Which of these nuclei is stable? What Types of radioactive decay would the other two undergo? Calculate the

binding energy difference between ^{15}N and ^{15}O . Assuming this difference comes from the Coulomb term in the semi-empirical binding energy equation, calculate the nuclear radius.

C) Define the following items

Mass stopping power of a charged particle in matter, equivalent dose, exposure dose
Auger electron

D) What is the specific activity of Rd-226

E) Calculate the mass absorption coefficient of 1-MeV γ -ray for NaI ($\mu_a \text{Na} = 2.32 \text{ b atom}^{-1}$, $\mu_a \text{I} = 12.03 \text{ b atom}^{-1}$),

2) Given 2.00 kg of $^{238}_{92}\text{U}$ ($T_{1/2} = 4.5 \times 10^9$) the stable decay product in this series is $^{206}_{82}\text{Pb}$

A) To which naturally occurring series U-92 belong to

B) What weight of U-92 is left after 3×10^9 y.

C) What weight of Pb-82 is produced in this time

D) For the following nuclear equations



Complete the decay equation of Rh-106

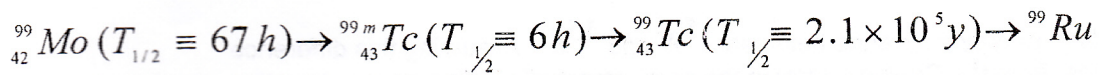
From the two equations calculate the mass of Rh-106 (the mass of Pd-106 = 105.9035 u)

E) Define the following items

Photo electric effect, Compton scattering, Gray, absorbed dose

F) How long 60-mg of Co-59 has to be placed in a flux of $5 \times 10^{13} \text{ n/cm}^2/\text{sec}$ to make 10 mCi of Co-60 . What type of nuclear reaction we used in this experiment

3) For the following nuclear decay



A) What are the modes of decay of Mo-99, ${}^{99\text{m}}\text{Tc}$ and ${}^{99}\text{Tc}$

B) Calculate the total number of atoms and the total mass in 15 mCi (555 MBq) of Mo-99 activity

C) Calculate the activity of ${}^{99\text{m}}\text{Tc}$ after 6 hours and 60 hours decay of Mo-99 if the initial activity is 15mCi

D) Calculate the time for the maximum activity of ${}^{99\text{m}}\text{Tc}$

E) A radionuclide has initial activity of 2.0×10^6 dis./min. and after 4.0 days its activity is 9×10^5 dis./min.. Calculate the activity in the sample after 40 days

F) U-235 ($T_{1/2} = 7.04 \times 10^8 \text{ y}$) emits α particle to form Th-231 ($T_{1/2} = 25.5 \text{ h}$).

Determine the following

The atomic ratio of Th-231 to the initial U-235

The ratio of the total activity (rate of particle emission to the initial value) after 50 h

G) Define the following items

Bremstrahlung emission , pair production , G-value , specific ionization , photonuclear reaction

Constants ; $m_{\text{H-2}} = 2.0141018 \text{ u}$, $m_{\text{p}} = 1.00727 \text{ u}$, $m_{\text{n}} = 1.00866 \text{ u}$, $N_{\text{A}} = 6.023 \times 10^{23} \text{ mole}^{-1}$

Periodic Table of Elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18		
1 H Hydrogen 1.00794	2 He Helium 4.002602											3 Li Lithium 6.941	4 Be Beryllium 9.012182	5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.0067	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797
11 Na Sodium 22.98976928	12 Mg Magnesium 24.3050											13 Al Aluminum 26.9815386	14 Si Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.065	17 Cl Chlorine 35.453	18 Ar Argon 39.948		
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955912	22 Ti Titanium 47.88	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938045	26 Fe Iron 55.845	27 Co Cobalt 58.933195	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.63	33 As Arsenic 74.9216	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.798		
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.96	43 Tc Technetium (97.9072)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.293		
55 Cs Cesium 132.9054519	56 Ba Barium 137.327	57-71		72 Hf Hafnium 178.49	73 Ta Tantalum 180.94788	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.084	79 Au Gold 196.966569	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98040	84 Po Polonium (209.9824)	85 At Astatine (209.9871)	86 Rn Radon (222.0176)	
87 Fr Francium (223)	88 Ra Radium (226)	89-103		104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (264)	108 Hs Hassium (277)	109 Mt Meitnerium (268)	110 Ds Darmstadtium (271)	111 Rg Roentgenium (272)	112 Cn Copernicium (285)	113 Uut Ununtrium (284)	114 Fl Flerovium (289)	115 Uup Ununpentium (288)	116 Lv Livermorium (292)	117 Uus Ununseptium (293)	118 Uuo Ununoctium (294)	
<div><div>Alkali metals</div><div>Alkaline earth metals</div><div>Actinoids</div><div>Lanthanoids</div><div>Metals</div><div>Transition metals</div><div>Poor metals</div><div>Other nonmetals</div><div>Noble gases</div><div>Nonmetals</div></div>																			

Alkali metals
 Alkaline earth metals
 Lanthanoids
 Actinoids
 Metals
 Transition metals
 Poor metals
 Nonmetals
 Other
 Noble gases

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

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57 La Lanthanum 138.90547	58 Ce Cerium 140.116	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.242	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92535	66 Dy Dysprosium 162.500	67 Ho Holmium 164.93032	68 Er Erbium 167.259	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.054	71 Lu Lutetium 174.9668
89 Ac Actinium (227)	90 Th Thorium 232.03806	91 Pa Protactinium 231.03588	92 U Uranium 238.02891	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

(6)

6h -							
5s +				-	$6h_{11/2} = 1h_{11/2}$	12	82
5d +				+	$5d_{3/2} = 2d_{3/2}$	4	70
				+	$5s_{1/2} = 3s_{1/2}$	2	66
				+	$5g_{7/2} = 1g_{7/2}$	8	64
5g +				+	$5d_{5/2} = 2d_{5/2}$	6	56
				+	$5g_{9/2} = 1g_{9/2}$	10	50
4p -				-	$4p_{1/2} = 2p_{1/2}$	2	40
4f -				-	$4f_{5/2} = 1f_{5/2}$	6	38
				-	$4p_{3/2} = 2p_{3/2}$	4	32
				-	$4f_{7/2} = 1f_{7/2}$	8	28
3s +				+	$3d_{3/2} = 1d_{3/2}$	4	20
3d +				+	$3s_{1/2} = 2s_{1/2}$	2	16
				+	$3d_{5/2} = 1d_{5/2}$	6	14
2p -				-	$2p_{1/2} = 1p_{1/2}$	2	8
				-	$2p_{3/2} = 1p_{3/2}$	4	6
1s +				+	$1s_{1/2} = 1s_{1/2}$	2	2

(1)

Final Exam of (321-C)

Question No. One:

(17 Marks)

From your study of coordination compounds expect the write facts and put (✓) in front and expect those wrong ones and put (x) in front:

- a) The double salts lose their identity in solution but the coordination compounds retain their identity in solution. ()
- b) Primary valency is the ionizable valency and secondary valency is the non ionizable valency ()
- c) In an octahedral complex $\text{CoCl}_3 \cdot 4\text{NH}_3$ the three chlorines act as primary valency. ()
- d) Depression in freezing point measurements depend on the number of charges present and on the concentration of solute. ()
- e) The electrical conductivity of a solution depends on the number of particles present. ()
- f) The tendency to attain an inert gas configuration (e.a.n.rule) is a significant factor but not a necessary condition for complex formation. ()
- g) In an octahedral complex the e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) point in between the axes x,y and z and the t_{2g} orbitals (d_{x-y} , d_{x-z} and d_{y-z}) are directed a long the axes. ()
- h) The difference in energy between the two d levels e_g and t_{2g} is given by the symbol Δ or $10Dq$. ()
- i) As the charge on the central metal ion of complex increase the magnitude of Δ decrease ()
- j) The crystal field stabilization energy is zero in case of electronic configuration 1,2 and 3 in an octahedral complex ()
- k) In an octahedral complex distortion from uneven filling of the e_g orbitals is too small and not important ()
- l) Chelated complexes are less stable than similar complexes with unidentate ligands ()
- m) Tetrahedral complexes are favoured where the ligands small and strong ()
- n) In a complex the negative ion is named first followed by positive ion ()
- o) If the complex contain two or more metal atoms, it termed mononuclear ()
- p) The exchange of groups between the complex ion and ions out side it gives rise to coordination isomerism ()
- q) Optical isomerism is common in octahedral complexes involving bidentate groups ()

Question No. Two:

(2)

(16Marks)

For the 1st transition series elements discuss only Three of the following:

- a) Formation of complexes and their stability (use hard – soft theory)
- b) Colour and spectral properties.
- c) Chemical reactivity of mercury.
- e) Titanium – tin relationship.

Question No. Three:

a) Give reasons for **Five** only of the following:

(5 Marks)

- i) Compounds of Zn(ii) are colourless while many compounds of Hg(ii) are highly coloured.
- ii) $[\text{MnF}_6]^{4-}$ is pale while $[\text{Mn}(\text{CN})_6]^{4-}$ is highly coloured.
- iii) KMnO_4 solution should be maintained in brown bottles.
- iv) Freshly precipitated $\text{Mn}(\text{OH})_2$ turns brown on standing.
- v) In contrast to $[\text{Fe}(\text{CN})_6]^{4-}$, the hexacyanoferrate (iii) is labile and quite poisonous.
- vi) Formation of blue compounds when acidified dichromate solutions are treated with H_2O_2 in presence of diethyl ether.

b) Complete the following sentences with the correct choice (between brackets) (4 Marks)

i) Crystallizes in an essentially molecular lattice.

(HgF_2 – HgCl_2 – ZnCl_2 – CuCl_2)

ii) Co^{2+} ions are easily oxidized in

(alkaline medium – acidic medium – neutral solutions)

iii) The ions are unstable and can be stabilized by precipitation as acetate.

(V^{2+} - V^{3+} - Cr^{2+} - Cr^{3+})

iv) Disproportionation of is favoured in presence of S^{2-} , OH^- or CN^- ions.

(Cu_2O – K_2MnO_4 – $\text{Hg}(\text{NO}_3)_2$ – $\text{Hg}_2(\text{NO}_3)_2$)

c) What is the effect of dilute HCl on only **Four** of the following:

(4 Marks)

i) K_2MnO_4

ii) Na_3VO_4

iii) $\text{Co}(\text{OH})_3$

iv) $[\text{Au}(\text{CN})_2]^-$

v) $\text{K}_2\text{Cr}_2\text{O}_7$ in presence of conc. H_2SO_4

d) Describe a method for preparing only **Four** of the following:

(4 Marks)

i) Sodium nitroprusside.

ii) Isolation of pure Cu from copper pyrite.

iii) K_2MnO_4 and its conversion to KMnO_4 .

iv) Cr_2O_3 from chrom iron stone.

v) Titanium from rutile.

Environmental Anal. Chem. Examination (343-C)

Answer the following questions: (50Marks)

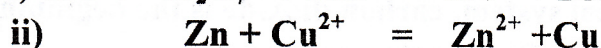
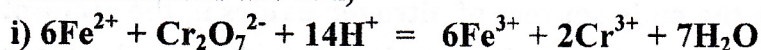
I- a) Write briefly on: (4.5 Marks)

Reference electrodes ; Normal hydrogen electrode ; Alkaline error

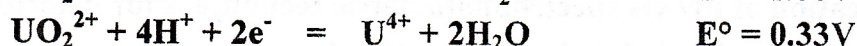
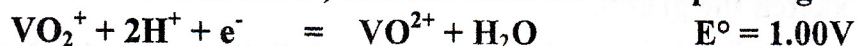
Location of the end point in a pH-metric titration.

b) Answer Four Only: (12 Marks)

1) Write the equivalent galvanic cells for the following reactions (assume all concentrations are 1M)



2) From the standard potentials of the following half-reactions, determine the reaction that will occur, and calculate the corresponding cell voltage.



3) A solution is 10^{-3} M in $\text{Cr}_2\text{O}_7^{2-}$ and 10^{-2} M in Cr^{3+} . If the pH is 2.0, what is the potential of the half-reaction. ($E^\circ\text{Cr}_2\text{O}_7^{2-}, \text{Cr}^{3+} = 1.33\text{V}$)

4) Given that the standard potential of the calomel electrode is 0.268 V and that of $\text{Hg} / \text{Hg}_2^{2+}$ electrode is 0.789 V, calculate the K_{sp} for calomel(Hg_2Cl_2).

5) A glass electrode – SCE pair is calibrated at 25°C with a pH 4.01 standard buffer, the measured voltage being 0.814V. Calculate the pH of an unknown solution for which the measured voltage is 0.467V.

II- a) Write briefly on: (4.5 Marks)

i) Aeration ii) Coagulation iii) UV radiation as a disinfecting agent.

b) Answer Four Only: (12 Marks)

1) Describe Winkler's method, for quantification of dissolved oxygen in water.

2) A 50.00 ml sample of oxygenated water at 0°C is treated with Winkler method. The liberated I_2 is titrated against $0.01136\text{ mol L}^{-1} \text{Na}_2\text{S}_2\text{O}_3$, of which 8.11 ml are required to reduce all the I_2 . Calculate the solubility of O_2 in water at 0°C .

3) A water supply contains 40 ppm of calcium in the form of $\text{Ca}(\text{HCO}_3)_2$. What mass of lime should be used to soften $2.2 \times 10^4\text{L}$ of this water?

(At. wts. $\text{Ca} = 40$, $\text{C} = 12$, $\text{O} = 16$, $\text{H} = 1$).

4) Explain why:

i) The pH is not a good guide to alkalinity.

ii) Ground water tends to be less contaminated than surface water.

iii) Soft water has a low alkalinity.

iv) All disinfecting agents, must be followed with a low dose of Cl_2 .

أنظر خلفه باقى الاسئلة،،،

5) What are the pH and the total carbonate concentration of a sample of water in equilibrium with air?

$$K_H \text{ (for CO}_2 \text{ in water)} = 3.4 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1}.$$

$$P(\text{CO}_2)_g = 3.0 \times 10^{-4} \text{ atm.} \quad ; \quad K_{a1} (\text{H}_2\text{CO}_3) = 4.2 \times 10^{-7}.$$

III- a) Define or characterize: (3 Marks)

i) Spot test and sampling. ii) Absorptivity iii) Molar absorptivity.

b) Describe the main objectives of pollution monitoring in environmental analysis. (2 Marks)

c) Answer Four Only: (12 Marks)

- 1) Why is nitrogen gas inert? What is meant by the terms nitrification and denitrification? What are the main sources of nitrogen oxides in the atmosphere?
- 2) Carbon is the key element in biological system, carbon dioxide is the beginning and the end product of biological processes. Discuss this statement.
- 3) Describe the photometric titration of a mixture of Bi^{3+} and Cu^{2+} with standard EDTA solution, sketch the graph.
- 4) Discuss the application of uv/ vis spectrophotometric techniques for determination of the stoichiometry of metal chelate by Job's method.
- 5) The molar absorptivity for the complex formed between Bi^{3+} and thiourea is $9.32 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 470nm. Calculate the range of permissible concentrations for the complex if the absorbance is to be no less than 0.15 nor greater than 0.80 when the measurements are made in 1.0 cm cell.

Good Luck,,,

Examiners: Prof. Dr. Hassan Sedira.

Prof. Dr. Elham Y. Hashem.