

Section B (Spectroscopy):

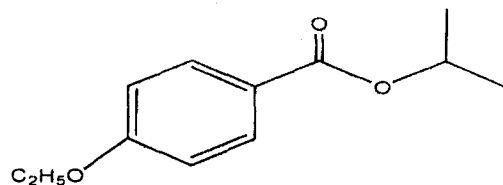
(34 Marks)

Answer the following questions:

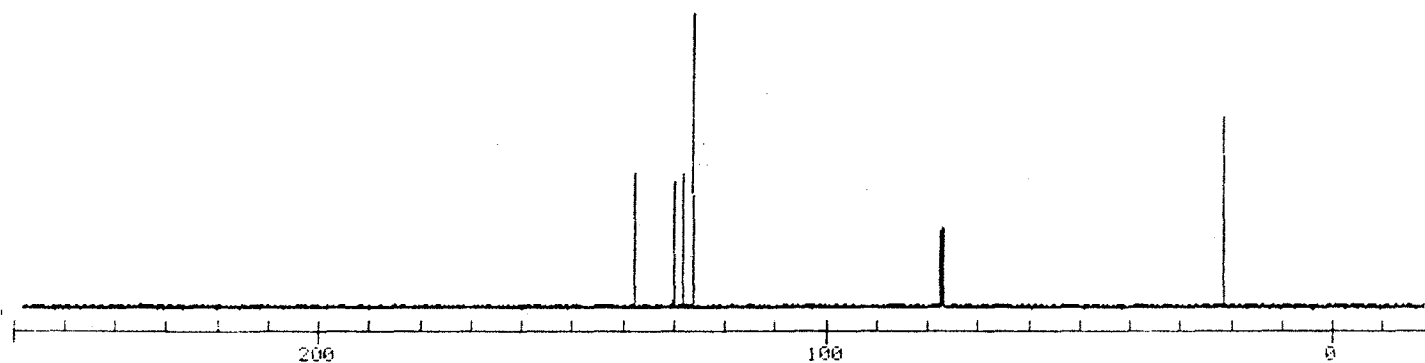
1) Describe briefly Only Two of the following: (5 Marks)

- (a) Isotope abundances in mass spectrometric analysis.
- (b) What is meant by β - cleavage with McLafferty rearrangement in the mass spectrometric analysis of carbonyl compounds ? (give one example)
- (c) The ortho effect in mass spectrometric analysis

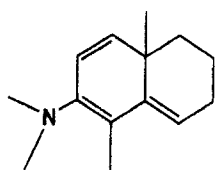
2) Sketch the ^1H NMR spectrum that you would expect for the molecule shown below. (2.5 Marks)



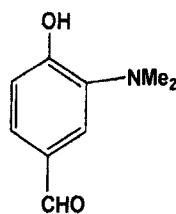
3) Below is the ^{13}C NMR spectrum of one of the three xylenes. (2.5 Marks)
Which one? Explain your reasoning. The triplet at 77 is CDCl_3 .



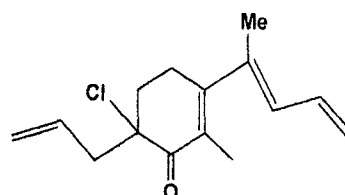
4) Calculate the UV maximum for Only Two of the following compounds. (4 Marks)
(See table page 10)



a



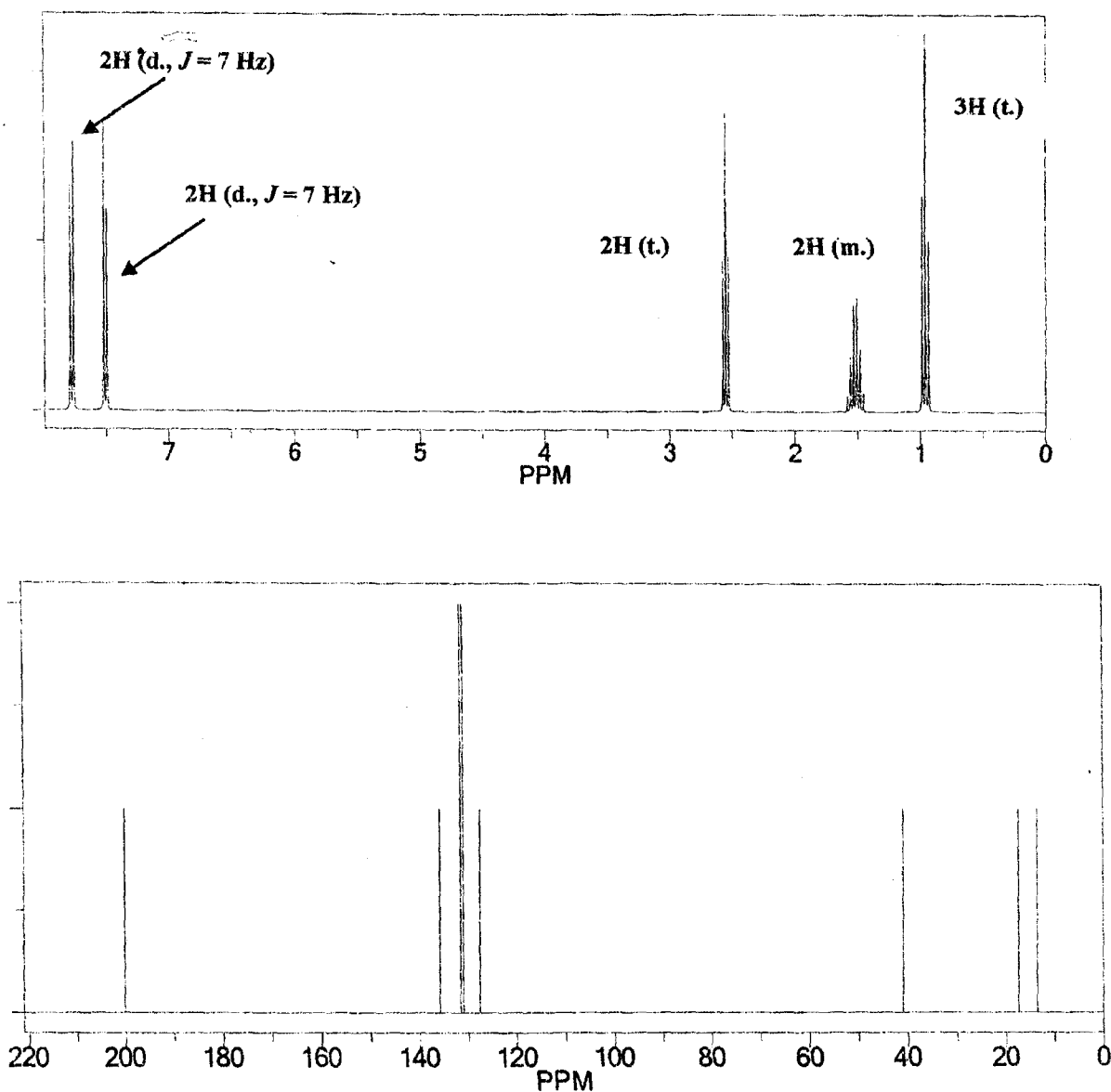
b



c

See the next page

- 7) Compound C has molecular formula $C_{10}H_{11}BrO$ with the both 1H NMR and ^{13}C NMR spectra shown below, and has two strong bands in the IR spectrum at 1690 and 810 cm^{-1} ; its mass spectrum shows peaks at $m/z = 228, 226, 198, 183, 155,$ and 147 . Provide your structural conclusions based on the spectral data provided and justify your answer by taking about fragmentation pattern of peaks with molecular weight lower than that of molecular ion peak, also, give brief explanation for appearance of two peaks at $m/z = 226$ and 228 . (See tables pages 6-9) (5 Marks)



See the next page

2- Write on two only of the following (using equations): (9 Marks)

a-The difference in electronic configuration between singlet and triplet nitrenes.

b-Compare between the hybridization of carbocation and carbanion (by drawing) .

c-The carbanion of cycloheptatriene is less acidic than the carbanion of cyclopentadiene (explain this statement).

Good Luck

Prof. A.A Abdel-Wahab , Prof. Y. A. Abdel Moez & Dr. M. A. Abdel Rahman

Aromatic Absorption Frequencies

	Stretching Vibrations			Bending Vibrations		
	Range (cm ⁻¹)	Intensity	Assignment	Range (cm ⁻¹)	Intensity	Assignment
Monosubstituted	3000-3070 1400-1600	med med-var	C-H (2 or 3-bands) C=C (ring, 2 or 3-bands)	730-770 & 680-720 950-1225 (2 or 3 bands)	str & str wk & sharp	=C-H bending (out-of-plane) (in-plane & ring torsion)
Di-substituted	3000-3070	med	C-H (2 or 3-bands)	735-770	str	C-H bending (out-of-plane)
<i>ortho</i>	1400-1600	med	C=C (ring, 2 or 3-bands)	685-720 & 750-810 & 810-900	str & str & med	
<i>meta</i>	1400-1600	med	C=C (ring, 2 or 3-bands)	800-860	str	
<i>para</i>	1400-1600	med	C=C (ring, usually 2-bands)			
Tri-substituted	3000-3070	med	C-H (2 or 3-bands)			=C-H bending (out-of-plane)
<u>1,2,3</u>	1400-1600	med	C=C (ring, 2 or 3-bands)	685-720 & 750-810	med & str	
<u>1,2,4</u>	1400-1600	med	C=C (ring, 2 or 3-bands)	800-860 & 820-900	str & med	
<u>1,3,5</u>	1400-1600	med	C=C (ring, usually 2-bands)	685-720 & 820-900	med & str	
Tetra-substituted	3000-3070	med	C-H (2 or 3-bands)			=C-H bending (out-of-plane)
<u>1,2,3,4</u>	1400-1600	med	C=C (ring, 2 or 3-bands)	800-840	str	
<u>1,2,3,5</u>	1400-1600	med	C=C (ring, 2 or 3-bands)	840-880	str	
<u>1,2,4,5</u>	1400-1600	med	C=C (ring, usually 2-bands)	840-880	str	
Pentasubstituted	3010-3040 1670	med med	=C-H C=C	840-880	str	=C-H bending (out-of-plane)

Typical Infrared Absorption Frequencies

	Stretching Vibrations			Bending Vibrations		
	Frequency (cm ⁻¹)	Intensity	Assignment	Frequency (cm ⁻¹)	Intensity	Assignment
Alkanes	2850-3000	str	C-H alkane	1350-1470 1370-1390 720-725	med med wk	CH ₂ & CH ₃ deformation CH ₃ deformation CH ₂ rocking
Alkenes	3020-3100 1630-1680 1900-2000	med var str	=C-H alkene C=C (symmetry reduces intensity) C=C asymmetric stretch	880-995 780-850 675-730	str med med	=C-H & =CH ₂ (out-of-plane bending) cis-RCH=CHR
Alkynes	3300 2100-2250	str var	≡C-H alkyne (usually sharp) C≡C (symmetry reduces intensity)	600-700	str	C-H deformation
Aromatic	3030 1400 - 1600 several bands	var med-wk	C-H aromatic C=C (benzene ring) (usually 2 or 3 bands)	690-900	str-med	C-H bending & ring puckering
Alcohols & Phenols	3580-3650 sharp 3200-3550 broad 1030-1250	var str str	O-H (free) O-H (H-bonded) C-O	1330-1430 650-770	med var-wk	O-H bending (in-plane) O-H bend (out-of-plane)
Amines	3400-3500 3300-3400 1000-1250	med-wk med-wk med	N-H (1°-amines), 2 bands N-H (2°-amines) one peak C-N	1550-1650 660-900	med-str var	NH ₂ scissoring (1°-amines) NH ₂ & N-H wagging (shifts on H-bonding)
	1630 - 1820	str	C=O (general)			
Aldehydes & Ketones	2690-2850 (2 bands) 1720-1740 1710-1720 1690	med str str str	C-H (aldehyde C-H) C=O (saturated aldehyde) C=O (saturated ketone) C=O α,β-unsaturation	1350-1360 1400-1450 1100	str str med	α-CH ₃ bending α-CH ₂ bending C-C-C bending
Carboxylic Acids & Derivatives	2500-3400 (acids) overlap C-H 1705-1720 (acids) 1210-1320 (acids) 1785-1815 (acyl halides) 1750 & 1820 (anhydrides) 1735-1750 (esters) 1630-1695 (amides)	str str med-str str str str str	O-H (H-bonded) (very broad) C=O O-C (sometimes 2-peaks) C=O C=O (2-bands) C=O C=O (amide)	1395-1440 1590-1650 1500-1560	med med med	C-O-H bending N-H (1 _i -amide) II band N-H (2 _i -amide) II band
Nitriles	2240-2260 sharp	med	C≡N			

-6-

5) Answer Only Two of the following: (5 Marks)

- a) Explain by diagram and short notes why the aromatic protons in toluene appears at δ 7-8 ppm, while the methyl protons appear at δ 2.3 ppm.
- b) Explain why a polar (protic or aprotic) solvent usually shifts the K band to longer wavelengths (red shift) while shifts the R band to shorter wavelengths (blue shift) during the UV measurements of mesityl oxide.
- c) Molecular vibrations in IR spectroscopy.
- 6) Choose the best answer from a, b, c or d for the following questions: (5 Marks)
- i) Compound A has molecular formula $C_5H_{11}NO$ and with the 1H NMR spectrum showing five signals at δ (ppm) = 1.14 (3H, t.), 1.21 (3H, t.), 2.22(2H, q.), 3.24 (2H, q.), 8.01(1H, broad s.).
- a) $CH_3CH_2CONHCH_2CH_3$ b) $CH_3CH_2COCH_2NHCH_3$ c) $CH_3NHCOCH_2CH_2CH_3$ d) $CH_3NHCH_2CH_2CH_2CHO$

ii) Which C=O function has the lowest stretching frequency in the IR?

- a) acetaldehyde b) formamide c) benzyl acetate d) benzoyl chloride

iii) Which hydrocarbon gives the highest field 1H NMR signal?

- a) 1-butyne b) cyclohexane c) 1, 4-cyclohexadiene d) benzene

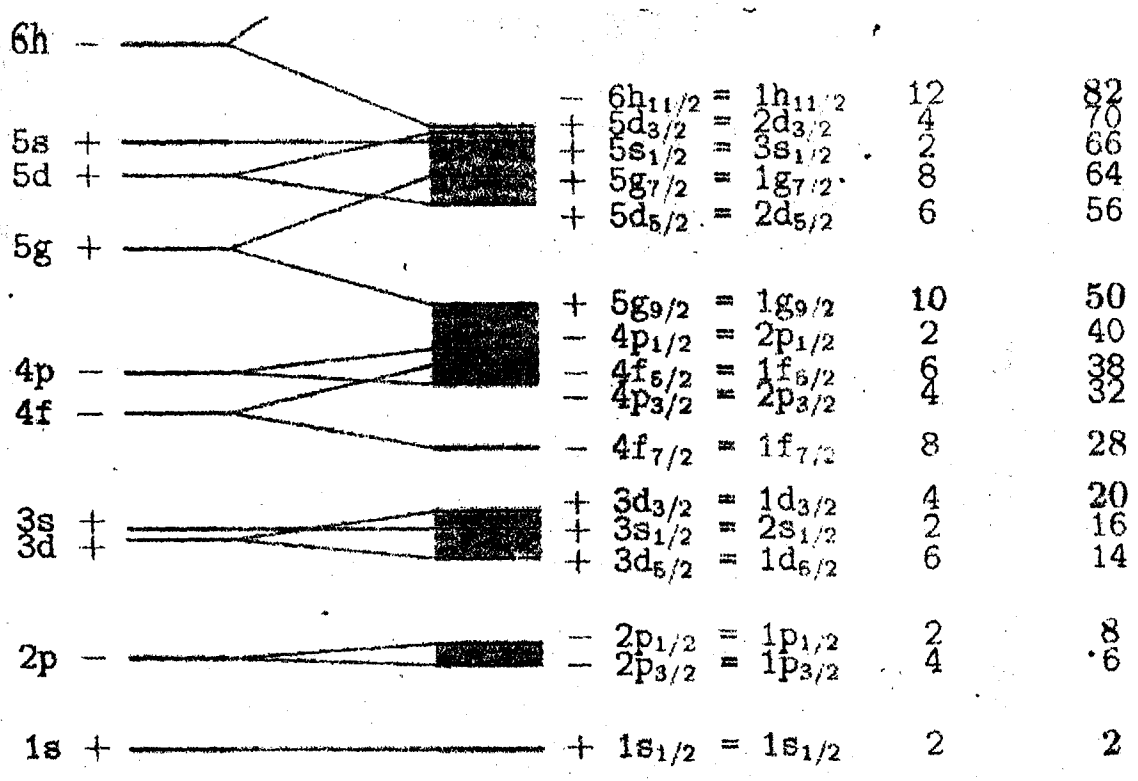
iv) Assuming all the compounds listed below yield an observable molecular ion, which would have an even number m/z value for this ion?

- a) $C_9H_{15}F$ b) $C_7H_{10}NO$
c) $C_8H_{10}N$ d) All the above have even mass molecular

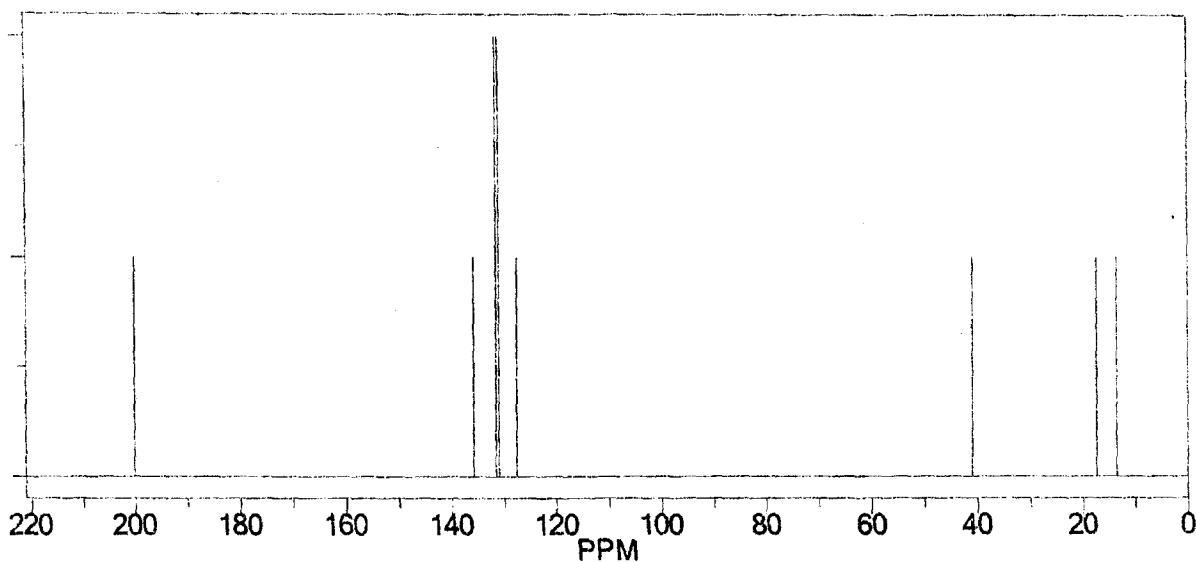
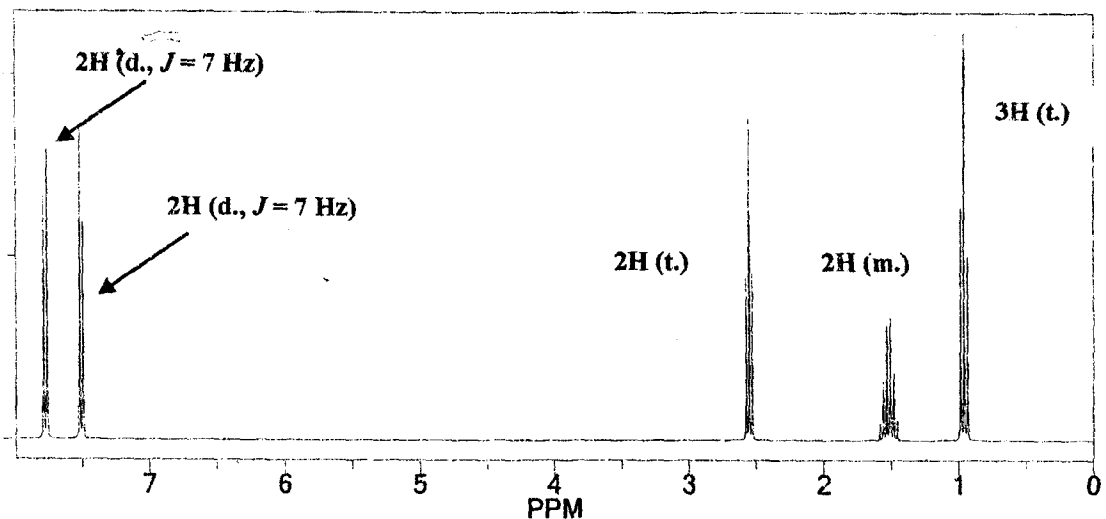
v) Compound B has the following 1H NMR signals at δ (ppm) = 7.47 (2H, m.) , 7.63(1H, m.), and 8.07 (2H, m.). Also it has 5 peaks in the ^{13}C NMR spectrum at δ (ppm) = 167.9, 135.4, 133.3, 131.4(2 carbon atoms), and 129.1 (2 carbon atoms).

- a) 4-chlorobenzaldehyde b) 2-chlorobenzaldehyde
c) benzoyl Chloride c) benzaldehyde

3



- 7) Compound C has molecular formula $C_{10}H_{11}BrO$ with the both 1H NMR and ^{13}C NMR spectra shown below, and has two strong bands in the IR spectrum at 1690 and 810 cm^{-1} ; its mass spectrum shows peaks at $m/z = 228, 226, 198, 183, 155,$ and 147 . Provide your structural conclusions based on the spectral data provided and justify your answer by taking about fragmentation pattern of peaks with molecular weight lower than that of molecular ion peak, also, give brief explanation for appearance of two peaks at $m/z = 226$ and 228 . (See tables pages 6-9) (5 Marks)



See the next page

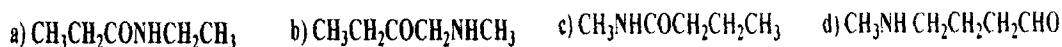
5) Answer Only Two of the following:

(5 Marks)

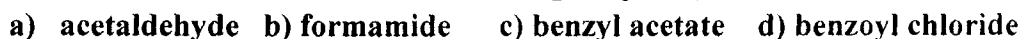
- a) Explain by diagram and short notes why the aromatic protons in toluene appears at δ 7-8 ppm, while the methyl protons appear at δ 2.3 ppm.
- b) Explain why a polar (protic or aprotic) solvent usually shifts the K band to longer wavelengths (red shift) while shifts the R band to shorter wavelengths (blue shift) during the UV measurements of mesityl oxide.
- c) Molecular vibrations in IR spectroscopy.

6) Choose the best answer from a, b, c or d for the following questions: (5 Marks)

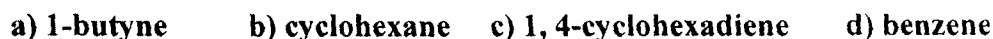
- i) Compound A has molecular formula $C_5H_{11}NO$ and with the 1H NMR spectrum showing five signals at δ (ppm) = 1.14 (3H, t.), 1.21 (3H, t.), 2.22(2H, q.), 3.24 (2H, q.), 8.01(1H, broad s.).



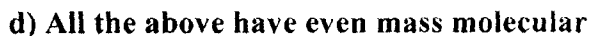
- ii) Which C=O function has the lowest stretching frequency in the IR?



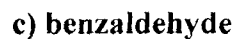
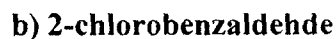
- iii) Which hydrocarbon gives the highest field 1H NMR signal?



- iv) Assuming all the compounds listed below yield an observable molecular ion, which would have an even number m/z value for this ion?



- v) Compound B has the following 1H NMR signals at δ (ppm) = 7.47 (2H, m.), 7.63(1H, m.), and 8.07 (2H, m.). Also it has 5 peaks in the ^{13}C NMR spectrum at δ (ppm) = 167.9, 135.4, 133.3, 131.4(2 carbon atoms), and 129.1 (2 carbon atoms).



See the next page



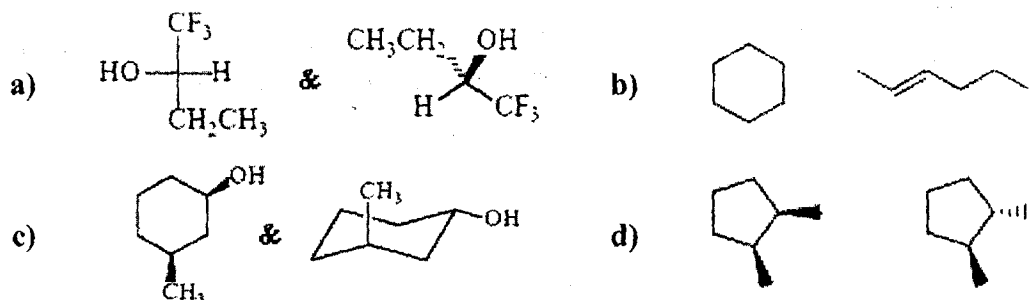
Final Exam of Organic Chemistry (311C) for the 3rd Level students

Section (A): Stereochemistry (16 Marks)

A- Answer *four* only of the following questions:

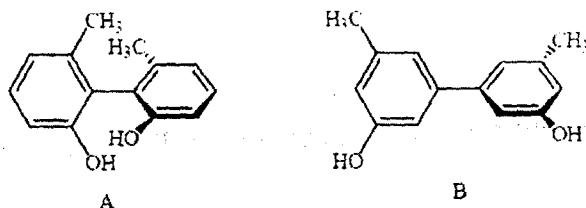
1- A solution of an unknown compound X (3.0 g of X per 20 mL), when placed in a polarimeter tube 2.0 dm long, was found to have an observed rotation of -1.8° . What is the specific rotation of X?

2- For each pair of the following pairs of compounds below, determine whether they are the same molecule, constitutional isomers, enantiomers, diastereomers, identical or different molecules?

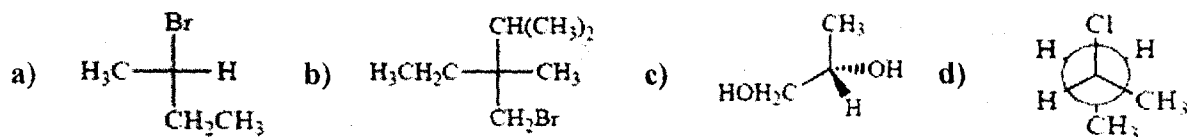


3- Use Fisher projections to draw all stereoisomers of 2-bromo-3-iodopentane. You do not need to assign absolute configurations. Number your unique isomers, and give the relationships between them (enantiomers, diastereomers, etc...)?

4- A- Which compound can be isolated in optically-active pure form? Explain your answer?



5- Indicate whether each of the following enantiomers has the R or S configuration?



ملحوظة هامة : (الإمتحان مكون من خمس صفحات)

Aromatic Absorption Frequencies

	Stretching Vibrations			Bending Vibrations		
	Range (cm ⁻¹)	Intensity	Assignment	Range (cm ⁻¹)	Intensity	Assignment
Monosubstituted	3000-3070 1400-1600	med med-var	C-H (2 or 3-bands) C=C (ring, 2 or 3-bands)	730-770 & 680-720 950-1225 (2 or 3 bands)	str & str wk & sharp	=C-H bending (out-of-plane) (in-plane & ring torsion)
Di-substituted	3000-3070	med	C-H (2 or 3-bands)	735-770	str	C-H bending (out-of-plane)
<i>ortho</i>	1400-1600	med	C=C (ring, 2 or 3-bands)	685-720 & 750-810 & 810-900	str & str & med	
<i>meta</i>	1400-1600	med	C=C (ring, 2 or 3-bands)	800-860	str	
<i>para</i>	1400-1600	med	C=C (ring, usually 2-bands)			
Tri-substituted	3000-3070	med	C-H (2 or 3-bands)			=C-H bending (out-of-plane)
<u>1,2,3-</u>	1400-1600	med	C=C (ring, 2 or 3-bands)	685-720 & 750-810	med & str	
<u>1,2,4-</u>	1400-1600	med	C=C (ring, 2 or 3-bands)	800-860 & 820-900	str & med	
<u>1,3,5-</u>	1400-1600	med	C=C (ring, usually 2-bands)	685-720 & 820-900	med & str	
Tetra-substituted	3000-3070	med	C-H (2 or 3-bands)			=C-H bending (out-of-plane)
<u>1,2,3,4-</u>	1400-1600	med	C=C (ring, 2 or 3-bands)	800-840	str	
<u>1,2,3,5-</u>	1400-1600	med	C=C (ring, 2 or 3-bands)	840-880	str	
<u>1,2,4,5-</u>	1400-1600	med	C=C (ring, usually 2-bands)	840-880	str	
Pentasubstituted	3010-3040 1670	med med	=C-H C=C	840-880	str	=C-H bending (out-of-plane)

Assiut University

Academic year 2016/2017

Faculty of Science

Time allowed: 3 hours

Chemistry Department

Final Exam. For Course no.333 (nuclear and radiochemistry)

Answer the Following question (18 marks)

From the nuclear data given below

Cs-132
6.47 d
ϵ, β^+
$\beta^- 0.8$
$\gamma 668, 465, 630..$

A) Sketch the decay scheme of Cs-132.

Write the complete decay equations of Cs-132.

How many Cs-atoms are present in 1 mCi of Cs-132 activity.

Insert spin and parity of parent and daughter nuclei.

What is the specific activity of Cs-132.

B) Define the following items

Exposure dose , Absorbed dose, LET, Mass stopping powder , Sievert ,Auger electron , Internal conversion , Specific ionization.

Calculate the activity of No-254 ($T_{1/2} = 55$ s) produced in a 1- minute irradiation of Pb-208 by Ca-48 atoms. Assume the Pb-208 target thickness is 0.5 mg/cm^2 , the Ca-48 beam current is $0.5 \mu\text{A}$ and the $^{208}\text{Pb}(^{48}\text{Ca}, 2n)^{254}\text{No}$ cross section is $3.0 \mu\text{b}$ ($1\text{A} = 6.24 \times 10^{18}$ electronic charge/s).

C) The exposure rate at a point near a cobalt-60 source was 235 R min^{-1} on October 15, 2016 . Calculate the exposure rate at the same point on August 15, 2017 and February 15, 2018 . Take 5.27 years as $T_{1/2}$ for Co-60.

Answer **TWO** questions only of the following

Question no. 2 (16 marks)

A) Define the following items

Inelastic collision of neutrons with matter , cross section of a nuclear reaction , Excitation function of a nuclear reaction , annihilation process , photoelectric effect.

B) How much time would it take for the decay of $8/9$ of a sample of Ge-68 whose half-life is 280 days.

Turn Over \longrightarrow

Environmental Analytical Chemistry Examination (343 C)

.....
Answer the Following Questions: (50 marks)

1- Answer Four Only: (12.5 marks)

- Describe the main objectives of pollution monitoring in environmental analysis
- Define and characterize " Spot test " and " Ultimate analysis " .
- What is meant by the terms " ground water " and " aquifer " .
- Draw a labeled diagram classifying the top and bottom layers of a lake in summer as rather oxidizing or reducing in character, and showing the stable forms of carbon, sulfur, nitrogen and iron in the two layers.
- Define the terms "BOD" and "COD", and explain why their values for the samples can differ slightly. Explain why natural water can have a high BOD.

2- Answer Four Only: (12.5 marks)

- How does temperature affect the solubility of O₂ in water? and explain what is meant by " Thermal pollution " .
- In water analysis distinguish between "batch sampling" and "Continuous sampling".
- What is meant by **pE** in aqueous solution? and what does a low and high values imply about the solution?
- Write about the different sources of water pollution and its effect on the human health.
- Write the balance chemical equation for the reaction by which organic carbon represented as CH₂O, is disproportioned by bacteria under anaerobic conditions.

3- Answer Four Only: (12.5 marks)

- Describe the poisoning effects of cadmium, lead and mercury ions in humans due to environmental contamination.
- Complete the following equations:
 - $2 \{ \text{CH}_2\text{O} \} + \text{SO}_4^{2-} + \text{H}^+ \rightarrow \dots + \dots + 2 \text{H}_2\text{O}.$
 - $\text{CdCl}^+ \text{ (chloro complex in sea water)} + \text{HS}^- \rightarrow \dots + \dots + \text{H}^+.$
 - $\text{HgCl}_2 \xrightarrow{\text{Methylcobalamin}} \dots + \dots$
- Show by equations how can arsenic may be converted to more mobile and toxic methyl derivatives by bacteria.
- Compare between the different methods for pre-treatment of environmental samples before analysis.
- Discuss the biological importance for both zinc and copper ions.

4- Answer Four Only: (12.5 marks)

- A 7.5×10^{-5} M solution of KMnO₄ has a transmittance of 36.4% when measured in 1 cm cell at 525 nm. Calculate the molar absorptivity of KMnO₄.
- Compare between Flame Atomic Absorption and Graphite Furnace Atomic Absorption spectrometric methods for analyzing metals in environmental samples.
- Define each of the following terms. The standard addition method – The acid rain – The calibration graph.
- Carbon mono oxide is poisonous. Explain this statement with equations.
- Describe briefly the advantages of Inductively Coupled Plasma Atomic Emission Spectroscopy as analytical method can be used for measuring contaminant metals in environmental samples.

.....
Good Luck

C) A sample of 1.00×10^{-10} g of Mo-99 ($T_{1/2} = 66$ h) is freshly purified at $t=0$

- What kind of equilibrium exist between Mo-99 and its daughter Tc-99m ($T_{1/2} = 6$ h)
- If this sample is left without further treatment, when will the amount of Tc-99m in it be a maximum.
- At that time of maximum growth what will be the weight of Tc-99m present.

Question no. 3 (16 marks)

A) Define the following items

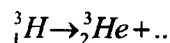
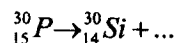
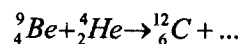
Compton scattering, Dose equivalent unit, isomeric transition, Gray, Anti-neutrino, neutron capture, Bremsstrahlung emission, Linear attenuation coefficient.

B) In the reaction $^{106}\text{Pd}(n, p)^{106}\text{Rh}$ the product Rh-106 ($T_{1/2} = 30$ s) decay by β^- emission with maximum kinetic energy of 3.5 MeV. Calculate the Q value of the reaction.

C) Calculate the mass absorption coefficient for 1 MeV γ -rays for sodium iodide (a_m for Na and I atoms are 2.32 and 12.03 b/atom respectively).

Question no.4 (16 marks)

A) Complete the following nuclear reactions



B) Calculate the barrier potential and the threshold energy for an alpha particle colliding with N-14 nucleus.

C) Calculate the maximum kinetic energy of the β^- emitted in the radioactive decay of He-6.

D) Cu-64 ($T_{1/2} = 12.700$ h) is known to decay by electron capture (61%) and β^- (39%). What are the partial half-life for EC and β^- decay? What is the partial width for EC decay?

Constants; $m_p = 1.00727$ u, $m_n = 1.00866$ u, $N_A = 6.023 \times 10^{23}$ mol $^{-1}$, $1\text{b} = 1 \times 10^{-24}$ cm 2 , $1\text{Ci} = 3.7 \times 10^{10}$ Bq

$m_{\text{He-6}} = 6.0188881$ u, $m_{\text{Li-6}} = 6.0151223$ u, $\hbar = 1.054589 \times 10^{-27}$ erg s

Good Luck

Prof. Dr. R. M. Mahfouz

C) Answer the following questions:

- 1- Explain the extraction process of either uranium or the lanthanides.
 - 2- Comment on **four** of the following:
 - a- The lanthanide contraction and its consequences.
 - b- Only Ce reacts with oxygen to give CeO_2 while other lanthanide give Ln_2O_3 .
 - c- The magnetic moment of the lanthanides is greater than the corresponding d-transition metals.
 - d- The first members of the actinides have larger numbers of oxidation states than the corresponding lanthanides.
 - e- Lanthanide ions are used for the calibration of spectral instruments.
 - f- On reaction with H_2 lanthanide metals, except Eu , give hydrides showing metallic characters.
-

Good Luck

Examiners: Prof.Dr.Asmaa.Ibrahiem.

Dr.Zaher.Abd El- Mohsen.

Final Examination For 3rd Level Students[Inorganic Chemistry (3)(C-324)]

Answer the following questions:

A) Answer **Only Four** of the following:

- 1- Bis (dimethylglyoximate) nickel (ii) is experimentally known to be diamagnetic. Predict on the basis of VBT and CFT whether the complex has a square planar or tetrahedral geometry.
- 2- On the basis of VBT discuss the following:
 - i- Huggin's suggestion of the square planar geometry of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion with $n=1$.
 - ii- The brown ring compound in nitrate test shows $\mu=3.8$ B.M.
- 3- Determine the number of unpaired electrons and CFSE in octahedral complexes of d^9 , d^3 , d^4 and d^5 when $\Delta_o > P$ and $\Delta_o < P$.
- 4- " Cu^{2+} ion forms square planar complexes rather than tetrahedral or octahedral complexes in both strong and weak fields". Explain.
- 5- Compare and contrast the assumptions of VBT and CFT.

B) Answer **Only Four** of the following:

- 1- The enthalpy of hydration of Cr^{2+} ion is -460 K cal mol^{-1} . In absence of CFSE the value is -435 K cal mol^{-1} . Calculate the value of Δ_o for $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ ion.
- 2- Soluble compounds of the complex ion $[\text{Co}(\text{NH}_3)_6]^{3+}$ have a maximum absorption of visible light at 437 nm. Calculate Δ_o and CFSE of this complex ion.
- 3- Calculate the number of unpaired electrons and magnetic moment for the following complex ions: $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ $[\text{Cr}(\text{NH}_3)_6]^{3+}$ $[\text{CoCl}_4]^{2-}$.
- 4- Draw Orgel diagrams for the different d^n electronic configurations in O_h weak field complexes.
- 5- Show the MO treatment of the disadvantages of both valence bond and crystal field theories.

(Atomic numbers) Cr=24 Fe=26 Co=27 Ni=28 Cu=29

أنظر باقي الأسئلة في الخلف

Final Inorganic Chemistry Exam(C-321)for third level students

Question Number One:

(17marks)

A) Answer Only Three of the following:

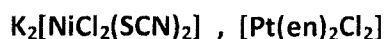
- i- What is meant by coordination number, primary valency and secondary valency according to Werner's theory?
- ii- Describe briefly the methods by which the presence of complex ion may be detected in solution.
- iii- Give the formula, number of charges, and number of particles for the complexes which agree with CaCl_2 and LaCl_3 solutions in molar conductivity and concentration 0.001M.
- iv- Draw the possible arrangement for six coordination number complexes.

B) Answer the following questions:

a) Write the formula of the following complexes.

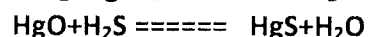
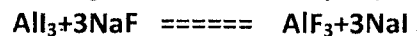
- (i) Bis(ethylenediamine)Co(III)- μ -hydroxo- μ -amidobis(ethylenediamine)Co(III)chloride
- (ii) Sodium amminebromochloronitritoplatinate(II).

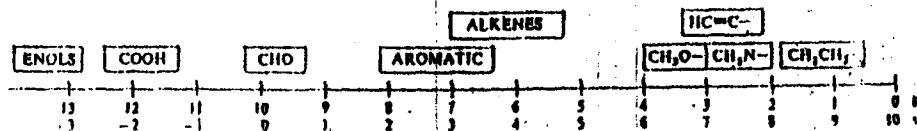
b) Write the IUPAC name of the following complexes.



c) What kind of isomerism that the two complexes [in point(b) above] possess?

d) In the light of HSAB concept , predict which direction the following reactions will go.





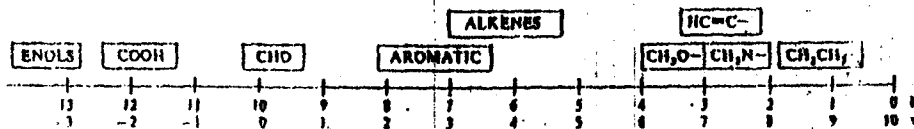
Approximate chemical shift positions for protons in organic molecules.

Chemical Shifts of Representative Types of Protons

Type of proton	Chemical shift (ppm)*	Type of proton	Chemical shift (ppm)*
$\text{H}-\text{C}-\text{R}$	0.9-1.8	$\text{H}-\text{C}-\text{NH}$	2.2-2.9
$\text{H}-\text{C}-\text{C}=\text{C}$	1.6-2.6	$\text{H}-\text{C}-\text{Cl}$	3.1-4.1
$\text{H}-\text{C}-\overset{\text{O}}{\parallel}{\text{C}}$	2.1-2.5	$\text{H}-\text{C}-\text{Br}$	2.7-4.1
$\text{H}-\text{C}\equiv\text{C}-$	2.5	$\text{H}-\text{C}-\text{O}$	3.3-3.7
$\text{H}-\text{C}-\text{Ar}$	2.3-2.8	$\text{H}-\text{NR}$	1-3†
$\text{H}-\text{C}=\text{C}$ (alkene)	4.5-6.5	$\text{H}-\text{OR}$	0.5-5†
$\text{H}-\text{Ar}$	6.5-8.5	$\text{H}-\text{OAr}$	6-8†
$\text{H}-\overset{\text{O}}{\parallel}{\text{C}}$	9-10	$\text{H}-\overset{\text{O}}{\parallel}{\text{C}}$	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.



Approximate chemical shift positions for protons in organic molecules.

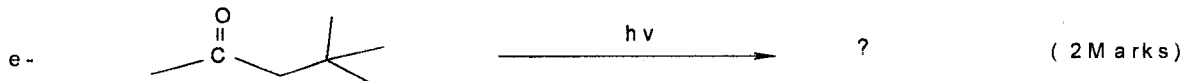
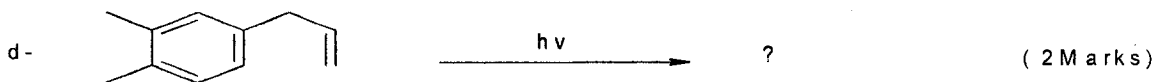
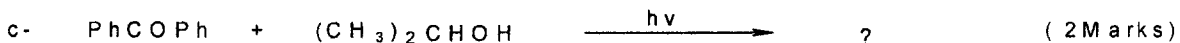
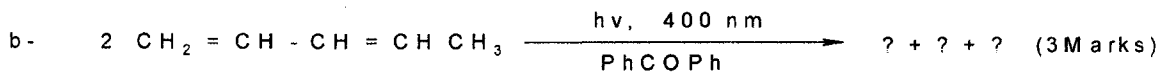
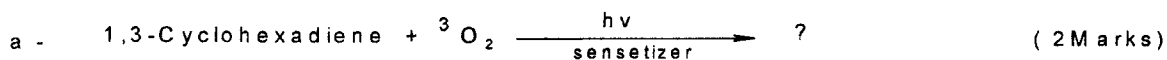
Chemical Shifts of Representative Types of Protons

Type of proton	Chemical shift (ppm)*	Type of proton	Chemical shift (ppm)*
$\text{H}-\text{C}-\text{R}$	0.9-1.8	$\text{H}-\text{C}-\text{NH}$	2.2-2.9
$\text{H}-\text{C}-\text{C}=\text{C}$	1.6-2.6	$\text{H}-\text{C}-\text{Cl}$	3.1-4.1
$\text{H}-\text{C}-\overset{\text{O}}{\parallel}{\text{C}}$	2.1-2.5	$\text{H}-\text{C}-\text{Br}$	2.7-4.1
$\text{H}-\text{C}\equiv\text{C}-$	2.5	$\text{H}-\text{C}-\text{O}$	3.3-3.7
$\text{H}-\text{C}-\text{Ar}$	2.3-2.8	$\text{H}-\text{NR}$	1-3†
$\text{H}-\text{C}=\overset{\diagup}{\text{C}}$	4.5-6.5	$\text{H}-\text{OR}$	0.5-5†
$\text{H}-\text{Ar}$	6.5-8.5	$\text{H}-\text{OAr}$	6-8†
$\text{H}-\overset{\text{O}}{\parallel}{\text{C}}$	9-10	$\text{H}-\overset{\text{O}}{\parallel}{\text{C}}$	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.

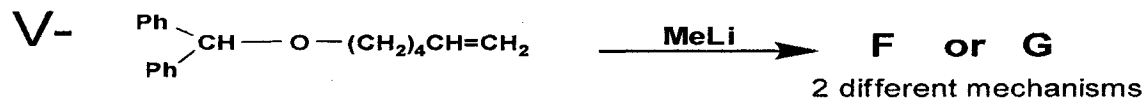
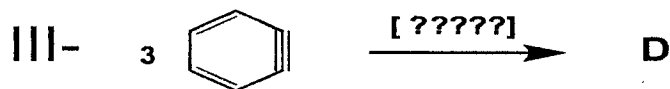
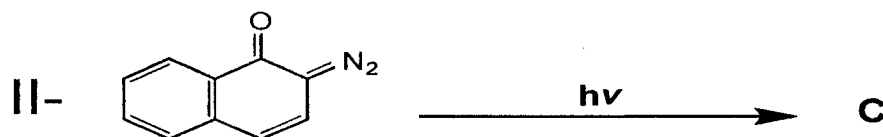
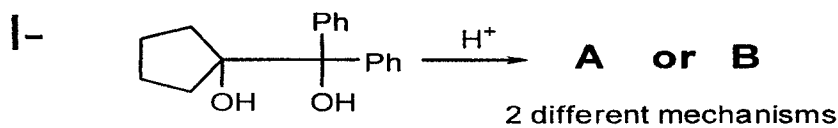
III] Complete **only Four** of the following reactions and discuss the reaction mechanism: [9 Marks]



Section (B) Reactive Intermediates:

(25 Marks)

1- Suggest the suitable product and mechanism for Only Four of the following reactions. Write the name of the suggested mechanism indicating each step using arrows. (16 Marks)



Photochemistry and Reactive Intermediates (313C)

Final Examination

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 criteria should be fulfilled by a compound to become photosensitizer ?, what is the importance of photosensitizers, using example?.
- 2- Explain the role of chemical Actinometer in Photochemistry? give an example.
- 3- Discuss briefly the phenomena of Photochromism ?.
- 4- Explain the role of Rhodopsin in the photochemistry of vision
- 5- Describe the mechanism of interaction of polar material with Microwave Radiation.

II] – Mark right (\checkmark) or wrong (X) on **only four** of the following statements, and explain your answer : (2 X 4 =8 Marks)

- 1- Liquid filters absorbing ≥ 300 nm radiations can be used in Visible light photolysis of organic compounds. ()
- 2- Photoisomerization is a thermodynamically controlled process. ()
- 3- Singlet \rightarrow Triplet transition is a Symmetry Forbidden transition. ()
- 4- Photopolymerization of Ethylene can be carried out successfully in the presence of Oxygen. ()
- 5- Vision is a photophysical process initiated by Emission of light. ()

Question Number Two:

(16 marks)

A) Write on the occurrence, extraction and physical properties of manganese metal.

B) Answer only Two of the following :

i- How the lower and higher oxidation states of transition metals can be stabilized?.

ii- Give the chemical formula and oxidation state of different metal ions for the following:

Vanadic acid - Permanganic acid - Sodium dichromate - Potassium ferrocyanide.

iii- Discuss the influence of carbon on the commercial varieties of iron.

C) Write on only one of the following:

i- Variation of acidic/basic character of the compounds of a given transition metal in various oxidation states.

ii- Metallic character and related properties of transition metals.

Question Number Three:

(17 marks)

A) Give reason(s) for only three of the following:

i- Ferrous salts act as strong reducing agents.

ii- Transition metals have variable oxidation states.

iii- In aqueous solution Cu exists only as Cu^{2+} ion.

iv- Most transition metals act as catalysts.

B) Write briefly on only one of the following:

i- Uses of Chromium and cobalt metals.

ii- Platinum black preparation and uses.

C) Answer only two of the following:

i- Explain the methods used for the purification of the extracted transition metals.

ii- The colour of transition metal complexes depends on the nature of both the metal ion and the ligand.

iii- Write on the action of H_2O and/or mineral acids on platinum metals and zinc group metals.

GOOD LUCK

المتتحنون: أ.د/ سعيد إبراهيم ، أ.د/ سحر الجيار ، أ.د/ أسماء إبراهيم

Section B (Spectroscopy):

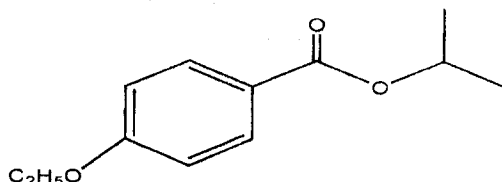
(34 Marks)

Answer the following questions:

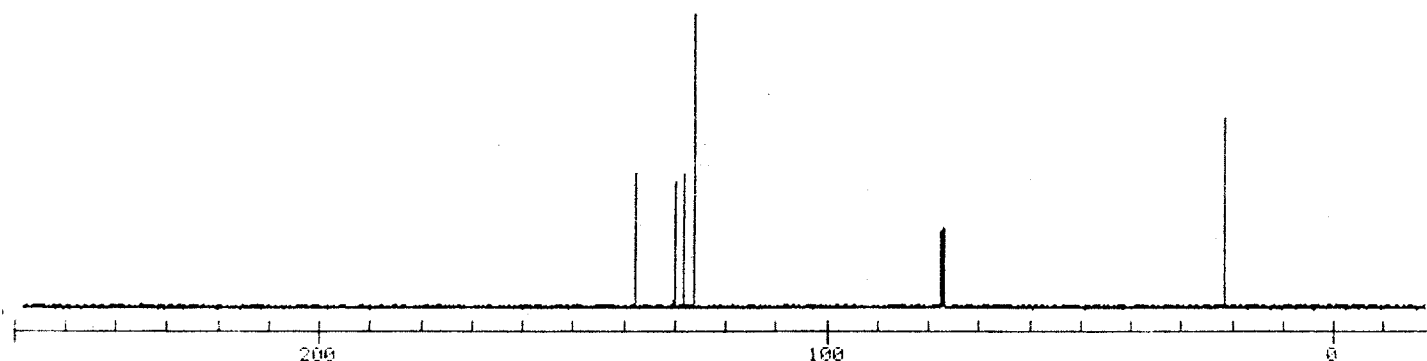
1) Describe briefly Only Two of the following: (5 Marks)

- (a) Isotope abundances in mass spectrometric analysis.
- (b) What is meant by β - cleavage with McLafferty rearrangement in the mass spectrometric analysis of carbonyl compounds ? (give one example)
- (c) The ortho effect in mass spectrometric analysis

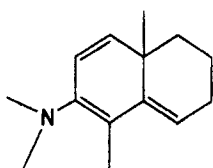
2) Sketch the ^1H NMR spectrum that you would expect for the molecule shown below. (2.5 Marks)



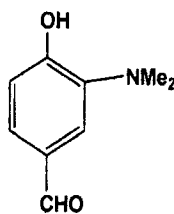
3) Below is the ^{13}C NMR spectrum of one of the three xylenes. (2.5 Marks)
Which one? Explain your reasoning. The triplet at 77 is CDCl_3 .



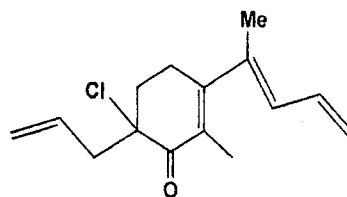
4) Calculate the UV maximum for Only Two of the following compounds. (4 Marks)
(See table page 10)



a



b



c

See the next page

Typical Infrared Absorption Frequencies

	Stretching Vibrations			Bending Vibrations		
	Frequency (cm ⁻¹)	Intensity	Assignment	Frequency (cm ⁻¹)	Intensity	Assignment
Alkanes	2850-3000	str	C-H alkane	1350-1470 1370-1390 720-725	med med wk	CH ₂ & CH ₃ deformation CH ₃ deformation CH ₂ rocking
Alkenes	3020-3100 1630-1680 1900-2000	med var str	=C-H alkene C=C (symmetry reduces intensity) C=C asymmetric stretch	880-995 780-850 675-730	str med med	=C-H & =CH ₂ (out-of-plane bending) cis-RCH=CHR
Alkynes	3300 2100-2250	str var	≡C-H alkyne (usually sharp) C≡C (symmetry reduces intensity)	600-700	str	C-H deformation
Aromatic	3030 1400 - 1600 several bands	var med-wk	C-H aromatic C=C (benzene ring) (usually 2 or 3 bands)	690-900	str-med	C-H bending & ring puckering
Alcohols & Phenols	3580-3650 sharp 3200-3550 broad 1030-1250	var str str	O-H (free) O-H (H-bonded) C-O	1330-1430 650-770	med var-wk	O-H bending (in-plane) O-H bend (out-of-plane)
Amines	3400-3500 3300-3400 1000-1250	med-wk med-wk med	N-H (1°-amines), 2 bands N-H (2°-amines) one peak C-N	1550-1650 660-900	med-str var	NH ₂ scissoring (1°-amines) NH ₂ & N-H wagging (shifts on H-bonding)
	1630 - 1820	str	C=O (general)			
Aldehydes & Ketones	2690-2850 (2 bands) 1720-1740 1710-1720 1690	med str str str	C-H (aldehyde C-H) C=O (saturated aldehyde) C=O (saturated ketone) C=O α,β-unsaturation	1350-1360 1400-1450 1100	str str med	α-CH ₃ bending α-CH ₂ bending C-C-C bending
Carboxylic Acids & Derivatives	2500-3400 (acids) overlap C-H 1705-1720 (acids) 1210-1320 (acids) 1785-1815 (acyl halides) 1750 & 1820 (anhydrides) 1735-1750 (esters) 1630-1695 (amides)	str str med-str str str str str	O-H (H-bonded) (very broad) C=O O-C (sometimes 2-peaks) C=O C=O (2-bands) C=O C=O (amide)	1395-1440 1590-1650 1500-1560	med med med	C-O-H bending N-H (1 _i -amide) II band N-H (2 _i -amide) II band
Nitriles	2240-2260 sharp	med	C≡N			

-6-

UV-VIS Calculation Tables

Conjugated Diene	
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	+60
Solvent correction ^a	+0
$\lambda_{calc} = \text{Total}$	

^aSee L. M. Fieser and M. Fieser, *Steroids*, New York: Reinhold, 1959, pp. 15-24; R. B. Woodward, *J. Am. Chem. Soc.*, 63, 1123 (1941); 64, 72, 76 (1942); A. I. Scott, *Interpretation of the Ultraviolet Spectra of Natural Products*, New York: Pergamon (Macmillan), 1964.

^aSolvents have negligible effects upon the λ_{max} of these $\pi \rightarrow \pi^*$ transitions.

Substituted Benzene	
ArCOR/ArCHO/ArCO ₂ H/ArCO ₂ R	λ_{max} (nm)
Parent chromophore: Ar = C ₆ H ₅	246
G = Alkyl or ring residue, (e.g., ArCOR)	250
G = H, (ArCHO)	250
G = OH, OAlk, (ArCO ₂ H and ArCO ₂ R)	230
Increment for each substituent on Ar:	
—Alkyl or ring residue	o-, m- +3 p- +10
—OH, —OCH ₃ , —OAlk	o-, m- +7 p- +25
—O ⁻ (oxyanion)	o- +11 m- +20
—Cl	p- +78 ^a o-, m- +0
—Br	p- +10 o-, m- +2
—NH ₂	p- +15 o-, m- +13
—NHCOCH ₃	p- +58 o-, m- +20
—NHCH ₃	p- +45
—N(CH ₃) ₂	p- +73 o-, m- +20
	p- +85

Conjugated Enone and Dienone	
	enone
	dienone
Base values (nm)	
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: —OH	α +35 β +30 δ +50
—OAc	α,β,δ +6
—OMe	α +35 β +30 γ +17 δ +31
—SAlk	β +85
—Cl	α +15 β +12
—Br	α +25 β +30
—NR ₂	β +95
Exocyclic double bond	+5
Homodiene component ^a	+39
Solvent correction (see table below)	Variable
$\lambda_{calc} = \text{Total}^a$	

^aTwo conjugated double bonds, both in the same ring.
^aThe calculated values usually fall within ± 3 nm of the observed values. The molar absorptivities of *cisoid* enones are usually less than 10,000, whereas the molar absorptivities of *transoid* enones are greater than 10,000.

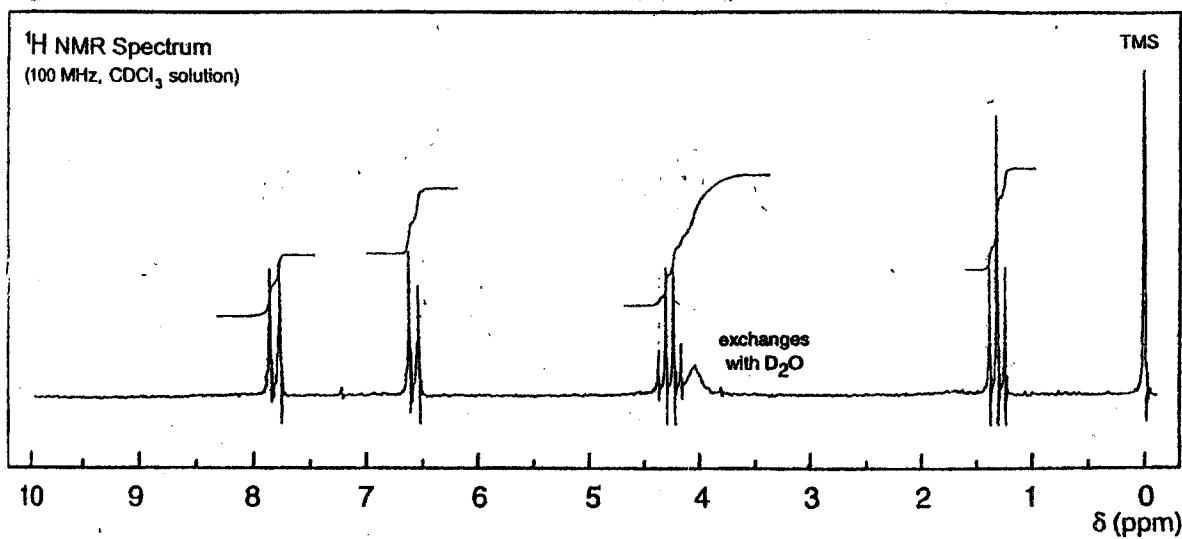
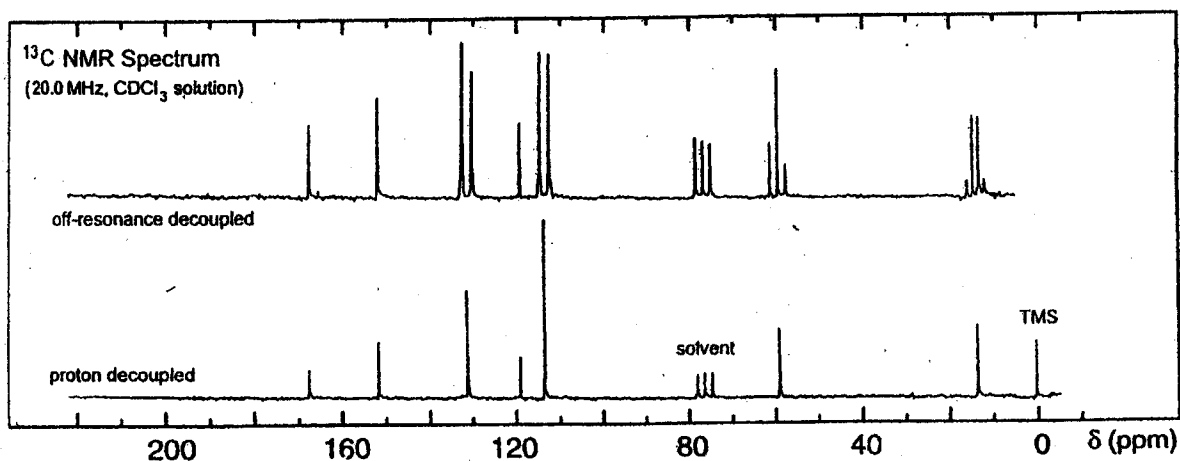
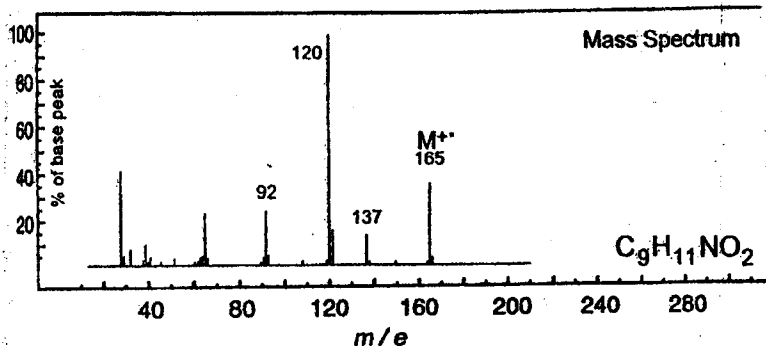
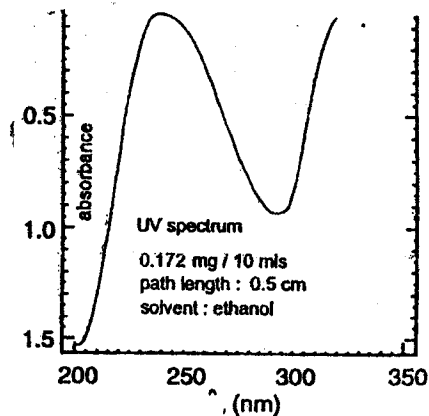
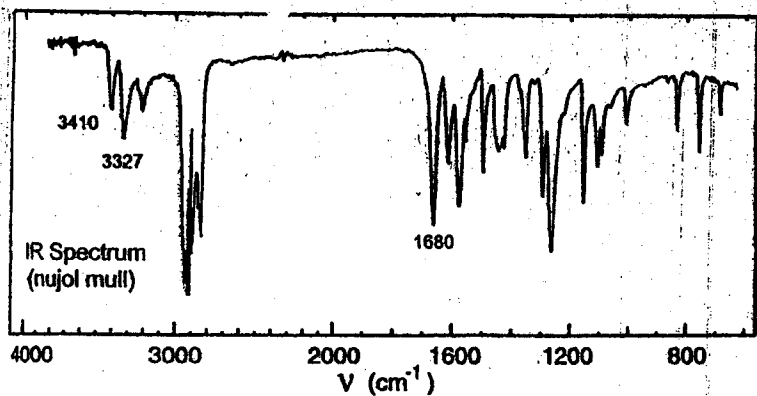
Terminology

	"homo-diene" homoannular diene
	"hetero-diene" heteroannular diene
EXOCYCLIC	
	Double bond has an atom that is part of a ring that the other is not.
	NOT EXOCYCLIC
	2-exocyclic components

8) You are provided with UV, IR, MS and ^1H NMR and ^{13}C NMR of compound D having the molecular formula $\text{C}_9\text{H}_{11}\text{NO}_2$: (5 Marks)

a) Write all the probable structures which can be represented by this formula.

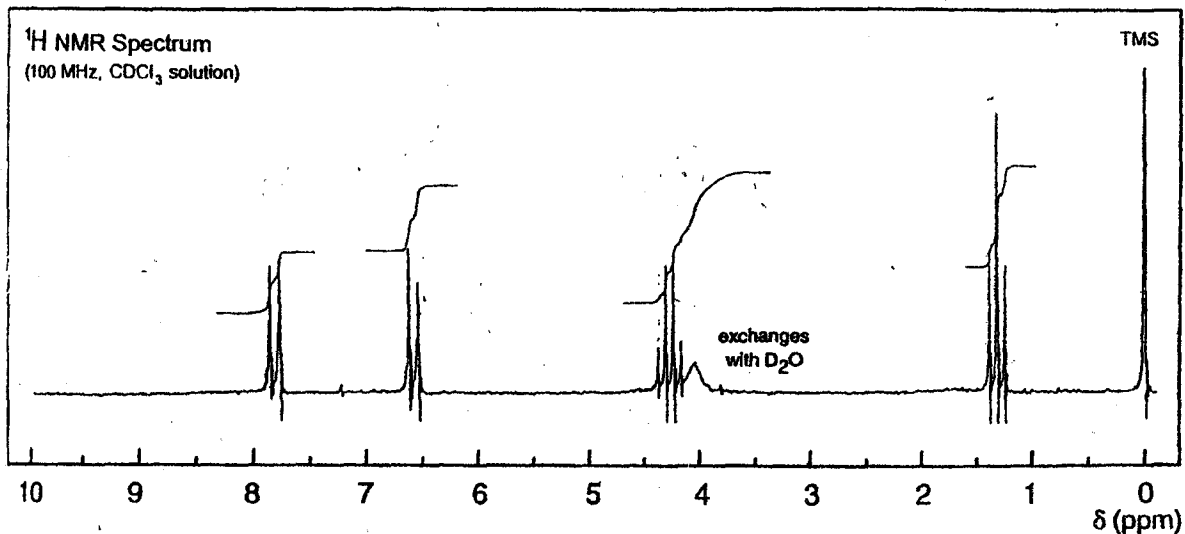
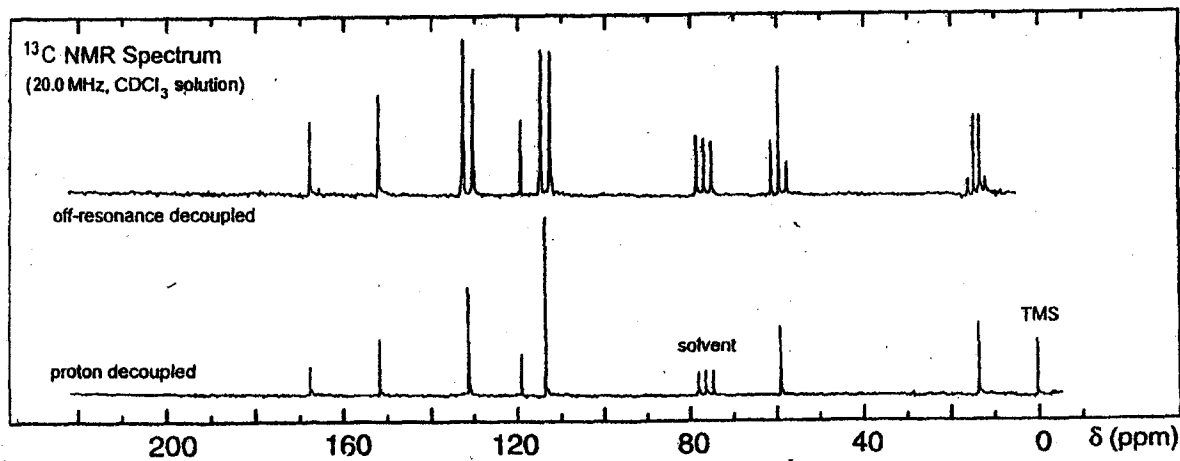
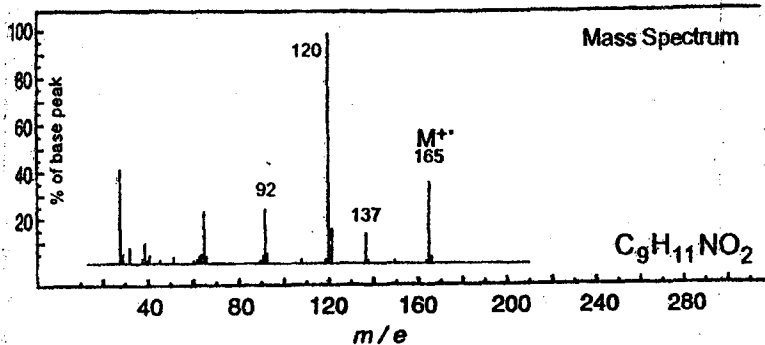
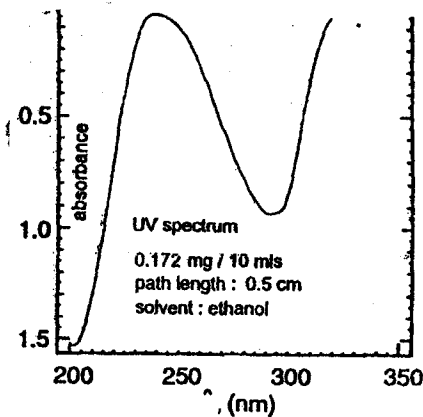
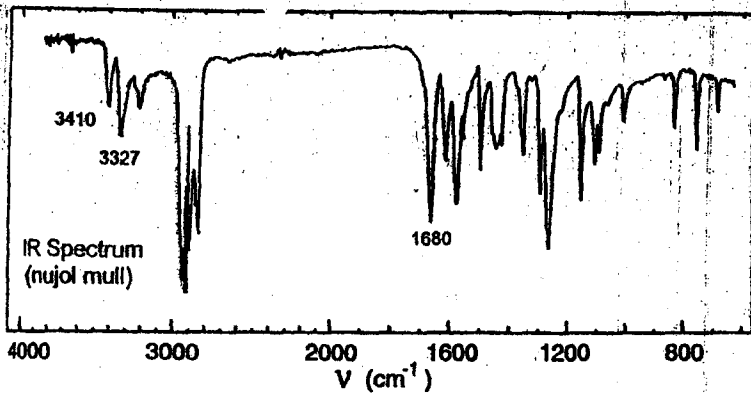
b) Assign the suitable structure which agrees with the provided spectra, give reason for your assignment and show the fragmentation pattern, IR, ^1H NMR and ^{13}C NMR peaks which confirm your answer. (See tables pages 6-9)



8) You are provided with UV, IR, MS and ^1H NMR and ^{13}C NMR of compound D having the molecular formula $\text{C}_9\text{H}_{11}\text{NO}_2$: (5 Marks)

a) Write all the probable structures which can be represented by this formula.

b) Assign the suitable structure which agrees with the provided spectra, give reason for your assignment and show the fragmentation pattern, IR, ^1H NMR and ^{13}C NMR peaks which confirm your answer. (See tables pages 6-9)



Periodic Table of Elements

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18

1	1	H	Hydrogen	1.00794
2	2	He	Helium	4.002602
3	3	Li	Lithium	6.941
4	4	Be	Beryllium	9.012182
5	5	B	Boron	10.811
6	6	C	Carbon	12.011
7	7	N	Nitrogen	14.00643
8	8	O	Oxygen	15.999
9	9	F	Fluorine	18.9984032
10	10	Ne	Neon	20.1797
11	11	Na	Sodium	22.98976928
12	12	Mg	Magnesium	24.30509
13	13	Al	Aluminum	26.9815386
14	14	Si	Silicon	28.0855
15	15	P	Phosphorus	30.973762
16	16	S	Sulfur	32.06
17	17	Cl	Chlorine	35.453
18	18	Ar	Argon	39.948
19	19	K	Potassium	39.0983
20	20	Ca	Calcium	40.078
21	21	Sc	Scandium	44.955912
22	22	Ti	Titanium	47.88
23	23	V	Vanadium	50.9415
24	24	Cr	Chromium	51.9961
25	25	Mn	Manganese	54.938045
26	26	Fe	Iron	55.845
27	27	Co	Cobalt	58.933195
28	28	Ni	Nickel	58.6934
29	29	Cu	Copper	63.546
30	30	Zn	Zinc	65.38
31	31	Ga	Gallium	69.723
32	32	Ge	Germanium	72.63
33	33	As	Arsenic	74.9216
34	34	Se	Selenium	78.96
35	35	Br	Bromine	79.904
36	36	Kr	Krypton	83.798
37	37	Rb	Rubidium	85.4678
38	38	Sr	Strontium	87.62
39	39	Y	Yttrium	88.90584
40	40	Zr	Zirconium	91.224
41	41	Nb	Niobium	92.90638
42	42	Mo	Molybdenum	95.94
43	43	Tc	Technetium	(98)
44	44	Ru	Ruthenium	101.07
45	45	Rh	Rhodium	102.90550
46	46	Pd	Palladium	106.42
47	47	Ag	Silver	107.8682
48	48	Cd	Cadmium	112.411
49	49	In	Indium	114.818
50	50	Sn	Tin	118.710
51	51	Sb	Antimony	121.757
52	52	Te	Tellurium	127.60
53	53	I	Iodine	126.90547
54	54	Xe	Xenon	131.29
55	55	Cs	Cesium	132.90545196
56	56	Ba	Barium	137.327
57	57-71	Lanthanoids		
58	58	Ce	Cerium	140.116
59	59	Pr	Praseodymium	140.90765
60	60	Nd	Neodymium	144.242
61	61	Pm	Promethium	(145)
62	62	Sm	Samarium	150.36
63	63	Eu	Eurium	151.964
64	64	Gd	Gadolinium	157.25
65	65	Tb	Terbium	158.92535
66	66	Dy	Dysprosium	162.500
67	67	Ho	Holmium	164.93032
68	68	Er	Erbium	167.259
69	69	Tm	Thulium	168.93421
70	70	Yb	Ytterbium	173.054
71	71	Lu	Lutetium	174.967
72	72	Hf	Hafnium	178.49
73	73	Ta	Tantalum	180.94788
74	74	W	Tungsten	183.84
75	75	Re	Rhenium	186.207
76	76	Os	Osmium	190.23
77	77	Ir	Iridium	192.222
78	78	Pt	Platinum	195.084
79	79	Au	Gold	196.966569
80	80	Hg	Mercury	200.59
81	81	Tl	Thallium	204.3833
82	82	Pb	Lead	207.2
83	83	Bi	Bismuth	208.9804
84	84	Po	Polonium	(209)
85	85	At	Astatine	(210)
86	86	Rn	Radon	(222)
87	87	Fr	Francium	(223)
88	88	Ra	Radium	(226)
89	89-103	Actinoids		
90	90	Th	Thorium	232.0377
91	91	Pa	Protactinium	231.03688
92	92	U	Uranium	238.02891
93	93	Np	Neptunium	(237)
94	94	Pu	Plutonium	(244)
95	95	Am	Americium	(243)
96	96	Cm	Curium	(247)
97	97	Bk	Berkelium	(247)
98	98	Cf	Californium	(251)
99	99	Es	Einsteinium	(252)
100	100	Fm	Fermium	(257)
101	101	Md	Mendelevium	(258)
102	102	No	Nobelium	(259)
103	103	Lr	Lawrencium	(262)

Metals

- Alkali metals
- Alkaline earth metals
- Lanthanoids
- Actinoids
- Transition metals
- Poor metals

Nonmetals

- Other nonmetals
- Noble gases

C Solid
Hg Liquid
H Gas
Rf Unknown

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

Periodic Table Design and Interface Copyright © 1997 Michael Dayah, <http://www.ptable.com/> Last updated: May 9, 2013

michael@dayah.com

For a fully interactive experience, visit www.ptable.com.

Michael Dayah