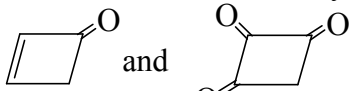
5. a) Arrange the following compounds in order of increasing enol content (in liquid)

$\underset{\text{I}}{MeCOCH_2COOEt}$, $\underset{\text{II}}{CH_3CO-CH_2-COCH_3}$,

$\underset{\text{III}}{CH_3COCHPhCOOEt}$, $\underset{\text{IV}}{PhCO-CH_2COMe}$

b) Which one of the following two carbonyl compounds will enolize and why? 1

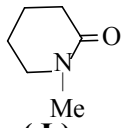

(I)

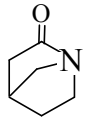
and

(II)

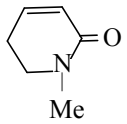
6. a) Monochlorination of propane is less selective (product ratio 60:40) than mono-bromination of propane (97:3). Explain the observation in the light of Hammond postulate. $1\frac{1}{2}$

b) Arrange the following amides in increasing order of basicity. Give reasons. 1


(I)


(II)

and



c) The first ionisation constant of maleic acid (*cis*-butenedioic acid) is greater than fumaric acid (*trans*-butenedioic acid). But the second ionisation constant of fumaric acid is greater than maleic acid — Explain. $1\frac{1}{2}$

B. Sc. Chemistry Examination, 2023

(1st Year, 2nd Semester)

CHEMISTRY (CORE)

Paper: Core/Chem/Th/03

Time : Two Hours Full Marks : 40

(20 marks for each unit)

Use a separate answer script for each unit.

UNIT - 2031-I

1. Answer all questions:

a) Considering Born-Haber cycles for CaF and CaF_2, calculate heat of formation of each using values provided below. From the obtained heat of formation, mention why CaF is non-existant.

[$\Delta H_S^{Ca} = 121$ KJ/mol; $\Delta H_{IP}^{Ca^+} = 590$ KJ/mol;

$\Delta H_{IP}^{Ca^{++}} = 1145$ KJ/mol; $\Delta H_{BD}^{F_2} = 157$ KJ/mol;

$\Delta H_{EA}^{F} = -335$ KJ/mol; $\Delta H_l^{CaF} = -795$ KJ/mol;

$\Delta H_l^{CaF_2} = -2805$ KJ/mol] $(1\times2)+\frac{1}{2}$

b) With the help of suitable calculations, derive the limiting condition for radius-ratio of cation to anion in a body-centred cubic lattice having coordination number four. Give an example of a compound that crystallizes in this structure. $1+\frac{1}{2}$

c) Using VSEPR explain shape of ICl_2^-. $1\frac{1}{2}$

d) Melting points of group II metal carbonates are provided in parentheses.
$BeCO_3$ (54°C); $MgCO_3$ (540°C); $CaCO_3$ (825°C); $SrCO_3$ (1494°C); $BaCO_3$ (811°C). Comment on thermal stability of group II metal carbonates. 1

e) Define i) Madelung constant, ii) Ion-pair energy. $\frac{1}{2}+\frac{1}{2}$

f) Radius of some ions are provided below.
Li^+ = 76 pm; Cl^- = 181 pm; Br^- = 196 pm and I^- = 216 pm. Predict structures of Li halides from radius-ratio calculations. Why then do these Li halides form face centred cubic lattice with octahedral arrangement of ions? $\frac{1}{2}+1$

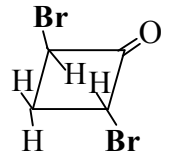
g) Using any theory of your choice, compare structures of HF, CO_2 and I_3^-. 1

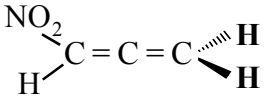
2. a) Explain Szilard-Chalmers effect. What is hot atom chemistry (HAC) in nuclear chemistry? $2+\frac{1}{2}$

b) What are doubly magic number nuclei? Give two examples. 2

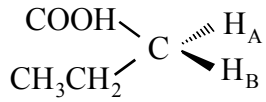
c) One microgram of phosphorous-32 was injected into a living system for biological tracer studies. The half-life of $^{32}P_{15}$ is 14.3 days. How long will it take for the radioactivity to fall to 10% of its initial value? $1\frac{1}{2}$

4. a) Assign the indicated pair of atoms as homotopic, enantiotopic or diastereotopic and justify. (any ***one***) 1

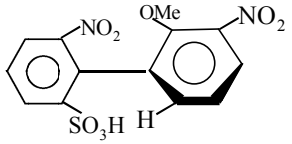
i) 

ii) 

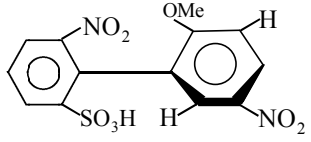
b) Identify the Pro-*R* and Pro-*S* hydrogen atoms (marked) in the following compound with explanation. 1



c) The rate of recemisation of (**A**) is much slower than that of (**B**) – explain. 1

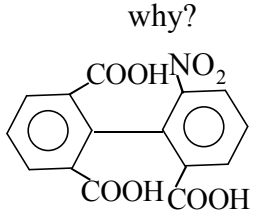


(**A**)

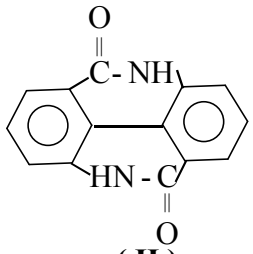


(**B**)

d) Which of the following compound is resolable and why? 1

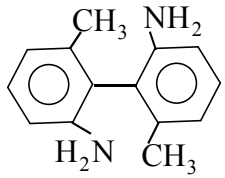


(I)

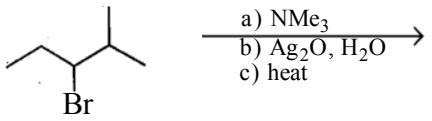


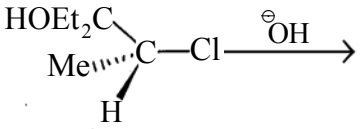
(II)

and



(III)

iv) 

v) 

b) Answer ***any two*** of the following questions: 2×2

i) Write down the product(s) formed when 3,3-dimethyl-2-butanol is heated in presence of conc. H_2SO_4. Identify the major product and justify with the plausible mechanism.

ii) Which member of the following pair of compounds results in higher ratio of substitution (S_N2) to elimination (E_2) when treated with NaOEt/EtOH?

$(CH_3)_2CHBr$, $(CH_3)_3CBr$

iii) Hydrolysis of *tert*-butyl bromide in 90% aqueous acetone at 50°C proceeds at about the same rate as in the presence of either LiBr or LiCl, whereas benzhydryl chloride (Ph_2CHCl) is only 3 times slower in the presence of LiCl as in the presence of LiBr.

d) Binding energy per nucleon for $^{238}U_{92}$ is about 7.5 MeV, whereas it is about 8.5 MeV for nuclei of half that mass. If $^{238}U_{92}$ nucleus were to split into two equal size nuclei, how much energy would be released in the process? 1

e) Explain the basic principle of (any one): 1

i) Shell model of the nucleus

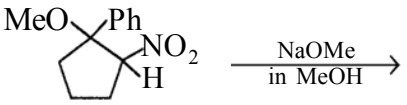
ii) Meson exchange theory

f) A piece of hair from an old cave gives 4 counts per minute from one gram of carbon. How old is the hair, if for a freshly-cut hair, the number of counts per minute per gram of carbon is 15.3 ($t_{1/2}$ for ^{14}C=5760 years)? 2

UNIT - 2032-O

3. a) Predict the product(s) of the following reactions and explain with plausible mechanism. Identify the major product (Answer ***any three***) 3×2

i) 

ii) 

iii)