Index Number: .....

Chemistry Olympiad Sri Lanka

Preliminary Selection Test – 2019

Answer ALL questions Number of Pages 16 Time: 2 hours + 10 minutes reading time

Do not open the question paper until told to do so.

Composition: **Section A: 16 Multiple Choice Questions (25%) and Section B: 3 Structured Questions (75%)**.

Section A: Multiple Choice Questions: Choose the best answer out of the five choices.

a. Should indicate all your answers in the answer boxes provided on page 2.
b. Select the best answer for each question and mark a cross using a carbon pen as shown below.

17.	A.	B.	C.	D.	E.

c. Mark only **one answer** to each question. (Marks will not be given for marking more than one answers.)
d. Clearly write your **index number** on top write hand corner of the booklet.

Section B: Structured Questions

e. **Use the given space** to write the answers. Rough sheets are provided for additional work but that cannot be attached with this booklet. Show your final answers clearly (underline or box)

Non programmable standard calculators are allowed, but any other electronic devices (smart watches) are not allowed.

PERIODIC TABLE OF THE ELEMENTS

1 1A																	18 8A
1 H 1.008	2 2A											13 3A	14 4A	15 5A	16 6A	17 7A	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Ds (281)	111 Rg (272)	112 Cn (285)	113 (Uut) (284)	114 Fl (289)	115 (Uup) (288)	116 Lv (293)	117 (Uus) (294)	118 (Uuo) (294)

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

Physical Constants

Gas Constant 8.314 J mol^{-1} K^{-1}	Avogadro Number 6.022×10^{23} mol^{-1}	0 °C = 273.15 K 1 atm = 760 mm Hg
Plank constant 6.6×10^{-34} m^2 kg s^{-1}	Standard temperature and pressure: 273 K and 100 kPa	

Answer boxes for Part A

1.	A	B	C	D	E	9.	A	B	C	D	E
2.	A	B	C	D	E	10.	A	B	C	D	E
3.	A	B	C	D	E	11.	A	B	C	D	E
4.	A	B	C	D	E	12.	A	B	C	D	E
5.	A	B	C	D	E	13.	A	B	C	D	E
6.	A	B	C	D	E	14.	A	B	C	D	E
7.	A	B	C	D	E	15.	A	B	C	D	E
8.	A	B	C	D	E	16.	A	B	C	D	E

Section A: Multiple Choice Questions

1. What is the electronic configuration of chlorine atom in potassium perchlorate ($KClO_4$)?
   A. $2s^2\ 2p^6$ B. $3s^1\ 3p^6$ C. $3s^2\ 3p^5$ D. $3s^1\ 3p^5$ E. $3s^2\ 3p^0$

2. One of the compounds given below has both oxidizing and reducing properties. This compound could be
   A. N_2O_5 B. HNO_3 C. NO_2 D. NH_3 E. Non of the above answers

3. Which one of the following molecules is the most polar?
   A. SF_6 B. $SnCl_4$ C. XeF_4 D. PCl_5 E. $TeCl_4$

4. Following data has been provided to explain the solubility of NaCl in water:

   ΔH_{solv} = +31 kJ mol^{-1}, $S(Na^+(aq))$ = 320.9 $JK^{-1}mol^{-1}$, $S(Cl^-(aq))$ = 56.5 $JK^{-1}mol^{-1}$, Entropy $S(NaCl(s))$ = 72.1 $JK^{-1}mol^{-1}$

   Consider the following statements

   I. Dissolution of NaCl in water is an endothermic reaction
   II. Entropy change of solvation of NaCl is positive
   III. Solvation of NaCl is spontaneous below 92.3 K
   IV. NaCl does not dissolve in water below 101.5 K

   Which of the above statement/s is/are true

   A. I only B. I & II only C. I & II and III only D. I, II and IV only E. All the statements

5. A spontaneous reaction occurs if Cl_2 and Br_2 are added to a solution containing Cl^- and Br^- ions. Select the statement that is true and justify the above reaction.
   A. Bromine has a higher electronegativity than chlorine, it will be reduced more easily.
   B. Chlorine has a higher electronegativity than bromine, it will be reduced more easily.
   C. Bromine has a higher electronegativity than chlorine, it will be oxidized more easily.
   D. Chlorine has a higher electronegativity than bromine, it will be oxidized more easily.
   E. None of the statements explain the above reaction.

6. Metal bromide (0.0005 mol) was dissolved in water. This solution required 40.00 cm^3 of 0.025 M silver nitrate solution to complete precipitate of silver bromide. These results are consistent with a metal bromide having the formula. (X is metal)
   A. X_2Br B. XBr C. XBr_2 D. XBr_3 E. X_2Br_3

7. Total number carboxylic acids and ester isomers that can be drawn for the molecular formula $C_4H_8O_2$ is (Carboxylic acids and esters have structural formula of R-COOH and R'COOR respectively.)
   A. 6 B. 5 C. 4 D. 3 E. 2

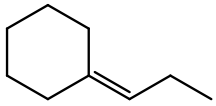
8. Which of the following compounds could not be prepared by oxidizing phosphorus trifluoride, PF_3?
   A. $Na_4P_2O_7.10H_2O$ B. $H_4P_2O_6$ C. KPF_6 D. $(NH_4)_2HPO_3.H_2O$ E. $Ca_5(PO_4)_3F$

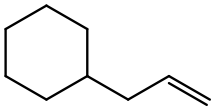
9. Calculate the volume of 3.0 M HCl needed to decompose 0.76 g of a rock sample. Assume that the sample is pure mineral dolomite $CaMg(CO_3)_2$ and you need 10% excess of the acid.
   A. 6.1 cm^3 B. 7.2 cm^3 C. 7.7 cm^3 D. 8.4 cm^3 E. None of the answers given

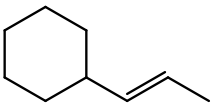
Question 10 is connected to question 9

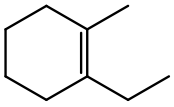
10. After decomposing the sample solution was boiled and then transferred to a 250 cm^3 volumetric flask Then deionized water was added to the mark. What would be the pH of this solution?
    pH = -log $[H^+]$ (negative log of H^+ concentration)
    A. 2.2 B. 2.5 C 2.7 D. 2.9 E. 3.1

11. It is known that highly substituted alkenes are more stable than less substituted alkenes. Consider the following alkenes.

(i) 

(ii) 

(iii) 

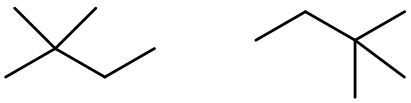
(iv) 

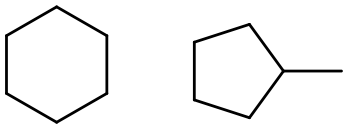
Which of the following answers shows the correct order of the increasing stability of the above alkenes?

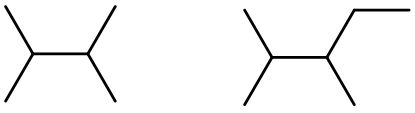
A. ii > iii > i > iv B. iv > ii > i > iii C. iii > iv > i > ii

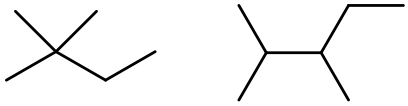
D. iv > i > iii > ii E. iv > i > ii > iii

12. Chain isomers have the same molecular formula, but different atomic arrangements. Which of the following pairs represent chain isomers?

A. 

B. 

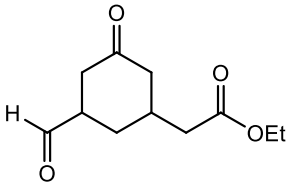
C. 

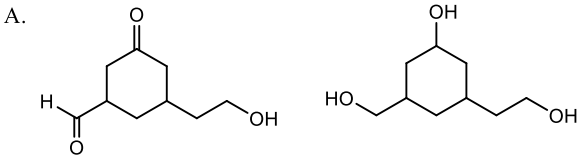
D. 

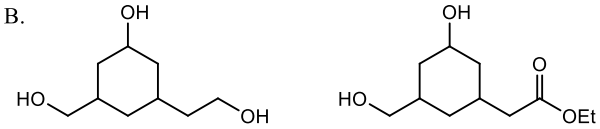
E. None of the above

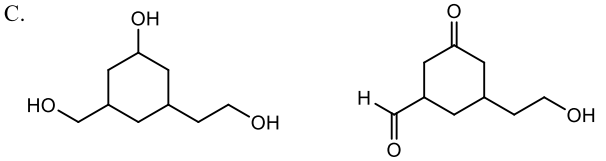
13. $LiAlH_4$ is a powerful reducing agent than $NaBH_4$. $LiAlH_4$ reduces aldehydes and esters into primary alcohols, and ketones in to secondary alcohols while $NaBH_4$ reduces only aldehydes and ketones in to primary and secondary alcohols, respectively. (A list of functional groups and their structures are given in page 14)

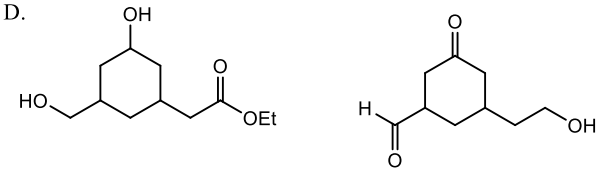
    Which of the following answers shows the reduced products of the following molecule when $LiAlH_4$ and $NaBH_4$, respectively?

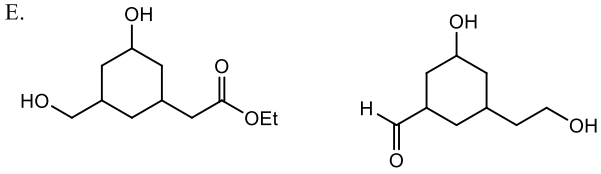


A. 

B. 

C. 

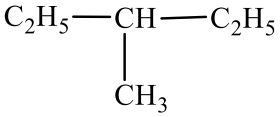
D. 

E. 

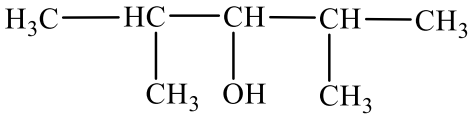
14. General formula for a non-cyclic alkane is C_nH_{2n+2}. Which pair represents the general formulae for an alkene (with double bonds) and alkyne (with triple bonds), respectively?
    A. C_nH_{2n} and C_nH_{2n-2}
    B. C_nH_{2n-4} and C_nH_{2n}
    C. C_nH_{2n-2} and C_nH_{2n-4}
    D. C_nH_{2n-2} and C_nH_{2n}
    E. C_nH_{2n} and C_nH_{2n-4}

15. The presence of an asymmetric carbon center is one of the structural features of a chiral molecule. Select the correct statement regarding the chirality of the following structures.

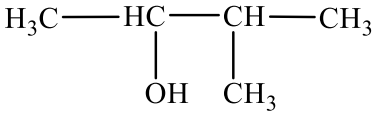
(i)



(ii)



(iii)



A. Only (i) is chiral
B. Only (ii) is chiral
C. Only (iii) is chiral
D. Both (i) and (ii) are chiral
E. All three structures are chiral compounds

16. The *de Broglie wavelength* is inversely proportional to the particle's momentum. Consider the following statements regarding *de Broglie wavelength:*

I. An electron traveling at the speed of light has a higher *de Broglie* wavelength than proton traveling at the same speed.
II. *de Broglie* wavelength of a cricket ball traveling at 100 km/h is significantly greater than an electron traveling at 1/100 of speed of light.
III. Since de Broglie wavelength of macroscopic particles like cricket ball is significantly higher than that of electrons, quantum effects are unobservable for the motion of macroscopic objects.

Which of the above statement/s is/are true?

A. Only I B. Only I and III C. Only II and III D. All three statements
E. None of the above three statements

Section B: Structured Questions

Question 1 (Total 25 marks)

I. An experiment was carried out to determine the acid concentration of a given solution using a mixture of iodate/iodide (IO_3^-/I^-). In the presence of an acid (H^+), IO_3^- and I^- react together to yield proportional amount of I_2. The reaction completes within 15 minute in the presence of strong acids. Iodine liberated can be determined by a titration with sodium thiosulfate ($Na_2S_2O_3$). {during the reaction with iodine (I_2), $S_2O_3^{2-}$ ions are oxidized to $S_4O_6^{2-}$)

(a) Draw the most acceptable Lewis structures of $S_2O_3^{2-}$ and $S_4O_6^{2-}$ ions (02 marks)

(b) Write the balanced equations for the two reactions mentioned above. (04 marks)

IO_3^- and I^-

I_2 and $S_2O_3^{2-}$

(c) In this experiment thiosulfate is added when concentration of H^+ in the medium is less. This is because in an acidic solution, thiosulfate undergoes an undesired side reaction that yields elemental sulfur. Write the balanced equation for this reaction. (You have to predict the product/s formed) {Hint: no gas or water will be formed} (02 marks)

(d) Following procedure was carried out to standardize (to determine the exact concentration) a solution of $Na_2S_2O_3$.

Pipette 20.00 cm^3 of the 0.05 M standard iodine solution (V_1) was pipetted into an Erlenmeyer flask, 25 cm^3 of distilled water was added and titrated with the thiosulfate solution until a colour change from colourless to pale yellow was observed. Then 3 cm^3 of the starch indicator was added and titration was continued until blue colour disappeared (V_2). Procedure was repeated 3 times. The titrant volumes are as follows.

V_2 (cm^3)	19.80	20.10	20.10

Determine the concentration of $Na_2S_2O_3$. (01 marks)

(e) Following procedure was carried out to analyze a strong acid solution

20.00 cm^3 of an unknown acid solution was pipetted out into the flask, 5 cm^3 of the KI solution and 5 cm^3 of the KIO_3 solution were added using the plastic transfer pipettes. The flask was stoppered and allowed to stand in the dark for 15 minutes. Then the produced iodine was titrated using the thiosulfate solution. Volume of thiosulfate solution required to reach the end point was 11.20 cm^3.

Assuming that there is an excess IO_3^-/I^- present, determine the concentration of the acid. (03 marks)

(f) One cannot apply the above procedure (part e) to determine the concentration of a weak acid such as oxalic acid ($C_2H_2O_4$) in a sample. Thus, in such a case, procedure can be slightly modified by converting the weak acid to an equivalent amount of strong acid.

Accordingly, 100.00 cm^3 of an unknown solution containing oxalic acid was taken into a flask. 5 cm^3 of the KI solution and 5 cm^3 of the KIO_3 solutions together with few grams of $\underline{CaCl_2}$ were added to the flask. The flask was stoppered and allowed to stand in the dark for 15 minutes. Produced iodine was titrated using the thiosulfate solution.

What is the additional chemical reaction occurred in this experiment? (Write a balanced equation) (02 marks)

(g) After adding $CaCl_2$, pH of the solution was 2.00. What should be the minimum amount of $CaCl_2$ needed to make this procedure a success? (Assume the sample only contained oxalic acid) {definition: pH = -log $[H^+]$ } (02 marks)

II. The Bray-Liebhafsky (BL) reaction is one of the fascinating chemical reactions in Chemistry because it can act as a Chemical Oscillator. During this reaction, hydrogen peroxide decomposed into oxygen and water in the presence iodate in acidic medium (shown below).

$$2H_2O_2 \xrightarrow{IO_3^-,\ H^+} 2H_2O + O_2$$

The above reaction is the result of **two reactions** where hydrogen peroxide acts as a reducing as well as an oxidizing agent. Accordingly, in the first reaction, H_2O_2 reacts with IO_3^- to form I_2 and in the second reaction, I_2 reacts with H_2O_2 to form IO_3^- again. Thus, sum of the two reactions yields the above decomposition of H_2O_2 and IO_3^- also acts as a catalyst. This reaction is known as a chemical oscillator because the concentration of iodine periodically oscillates as long as H_2O_2 remains in the mixture.

(a) Sketch (draw) the shape of H_2O_2 molecule (01 mark)

(b) Draw the Lewis structure of IO_3^- and it's resonance structures (2 marks)

(c) Obtain the **two reactions** taking place as mentioned above using relevant half reactions (04 marks)

(i) Reaction where H_2O_2 acts as a reducing agent.

(ii) Reaction where H_2O_2 acts as an oxidizing agent.

(d) During this reaction several iodine containing intermediates are formed. Based on your knowledge on molecular structure, circle which of the following cannot be an intermediate/intermediates in the reaction. (2 marks)

IOH IO_2H I_2O_3 I_2O I_3O IO_2H_2 IO_3H

Find the oxidation numbers of iodine in each intermediate.

Question 2 (25 marks)

I. Liquefied Petroleum Gas (LPG) is a vital source of energy for millions of people around the world. LPG is a mixture of propane (C_3H_8) and butane (C_4H_{10}).

In order to determine the ratio of propane and butane in domestic LPG the following experiment was conducted. Volume of 1.12 dm^3 of LPG was burnt in the excess of oxygen. The obtained carbon dioxide was blown through a solution of NaOH and was observed that 9.54 g of sodium carbonate and 8.40 g of sodium bicarbonate were formed. (Assume ideal gas behavior for calculations)

(a) Write balanced chemical equations for all the reactions that may have occurred in this experiment. (02 marks)

(b) Calculate the amount of CO_2 released and its approximate volume at 25^0C and 1 bar pressure (2 marks)

(c) Calculate the mass fraction of propane in the mixture. (02 marks)

II. In some countries you can find LPG cylinders with pure propane or pure butane. Consider the weight of LPG (propane or butane) in such a cylinder is 13 kg. A 'completely full' cylinder at a pressure of 140 psi (equal to 9.52 atm) is in fact only filled to about 87% capacity with liquid gas, the remaining volume being taken up by the vapour. The standard enthalpy change for the complete combustion of propane and butane are -2220 kJ mol^{-1} and -2877 kJ mol^{-1} respectively.

(a) Calculate the total amount of heat energy released by combustion of all the propane in a cylinder under standard temperature and pressure. (1 mark)

(b) Calculate the mass of carbon dioxide produced in kilograms when all of the propane in the cylinder is burnt completely. Thus, calculate the kilograms of CO_2 released to generate 1 kJ of heat. (2 marks)

(c) Repeat the calculations (above part a and b) for butane. (02 marks)

(d) Which gas causes less environmental impact in terms of CO_2 emission? Circle (01 mark)

C_3H_8 or C_4H_{10}

(e) Calculate the rate at which propane must leave the cylinder (in cm^3s^{-1}) to produce 15 kW (i.e. 15 kJ s^{-1}). (02 mark)

(f) According to the information given above, find SI unit equivalent to 1 psi. (01 mark)

III. Because pure propane and butane gases are odorless, small amounts of other compounds are usually added so that gas leaks can be detected. Ethyl Mercaptan (ethanethiol, C_2H_5SH) is one such compounds which gives a peculiar smell.

a) Draw the possible structure of ethyl mercaptan and predict the bond angle around the sulfur atom (02 mark)

b) Calculate the mass of Ethyl Mercaptan which must be added to 13 kg of propane to produce 0.02 molecules of ethyl mercaptan per million molecules of propane. (02 marks)

c) Arrange propane, butane, ethanol and ethyl Mercaptan in the order of decreasing boiling points. (Use English letters) (01 marks)

IV. Gases mentioned in this question (CO_2 and hydrocarbons) may deviate considerably from the ideal behavior. Therefore, these gases have significantly larger volume than ideal gasses. Van der Waals equation given below can be used to obtain much better value for molar volume.

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

P= pressure, *V*= Volume, *R*= Universal gas constant, *n* – number of moles
a and *b* are constants for a given gas.

a) Deduce the SI units of a and b? (1.5 marks)

b) Obtain an expression for the molar volume (V_m) using the Van der Waals equation (1.5 marks)

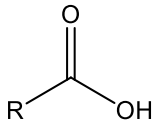
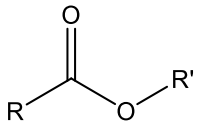
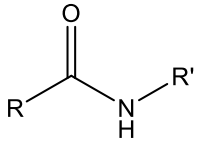
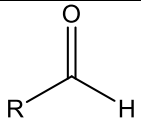
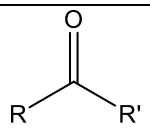
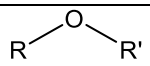
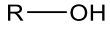
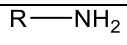
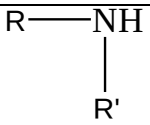
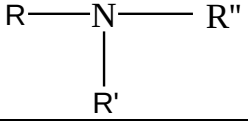
c) Further simplify the above expression in part b) and obtain a cubic equation of V_m to estimate the molar volume of CO_2 at Standard temperature and pressure in terms of *a* and *b*. (02 marks)

Question 3 (25 marks)

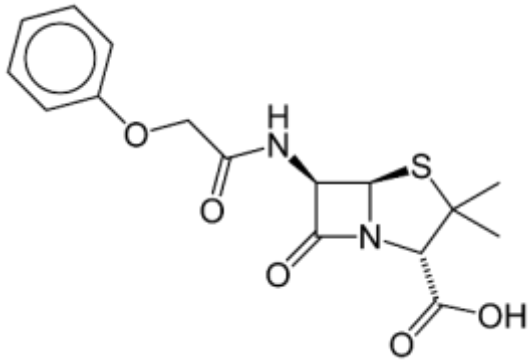
Functional groups are a group of atoms arranged in a particular way that is unique in all molecules. One molecule can contain a variety of functional groups.

A list of common organic functional groups and what they look like is shown in **Table 1**. Note that R, R', R" are used to symbolize further bonding to other carbon atoms that may contain other functionality, but will not affect the identification of the functional group.

Table 1: A list of common organic functional groups

Functional group	Symbol	Structure
Carboxylic acid	R-COOH	
Ester	R-COR'	
Amide	R-CO-NHR'	
Aldehyde	R-CHO	
Ketone	R-CO-R'	
Ether	R-O-R'	
Alcohol	R-OH	
Primary Amine	$R-NH_2$	
Secondary Amine	RR'NH	
Tertiary Amine	RR'R"N	

I. Structure of the antibiotic phenoxymethylpenicillin (Penicillin V) is shown below. It has several specific functional groups that are responsible for the characteristic chemical properties. Identify and circle the functional groups and name them (use English letters only).



(03 marks)

II. Structural isomers are molecules which have the same molecular formula but differ in the linkages of atoms (connections). Amines can be categorized as primary (RNH_2), secondary (RR'NH) and tertiary (RR'R"N) amines where R, R' and R" are alkyl groups.

a) Draw the structural isomers of $C_4H_{11}N$ which are primary amines?

b) Draw the structural isomers of $C_4H_{11}N$ which are secondary amines?

c) Draw the structural isomers of $C_4H_{11}N$ which are tertiary amines?

(07 marks)

III. Functional group isomers have the same molecular formula, but they have different functional groups. Draw the structures of the functional group isomers for each of the following. (04 marks)

a) C_3H_8O

b) $C_3H_6O_2$

IV. The unsaturation number of a molecule can be calculated using the following equation.

Unsaturation number = ½ {Maximum number of Hydrogens could be present in the molecule – Number of Hydrogens present in the molecule}

Maximum number of Hydrogens could be present in the molecule with n number of carbon atoms = 2n+2. When considering the number of hydrogens present in the molecule replace the halogens (if any) with hydrogens and add that to the actual number of hydrogens present in the molecule. Disregard any oxygens present in the molecule. Subtract each nitrogen (if any) from a hydrogen.

(i) Calculate the unsaturation number of $C_3H_4Cl_2$. (02 marks)

(ii) Draw two possible isomers of $C_3H_4Cl_2$. (02 marks)

V. Nucleophilic centers generally involve an atom that has a negative charge or a neutral atom with one or more lone pairs of electrons. Electrophilic centres are those that have a positive charge or are connected to an electron-withdrawing group.

Identify the following as nucleophilic (Nu), electrophilic (El) or neither (N). (Use English letters)

a) CH_3Br b) NH_3 c) CH_4 d) OH^-

(2 marks)