UNIVERSITY OF RUHUNA
BACHELOR OF SCIENCE GENERAL DEGREE–LEVEL II
(SEMESTER II) EXAMINATIONS – JANUARY 2018

SUBJECT: CHEMISTRY **TIME**: Three **(03)** hours
COURSE UNIT: CHE 2214

Answer **six (06)** questions only by selecting **two (02)** from each of the sections, **A**, **B**, and **C**

Physical Constants

Velocity of light, c	=	3×10^{8} m s^{-1}
Avogadro's number, N_A	=	6.022×10^{23} mol^{-1}
Universal gas constant, R	=	8.314 J K^{-1} mol^{-1}
Boltzmann constant, k	=	1.381×10^{-23} J K^{-1}
Faraday constant, F	=	9.6485×10^{4} C mol^{-1}
Electron charge, e	=	-1.602×10^{-19} C
Planck's constant, h	=	6.626×10^{-34} J s
Proton mass, m_p	=	1.673×10^{-27} kg
Electron mass, m_e	=	9.10×10^{-31} kg
Vacuum permittivity, ε_0	=	8.854×10^{-12} J^{-1} C^2 m^{-1}
Standard pressure	=	1.01325×10^{5} Pa
Atomic mass unit, *amu*	=	1.6606×10^{-27} kg

Useful Conversion Factors

1 atm = 760 mmHg = 1.01325 bar = 101325 Pa

2.303 (RT/F) = 59.15 mV at 298.15 K

1 eV = 1.6022×10^{-19} J

Section A

01. Answer **all** parts.

(a) Even though hydrogen is placed in Group 1 in the Periodic Table, it can be placed in Group 17 as well as Group 14. Explain this briefly.

(15 marks)

(b) The chemistry of Li is very similar to that of Mg even though they are placed in two different groups in the Periodic Table. Indicate the reason(s) for this. Give four examples to justify your answer.

(20 marks)

(c) Write balanced chemical equations for the following reactions:

(i) $SrCO_3(s) \xrightarrow{\Delta}$

(ii) $Ba(OH)_2(s) \xrightarrow{\Delta}$

(iii) $LiNO_3(s) \xrightarrow{\Delta}$

(iv) $Na_2O_2(s) + H_2O(l) \rightarrow$

(v) $CaO(s) + HCl(aq) \rightarrow$

(25 marks)

(d) Define the term "hydration enthalpy". Giving reasons arrange the following ions of alkali metals and alkaline earth metals in decreasing order of their hydration enthalpies.
Be^{2+}, Cs^+, Li^+, Mg^{2+}, Na^+

(20 marks)

(e) When considering the elements Ba, Ca, and Sr, which element is the strongest reducing agent? Give reasons for your answer.

(20 marks)

02. Answer **all** parts.

(a) Amorphous boron is reactive, while crystalline boron is comparatively unreactive.
Write balanced chemical equations for the synthesis of the following boron compounds.

(i) B_2O_3

(ii) BN

(iii) BCl_3

(iv) Na_3BO_3

(v) $B_2H_6.\ 2NH_3$

(vi) $B_3N_3H_6$

(30 marks)

UNIVERSITY OF RUHUNA
BACHELOR OF SCIENCE GENERAL DEGREE–LEVEL I
(SEMESTER II) EXAMINATIONS – FEBRUARY 2018

SUBJECT: CHEMISTRY **TIME:** Three **(03)** hours.
COURSE UNIT: CHE 1214

Answer **six (06)** questions only by selecting
One (01) from **section A,**
Three (03) from **section B**, and
Two (02) from **section C**.

Physical Constants

Velocity of light, c	=	3×10^{8} m s^{-1}
Avogadro's number, N_A	=	6.022×10^{23} mol^{-1}
Universal gas constant, R	=	8.314 J K^{-1} mol^{-1}
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Useful Conversion Factors

1 atm = 760 mmHg = 1.01325 bar = 101325 Pa

2.303 (RT/F) = 59.15 mV at 298.15 K

1 eV = 1.6022×10^{-19} J

(b) Explain the following statements using the relevant chemistry.

(i) "Even though B_2H_6 and Al_2Cl_6 have similar structures, their bonding is totally different" .

(ii) $N(CH_3)_3$ is pyramidal but $N(SiH_3)_3$ is planar.

(iii) Phosphorous trioxide and phosphorous pentoxide have dimeric structures.

(30 marks)

(c) In 1962, Neil Bartlett, then at the University of British Columbia, prepared a red coloured compound which was formulated as $O_2^+PtF_6^-$. Then he realised that the first ionization energy (IE) of O_2 (1175 kJ mol^{-1}) was almost identical to the first ionization energy of Nobel gas **A** (1170 kJ mol^{-1}). He made another red coloured compound $\mathbf{A}^+PtF_6^-$ by mixing PtF_6 and **A** in a 1:1 molar ratio. The reaction of elements, **A** and F in a 1:5 ratio under a pressure of 7 bar at 873 K temperature produced a colourless crystalline solid **B** which sublimed at 298 K. **B** readily hydrolysed even by traces of water giving a colourless explosive solid **C**. **B** reacts with SbF_5 to produce $[\mathbf{D}]^+[SbF_6]^-$.

(i) Identify **A-D**

(ii) Draw the shapes of molecules **B** and **C**

(iii) Give balanced chemical reactions for the conversion of **B** to **C**.

(40 marks)

Section B

03. Answer **all** parts.

(a) (i) Write brief accounts on the reactivity of the following categories of aliphatic compounds.

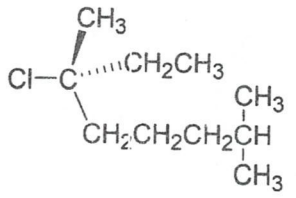
(I) alkanes

(II) alkenes

(III) alkynes

(15 marks)

(b) The neucleophilic substitution of (*R*)-6-chloro-2,6-dimethyloctane with water produces a racemic mixture of 3,7-dimethyloctan-3-ol. Explain this observation.



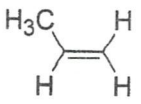
(*R*)-6-chloro-2,6-dimethyloctane

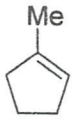
(15 marks)

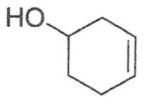
(c) Write down the major product(s) of the following reactions giving emphasis to the stereochemistry when necessary.

(I)  $\xrightarrow{H^+ / H_2O}$?

(II) $H_3CC{\equiv}CH \xrightarrow[\text{Liq. } NH_3]{NaNH_2}$? $\xrightarrow{CH_3CH_2Br}$?

(III)  $\xrightarrow[\text{2. } NaBH_4 / {}^-OH]{\text{1. } Hg(OAc)_2,\ H_2O,\ THF}$?

(IV)  $\xrightarrow[\text{2. } H_2O_2,\ NaOH,\ 25^oC]{\text{1. THF, } BH_3}$?

(V)  $\xrightarrow[CH_2Cl_2]{Ph(C{=}O)OOH}$?

(30 marks)

(d) Considering the following reactions of alkyl halides, answer the questions (i) and (ii).

(I) $H_3C-Br + (CH_3)_3CO^- \longrightarrow$

(II) $(CH_3)_3C-Br + CH_3O^- \longrightarrow$

(i) Propose the product of each of the above reactions.

(ii) Giving reasons name the reaction type involved in the formation of the proposed product in each of the above reactions.

(20 marks)

(e) Propose a plausible mechanism for the following conversion.

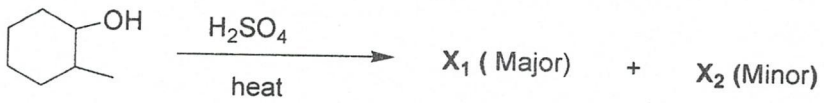
(20 marks)

04. Answer **all** parts.

(a) Compare the reactivity of aldehydes and ketones towards nucleophilic addition reactions.

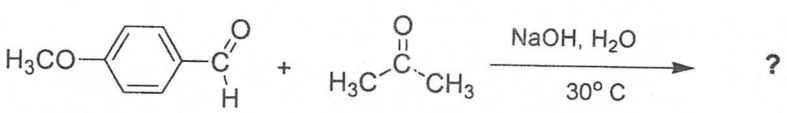
(10 marks)

(b) 2-Methylcyclohexanol has been subjected to acid catalyzed dehydration as shown below. Giving reasons identify the products X_1 and X_2.



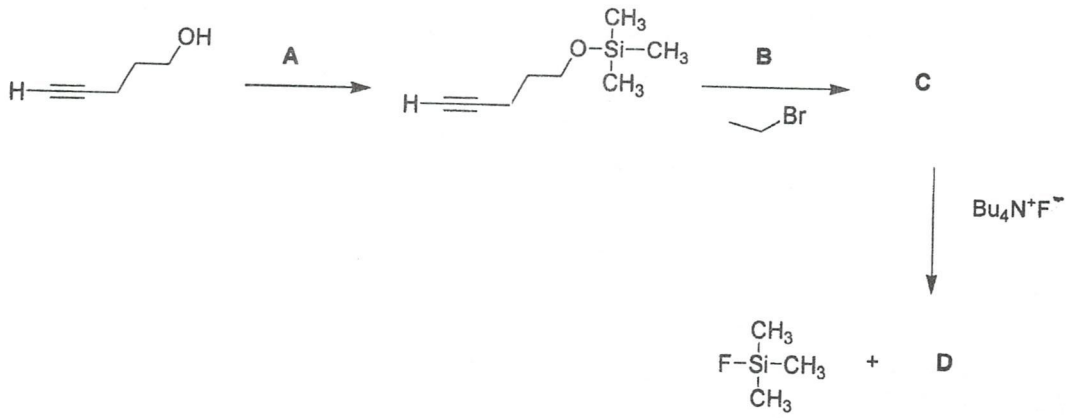
(15 marks)

(c) Giving a plausible reaction mechanism predict the product(s) of the following reaction.



(16 marks)

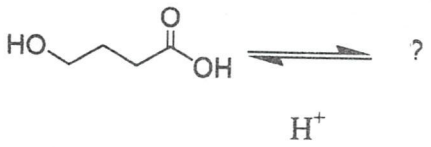
(d) Identify the reagents and intermediates **A-D** in the following reaction sequence.



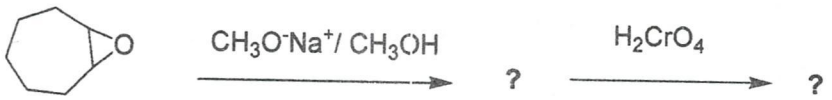
(16 marks)

(e) Write down the chemical structure of the product(s) of the following reactions.

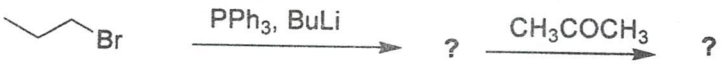
(i)



(ii)



(iii)



(25 marks)

(f) Giving suitable reagents and reaction conditions show how you would carry out the following conversions.

(i)

(ii)

(18 marks)

05. Answer **all** parts.

(a) (i) What are the special characteristics associated with aromaticity?

(ii) How can above mentioned characteristics be explained using structure of benzene based on hybridization theory?

(20 marks)

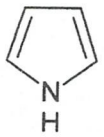
b) (i) How can "Frost circle" be used to draw π-molecular orbital energy level diagram of cyclic polyene? Consider benzene as an example to explain your answer.

(ii) Use π molecular orbital diagram of benzene to explain its stability.

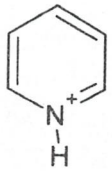
(30 marks)

c) (i) State Huckel rule in aromaticity.

(ii) Comment on the aromaticity of the following two molecules/ion(s), applying Huckel rule.



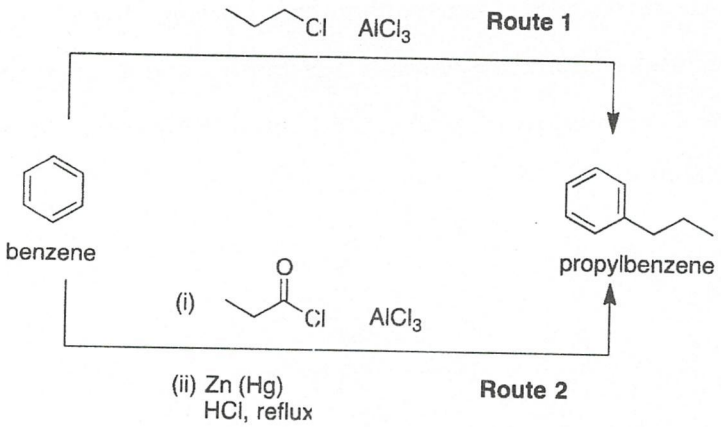
pyrrole



pyridinium ion

(20 marks)

(d) A student proposes the following two routes for the synthesis of propylbenzene from benzene.



(i) Draw the electrophiles involved in the route 1 and route 2.

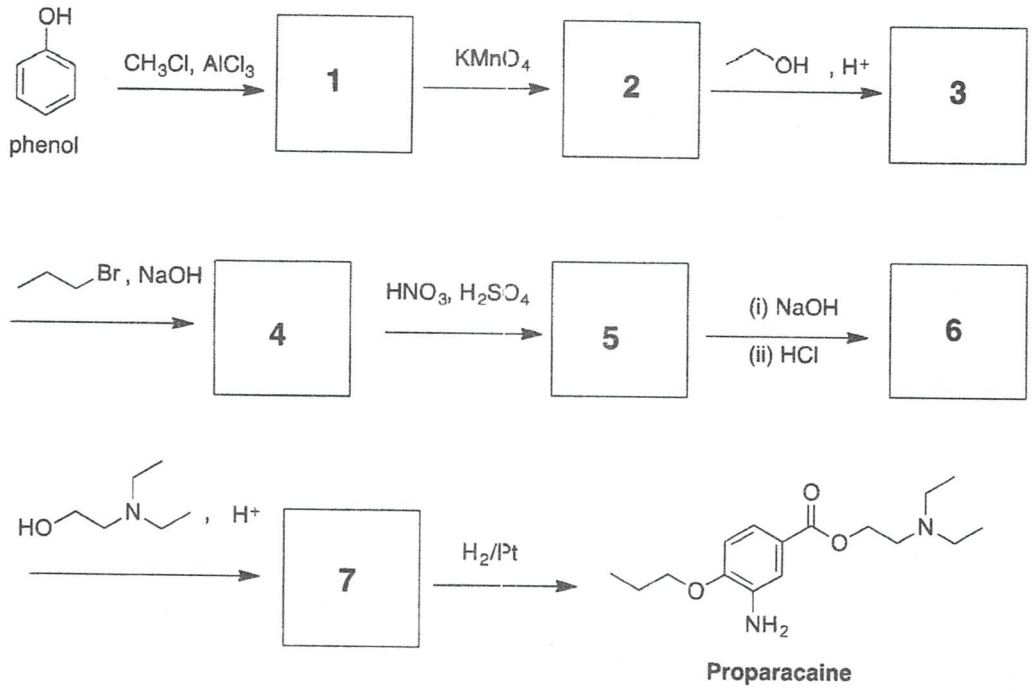
(ii) Which route is better for synthesizing propylbenzene? Give a reasonable explanation for your answer.

(iii) Draw a plausible mechanism for the formation of the product from the step (I) of route 2.

(30 marks)

06. Answer **all** parts.

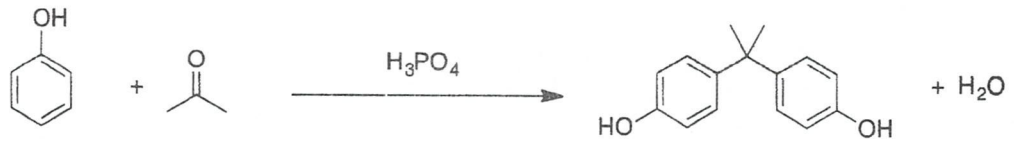
(a) Given below is a multistep synthetic scheme for *proparacaine*, a local anesthetic. Draw the structures of intermediates from **1** – **7** by considering the reagents and reaction conditions shown on each step.



Proparacaine

(30 marks)

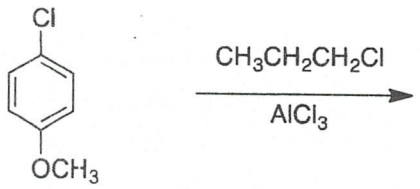
(b) Bisphenol A (BPA) is an important monomer in the production of polycarbonate. It is suspected as a hazardous food contaminant arising from its use in reusable polycarbonate food containers such as water bottles and kitchen utensils. Following reaction shows the synthesis of BPA from phenol. Propose a reasonable mechanism for this conversion.



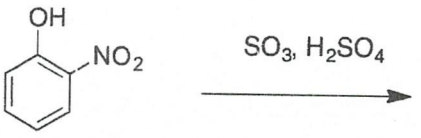
Bisphenol A (BPA)

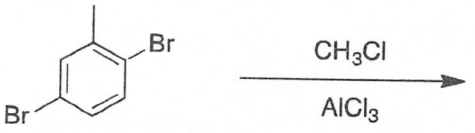
(20 marks)

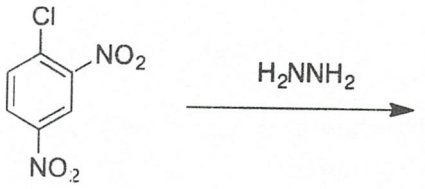
(c) Give the major product(s) of each of the following reactions:

(i) 

(ii) 

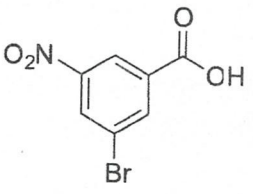
(iii) 

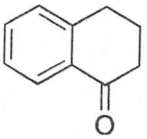
(iv) 

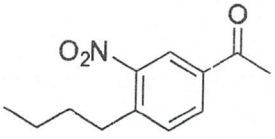
(v) 

(20 marks)

(d) Giving necessary reagents, reaction conditions and intermediates formed; show how you would synthesize the following compounds from benzene.

(i) 

(ii) 

(iii) 

(30 marks)

Section C

7. Answer **all** parts.

(a) Write short notes on the following pairs by comparing and contrasting. Give examples whenever necessary:

(i) Intensive properties and extensive properties

(ii) Adiabatic and isothermal processes

(iii) State functions and path functions

(iii) Constant pressure heat capacity (C_p) and constant volume heat capacity (C_v)

(40 marks)

(b) Consider a gas confined in a cylinder with a mass-less frictionless piston which undergoes an isothermal expansion from volume V_1 to V_2 against an external pressure of p_{ex}. Show that the amount of work (w) involved in this process is given by

(i) $w_{irr} = -p_{ex}(V_2 - V_1)$ for an irreversible expansion.

(ii) $w_{rev} = -\int_{V_1}^{V_2} p_{ex}\,dV$ for a reversible expansion.

(iii) Hence show that $w_{rev} = -nRT \ln(V_2/V_1)$ for n moles of an ideal gas at temperature T.

(25 marks)

(c) 2.50 mol of an ideal gas expands from an initial volume of 12.0 dm^3 and a temperature of 300 K to a final volume of 24.0 dm^3 and a temperature of 400 K.

Calculate (i) the work done,

(ii) the change in internal energy,

(iii) the heat absorbed, for each of the following paths:

(A) A reversible isothermal expansion at 300 K from 12.0 dm^3 to 24.0 dm^3 followed by heating at constant volume to 400 K.

(B) Heating at constant volume (12.0 dm^3) to 400 K followed by a eversible isothermal expansion at 400 K to 24.0 dm^3.

[Note: $C_V = 20.0\ J\ K^{-1}\ mol^{-1}$ and does not depend on T]

(35 marks)

08. Answer **all** Parts.

Decomposition N_2O_4 gas to NO_2 gas at 288 K was found to be first order and the decomposition is given by the elementary reaction,

$$N_2O_4(g) \longrightarrow 2NO_2(g).$$

(a) Starting from the differential rate law, show that the concentration of N_2O_4 at any time during the reaction is given by

$$\ln[N_2O_4] = \ln[N_2O_4]_0 - k_1 t,$$

where $[N_2O_4]_0$ and k_1 are initial concentration of N_2O_4 and first order rate constant respectively.

(30 marks)

(b) Show that the half-life of the reaction is independent of N_2O_4 concentration and it is inversely proportional to the rate constant.

(25 marks)

(c) Arrhenius equation accounts for the temperature dependence of a reaction rate and it is given by the equation ,

$$k = Ae^{\frac{-E_a}{RT}}.$$

Activation energy of the above reaction is 58.0 kJ mol^{-1}.

(i) At a certain temperature, T, the half-life of the reaction is 6.93×10^{-5} s. Calculate the rate constant at this temperature.

(10 marks)

(ii) If the rate constant of this reaction at 288 K is 4.5×10^3 s^{-1}, calculate the temperature T in part (i).

(25 marks)

(iii) Discuss the temperature dependence of the rate constant.

(10 marks)

09. Answer **all** parts.

(a) Distinguish between,

(i) The number of constituents and components of a system.
(ii) Critical point and triple point of one component system.

(20 marks)

(b) (i) Sketch phase diagrams of systems of two components, A and B to illustrate,

(I) Positive deviation from Raoult's law

(II) A low boiling azeotropic mixture.

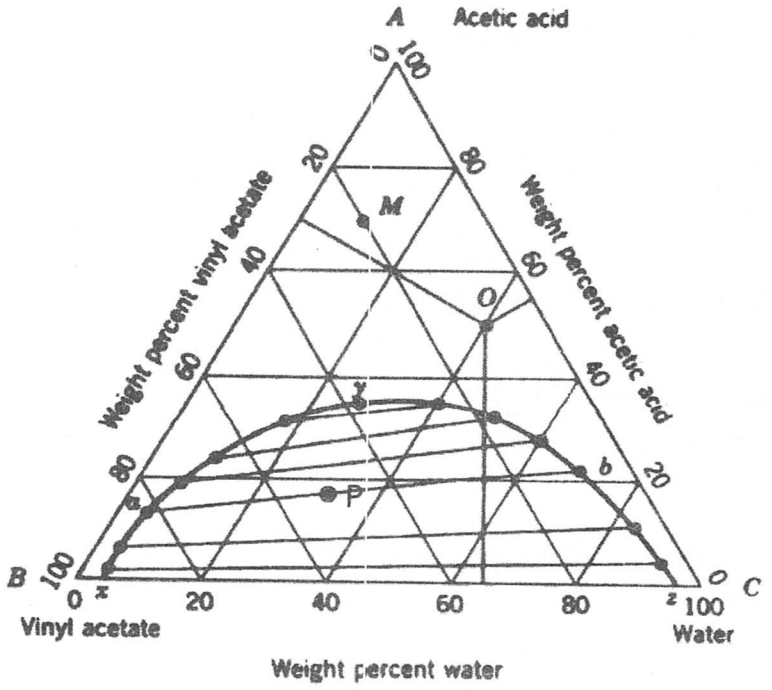
(III) A congruently melting compound A_2B

(30 marks)

(ii) Write down the principle behind steam distillation and give the advantage(s) of the method.

(15 marks)

(c) Three component equilibrium phase diagram of water, vinyl acetate and acetic acid at 25 °C and 1 atm showing regions of miscibility is given below. Answer the following questions using this phase diagram.



(i) Give the composition of the systems represented by the points M, and O on the diagram and find the degrees of freedom pertaining to them. Comment on the miscibility of all three components in each of the system.

(ii) Give the approximate weight ratio of phases *a* and *b* in equilibrium that are represented by the point P.

(35 marks)

@@@@@@@@@@@@@

Section A

01. Answer **all** parts.

(a) (i) Determine the oxidation state of the metal in each of the following organometallic compounds.

(I) $HCo(CO)_4$

(II) $(\eta^4\text{-}C_8H_{12})Fe(CO)_3$

(III) $Ir(CO)Cl(PMe_3)_2$

(IV) $(\eta^6\text{-}C_6H_6)Mo(CO)_3$

(05 x 4 marks)

(ii) The following organometallic compounds/ions obey the eighteen electron rule. Draw their structures indicating the hapticity of the Cp ligand.

(I) $Cp_2W(CO)_2$

(II) $CpMo(H)(CO)_3$

(III) $[Cp_2FeH]^+$

(05 x 3 marks)

(b) (i) Of the following ligands, which one would be the best σ-donor in forming organometallic compounds?

PMe_3, PF_6, PPh_3

(05 marks)

(ii) By using a suitable labeled diagram, explain the metal-carbon bonding in a metal carbonyl.

(10 marks)

(iii) Predict the possible product(s) of the following reactions.

(I) $(\eta^5\text{-}Cp)_2Fe + HBF_4 \rightarrow$

(II) $NaCp + FeCl_2 \rightarrow$

(III) $Mn_2(CO)_{10} + Br_2 \rightarrow$

(05 x 3 marks)

(c) The carbonyl stretching frequencies (ν_{CO}) of the IR spectra of $[Re(CO)_5]^+$, $[Os(CO)_6]^{2+}$, $W(CO)_6$ and $[Ir(CO)_6]^{3+}$ are given below. They are not given in the correct order.

1977 cm^{-1}, 2254 cm^{-1}, 2085 cm^{-1}, and 2190 cm^{-1}

Match the correct ν_{CO} value to each of the above organometallic compounds.

(05 x 4 marks)

Give reasons for your answer.

(15 marks)

02. Answer **all** parts

(a) (i) Giving balanced chemical equations whenever necessary, describe the sulphate process of the manufacture of TiO_2.

(20 marks)

(ii) Briefly discuss the importance of controlling the final heating temperature of the above process.

(05 marks)

(iii) Giving reasons explain how you would change the reaction conditions if the final product of the above process (TiO_2) is going to be used in the paper and garment production industries.

(20 marks)

(b) Chromite is the only naturally occurring economically important ore of Cr. When chromite is fused with NaOH in air, at 1100 ^{0}C a yellow coloured solution **(A)** and water insoluble metal oxide **(B)** are formed. After the separation of the precipitate, acidification and the evaporation of the liquid **(A)** gives an orange coloured crystalline product **(C).** Reduction of the product **(C)** with coke gives a green coloured product **(D).**

(i) Write the chemical formulae of the products **A** to **D**.

(ii) Write balanced chemical equations for the formation of the products **A** and **D**.

(iii) Explain how the yellow product **A** is used in the analysis of Ag^+ ions in deodorants.

(30 marks)

(c) Explain how you would distinguish the two Co complexes, $[Co(H_2O)_6]^{2+}$ and $[Co(NH_3)_6]^{3+}$ using their magnetic properties. Show the necessary calculations you would use in the explanation.

(25 marks)

03. Answer **all** parts

(a) The use of ionic liquids as reaction media is relatively a new field in chemistry.

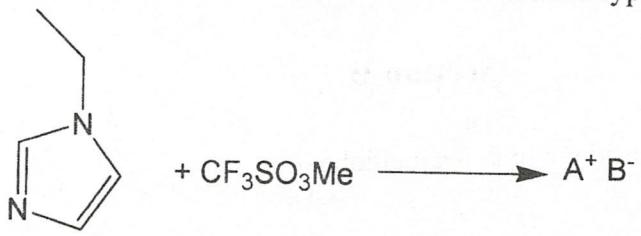
(i) What are ionic liquids?

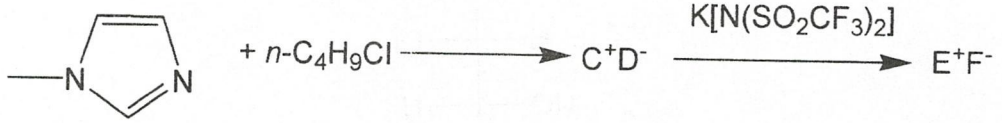
(05 marks)

(ii) Briefly explain why ionic liquids have a green advantage over organic solvents.

(05 marks)

(iii) Two methods used for the preparation of ionic liquids are given below. Identify the ion(s) labelled from A^+ to F^- and the related reaction type(s).

(I) 

(II) 

(20 marks)

(iv) Give **one** advantage of the second preparation method over the first preparation method in (iii) above.

(05 marks)

(b) Predict the product(s) of the following reactions and write balanced chemical equations.

(i) HF with SiO_2
(ii) SO_2Cl_2 with NH_3
(iii) Li with N_2O_4

(15 marks)

(c) (i) Draw the structures of the following.

(I) C_8 cubic carbon
(II) graphene
(III) cyanuric chloride ($C_3N_3Cl_3$)
(IV) trimetaphosphoric acid
(V) γ-SO_3

(25 marks)

(ii) State **two** differences between C_8 cubic carbon and graphene.

(05 marks)

(d) Predict the product(s) of the following reactions giving balanced chemical equations.

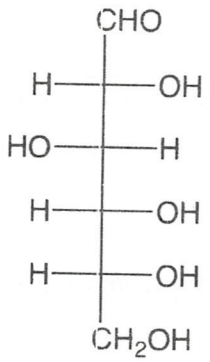
(i) $HCN + NO_2 \longrightarrow$
(ii) $LiCH_3 + SiCl_3 \longrightarrow$
(iii) $P_4 + NaOH + H_2O \longrightarrow$
(iv) $SO_3 + SCl_2 \longrightarrow$

(20 marks)

Section B

04. Answer **all** parts

(a) Glucose is a monosaccharide, which is an aldohexose.



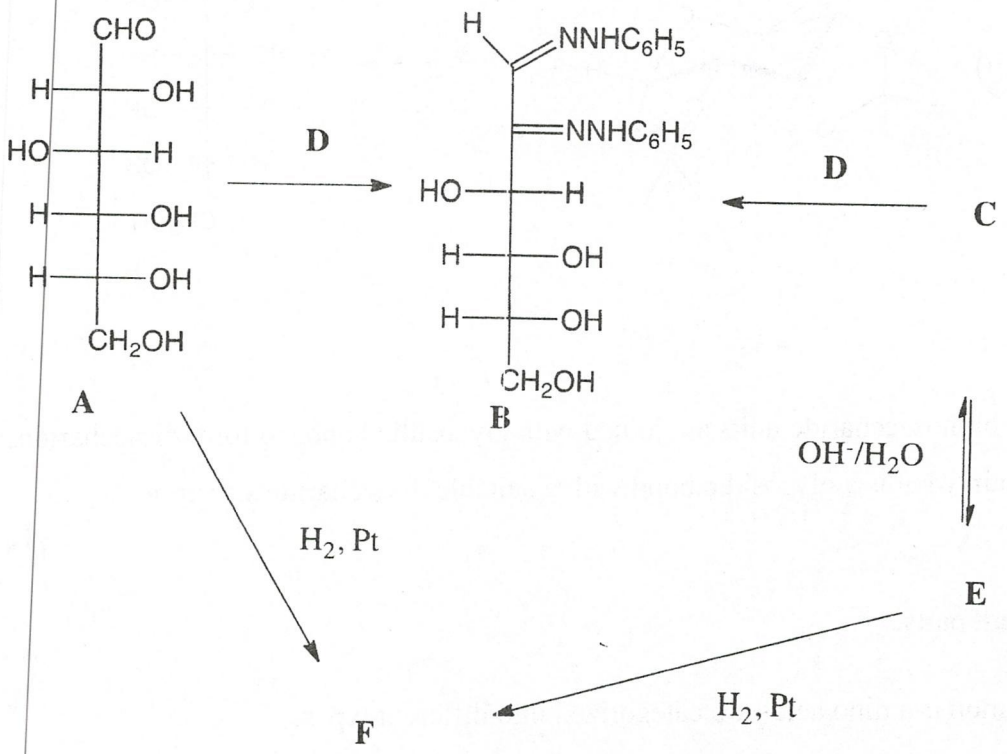
(i) Write down the basis of assigning configuration as D or L of sugars. Based on that what is the configuration of above molecule.

(ii) Draw the Haworth projection of six membered cyclic structure(s) formed by glucose and name it accordingly.

(iii) Glucose is a reducing sugar. Explain this with suitable reactions.

(25 marks)

(b) Answer the following questions based on the reaction scheme given below.



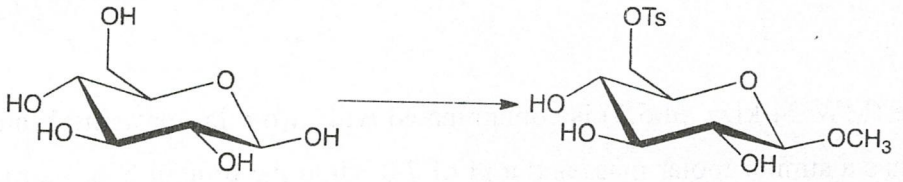
(i) Draw the structures of missing intermediates and reagents **C, D, E** and **F**.

(ii) What is the relationship between **A** and **C**? Explain why both **A** and **C** are forming only one product with the reaction with **D**.

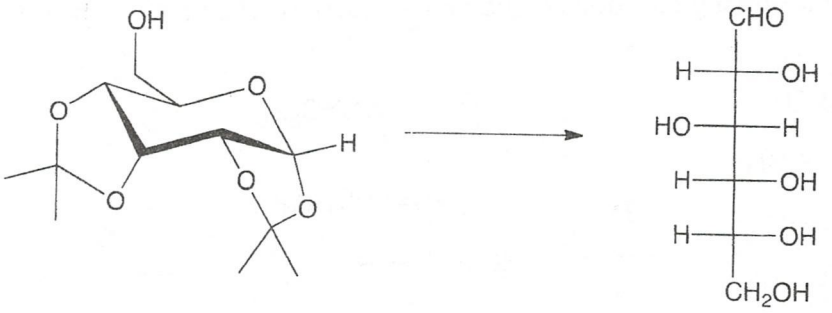
(iii) Give a reasonable mechanism for the conversion of **C** to **E**.

(30 marks)

(c) Giving necessary reagents, reaction conditions and intermediates formed, show how you would carry out the following conversions.

(i) 

(ii)



(30 marks)

(d) Two monosaccharide units are joined with glycosidic bonds to form disaccharides. Explain what is a glycosidic bond with a suitable disaccharide structure.

(15 marks)

05. Answer **all** parts.

(a) Common α-amino acids are categorized into different types.

(i) Name <u>four</u> α-amino acids having aliphatic side chains which might be involved in non-polar hydrophobic interactions.

(ii) Draw the chemical structures and give three-letter codes of them.

(20 marks)

(b) Alanine is synthesized from acetaldehyde by Strecker synthesis. Write necessary steps to illustrate this synthesis.

(20 marks)

(c) An enzyme (MW 24 kDa, pI 5.5) is contaminated with two other proteins **X** and **Y**. The protein **X** has a similar molar mass and a pI of 7.0 while the protein **Y** has a molar mass of 100 kDa and a pI of 5.4. Suggest a suitable method to purify the contaminated enzyme.

(20 marks)

(d) Acid hydrolysis of a polypeptide **P** gives Ala_2, Arg, Lys_2, Met, Phe, Ser_2. Deduce the amino acids sequence of polypeptide **P** using the following results for the given treatments:

(i) carboxypeptidase gives Ala;

(ii) chymotrypsine gives a tripeptide and hexapeptide with the compositions of:

[Ala, Arg, Phe] and [Ala, Lys_2, Met, Ser_2].

(iii) trypsin gives a dipeptide and two tripeptides with the compositions of:

[Ala, Arg] and [Lys, Phe, Ser], [Ala, Met, Ser] and free Lys.

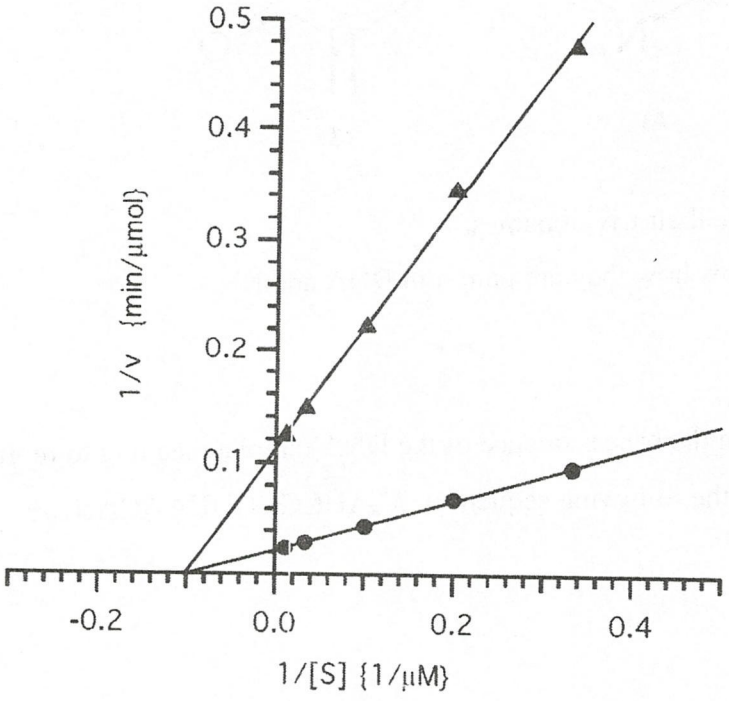
(iv) CNBr gives a dipeptide and a heptapeptide with the compositions of:

[Ala, Ser] and [Ala, Arg, Lys_2, Met, Phe, Ser]

(40 marks)

06. Answer **all** parts

(a) Shown below is a Lineweaver-Burk plot of enzyme kinetics for an enzyme catalyzed reaction that was conducted with 800 pmol of enzyme in both the presence (▲) and absence (•) of a 100 μM concentration of an inhibitor.



Answer the following questions using the above plot:

(i) What are the V_{max} and K_M values for the inhibited and uninhibited reaction? (Show your calculations with appropriate units.)

(ii) What type of inhibition is displayed by this inhibitor? Give reasons for your answer.

(iii) What is the turnover number of the enzyme in the absence of the inhibitor?

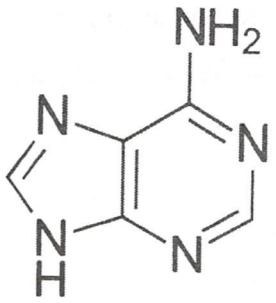
(iv) Indicate whether the maximum rate for the uninhibited reaction has reached to the diffusion limit.

(v) Where does this inhibitor most likely bind on the enzyme? Explain.

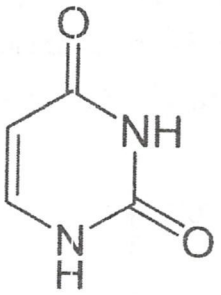
(vi) Calculate the value for the dissociation constant, K_I, of the inhibitor-enzyme complex?

(50 marks)

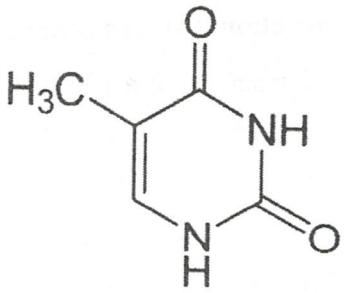
(b) **A**, **B**, and **C** are three common nitrogen bases found in DNA and RNA molecules.



(A)



(B)



(C)

(i) Give their trivial names.

(ii) Show how they are paired in DNA and RNA.

(30 marks)

(c) Write down the base sequence of the DNA template leading to replication of a strand of RNA with the following sequence: 5'-AUCGCGUUAACAUG-3'.

(20 marks)

Section C

07. Answer **all** parts.

(a) Predict whether ΔS is positive or negative for each of the following processes, assuming that each occurs at constant temperature: Briefly justify your answers.

(i) Thermal decomposition of calcium carbonate.

(ii) Reaction of HCl(g) and NH_3(g) at room temperature.

(iii) Rusting of iron exposed to air.

(iv) Nitric oxide generation by lightning discharges.

(v) Precipitation of AgCl from its ions in solution.

(20 marks)

(b) (i) What is the criterion for spontaneity of a process in a closed isothermal system at constant pressure? (derivation is not required).

(10 marks)

(ii) What are the <u>four</u> different ways that can be used to calculate the Gibbs free energy change of a chemical reaction under standard state conditions?

(20 marks)

(iii) Methyl isonitrile was heated to a constant temperature of 240 ^{0}C and the following rearrangement reaction was allowed to proceed until equilibrium was reached.

$$CH_3NC\ (g) \rightleftharpoons CH_3CN\ (g)$$

The equilibrium mixture was found to contain 1.6 mol of methyl isonitrile and 2.8 mol of acetonitrile. Calculate the standard Gibbs free energy change of the reaction.

(10 marks)

(c) (i)Starting from the Gibbs-Helmholtz Equation:

$$\left[\frac{\partial(\Delta G/T)}{\partial T}\right]_p = -\frac{\Delta H}{T^2}$$

derive an equation which shows how the equilibrium constant for a reaction ,K, varies with temperature, stating any assumptions you make.

(20 marks)

(ii) For the equilibrium $CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g)$ in the temperature range 900 to 1000 K, the equilibrium constant is given by the following equation:

$$\ln K = 12.745 - \frac{6341}{T(K)}$$

Calculate ΔG^0 for this reaction at 1000 K.

(20 marks)

08. Answer **all** parts.

(a) Compounds can be categorized as strong electrolytes, weak electrolytes, or nonelectrolytes.

(i) Giving examples distinguish between electrolytes and non-electrolytes.

(10 marks)

(ii) Write down the equation used for calculation of the ionic strength of an electrolytic solution and name all the symbols in it.

(10 marks)

(iii) Calculate the ionic strength of a solution containing 0.1 mol kg^{-1} KCl and 0.2 mol $kg^{-1}CuCl_2$.

(15 marks)

(b) Electroanalytical methods are selective, sensitive, rapid and provide easy techniques applicable to analyses in many fields.

(i) Distinguish between a galvanic cell and an electrolytic cell.

(16 marks)

(ii) Sketch the diagram of a galvanic cell in which the following reaction takes place.

$$2\ Al(s) + 3\ ZnSO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3\ Zn(s)$$

Label the electrodes and indicate the flow of electrons for this cell in your sketch. Assume that the concentrations of $Al_2(SO_4)_3$ and $ZnSO_4$ are c_1 mol dm^{-3} and c_2 mol dm^{-3}, respectively.

(15 marks)

(iii) Write down the half-cell reactions of the anode and the cathode.

(10 marks)

(iv) Write down the standard cell notation for the above mentioned galvanic cell.

(12 marks)

(v) In an electrochemical cell containing 1.2 mol dm^{-3} Al^{3+} and 2.5 mol dm^{-3} Fe^{3+} the reaction given below has taken place.

$$Al^{3+}(aq) + Fe(s) \rightleftharpoons Al(s) + Fe^{3+}(aq)$$

If E^{O}_{cell} is -1.62 V for this cell, calculate the cell potential at 298 K.

(12 marks)

09. Answer **all** parts

(a) "Light appears to be wavelike in some observations and particle-like in others and this is what we call the wave-particle duality of light. Louis de Broglie, a young French scientist, proposed in 1924 that if light can display wave-particle duality, then microscopic matter might also display wavelike properties."

(i) Briefly discuss this statement paying special attention to underlined phrases.

(ii) Using Einstein's equation $E = mc^2$, derive an expression for the *de Broglie wavelength.*

(iii) Calculate the de Broglie wavelength for a cricket ball of mass 280 g bowled at a speed of 45 m s^{-1}.

(iv) Calculate the de Broglie wavelength of an electron traveling at 1% of the speed of light.

(v) Typical wavelength of X – rays is around 250 pm. What can you deduce from your answers obtained for (iii) and (iv) and comparing them to wavelength of X – rays?

(50 marks)

(b) A particle of mass **m** is confined to a one dimensional box of length **a**. The potential energy of the system is defined as:

$$V(x) = \begin{cases} 0 & 0 \le x \le a \\ \infty & 0 > x \text{ and } x > a \end{cases}$$

(i) Write the Schrodinger equation for this system showing separate equations for the inside and outside of the box and hence show that the particle has zero probability of staying outside of the box.

(15 marks)

(ii) Assume a solution (inside the box) of the form $\psi(x) = A \sin(\alpha x) + B \cos(\alpha x)$ and prove by substitution that this is a satisfactory solution to the Schrodinger equation in (i) for inside the box. Using boundary conditions and then normalizing, show that

$$\Psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \quad \text{and} \quad E_n = \frac{n^2 h^2}{8ma^2}$$

where n = 1,2,3,.....

[$\cos 2\beta = 1 - 2\sin^2\beta$ and $\int \cos(ax)\,dx = \frac{1}{a}\sin(ax)$]

(30 marks)

(iii) Explain why n = 0 is not possible.

(05 marks)

[Note: The general form of the Schrodinger equation is given by

$$\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\Psi = 0\,]$$

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