UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE GENERAL DEGREE LEVEL II (SEMESTER II) EXAMINATIONS-NOVEMBER/DECEMBER-2016

SUBJECT: Chemistry

COURSE UNIT: *CHE 2214*

TIME: Three (03) hours

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

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 $J \cdot K^{-1} mol^{-1}$
		0.0821 dm^3 atm K^{-1} mol^{-1}
Boltzmann constant, k	=	1.381×10^{-23} $J \cdot K^{-1}$
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
Atomic mass unit (amu)	=	1.6606×10^{-27} kg
Standard pressure	=	1.01325×10^{5} Pa

Important conversation 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) (i) State the eighteen electron rule.

[05 marks]

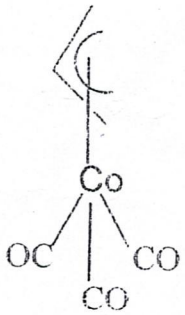
(ii) Show whether the following organometallic compounds agree or do not agree with the eighteen electron rule.

(I) $Cr(CO)_3(\eta^6\text{-}C_6H_6)$

(II) $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$

(III) $(\eta^5\text{-}C_5H_5)Ir(CH_3)_4$

(IV)



[05x4 marks]

(iii) State the oxidation state of the metal in each of the above organometallic compounds.

[05 marks]

(b) (i) Identify each of the organometallic compounds given below as ionic, covalent or electron deficient.

(I) $(CH_3)_2Hg$

(II) $Al_2(CH_3)_6$

(III) $(CH_3)_4Si$

(IV) $K(\eta^5\text{-}C_5H_5)$

(V) $[Be(CH_3)_2]_n$

[03x5 marks]

(ii) For each of the following pairs, identify the ions/molecules having the higher value for the given parameter/property. Give reasons for your answers.

(I) CO bond length $[Fe(CO)_4]^{2-}$, $[Cu(CO)_4]^+$

(II) π-acceptor property PF_3 , $P(C_2H_5)_3$

(III) Stability $[Mn(CO)_6]$, $[Mn(CO)_6]^+$

(IV) ν_{CO} stretching frequency in the IR spectrum $Na_2Fe(CO)_4$, $Fe(CO)_5$

[20 marks]

(c) (i) Predict the possible product(s) of the following reactions.

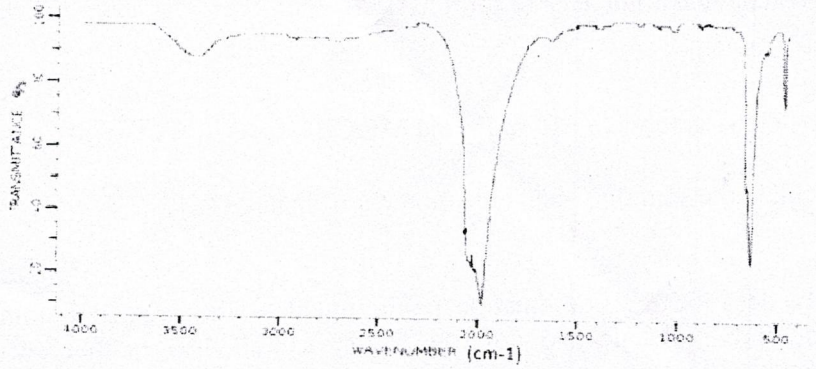
(I) $CH_3Cl + Li \rightarrow$

(II) $NaMn(CO)_5 + CH_3Cl \rightarrow$

(III) $Mn_2(CO)_{10} + Na/Hg \rightarrow$

[05x3 marks]

(ii) The IR spectrum of the diamagnetic compound $Mn_2(CO)_{10}$ is given below.



By using the above data and the Valence Bond Theory, predict the geometry of $Mn_2(CO)_{10}$and sketch its structure.

[20 marks]

02. Answer **all** parts

(a) Briefly explain the chemistry pertaining to the following statements.

(i) CrO_4^{2-} ion is used in the titrimetric determination of Ag^+ ions with Cl^- ions.

(ii) $K_2Cr_2O_7$is used in ethanol detectors.

[20 marks]

(b) Titanium is a light, strong and commercially important transition metal.

(i) Giving appropriate balanced chemical equations and necessary conditions describe how you would extract pure titanium from naturally occurring rutile.

[20 marks]

(ii) State **two** major disadvantages of the above extraction process.

[10 marks]

(iii) Explain why C or CO cannot be used as the reducing agent in the above extraction process.

[05 marks]

(c) **M** is an early transition element with varying oxidation states. **M** forms an orange coloured catalytically important metal oxide **X**. When **X** is reduced with calcium the pure metal **M** is obtained. The pure metal **M** reacts with Cl_2 gas to give a toxic red-brown liquid $\mathbf{MCl_4}$. Reaction between NaC_5H_5 and $\mathbf{MCl_4}$ in THF followed by extraction into chloroform gives an anticancer drug $M(C_5H_5)_2Cl_2$ (**R**). When the oxide **X** is reduced with SO_2, the dark blue amphoteric oxide $\mathbf{MO_2}$and SO_3 gas are formed. $\mathbf{MO_2}$ reacts with dilute HCl to form $\mathbf{MOCl_2}$.

(i) Identify **X, M.**

[05 marks]

(ii) Draw the structures of $\mathbf{MCl_4}$, **R**, and $\mathbf{MOCl_2}$

[10 marks]

(iii)Calculate the spin only magnetic moment of $\mathbf{[M(H_2O)_6]^{2+}}$.

[15 marks]

(d) Briefly describe the coordination environment at the oxygen binding site of the hemoglobin molecule and describe the structural changes that occur during the oxygen binding process.

[15 marks]

03. Answer **all** parts.

(a) Liquid HF and liquidN_2O_4 are two non-aqueous solvents used in research and industry.

(i) Write balanced chemical equations for the self-ionization of liquid HF and liquid N_2O_4.

(ii) Identify the acidic and basic species present in each ionized solvent.

(iii)Draw the structure of the basic species formed by the self-ionization of liquid HF.

(iv) In addition to the ionized basic product given in part (iii), $H_3F_4^-$ can be formed as an ionic product. Draw an acceptable structure for this ion.

(v) Giving relevant chemical equations, explain why liquid HF cannot be stored in glass bottles.

(vi) What product(s) would you expect when Na is added to liquidN_2O_4?

(vii) Predict the products and write balanced chemical equations for the following reactions.

(I) Sn + ClNO (in liquid N_2O_4)

(II) Cu + N_2O_4 (in the presence of CH_3CN)

(III) HF + CH_3COOH

[50 marks]

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

(i) $CS_2 + S_2Cl_2 \longrightarrow$

(ii) $PCl_5 + NO_2 \longrightarrow$

(iii) $Al_4C_3 + H_2O \longrightarrow$

(iv) $CFCl_3 + HF \longrightarrow$

(v) $P_4O_{10} + CH_2(CO_2H)_2 \longrightarrow$

(vi) $CH_3SiCl_3 + CH_3MgCl \longrightarrow$

[30 marks]

(c) Draw the structures of the following and indicate the oxidation state(s) of P, Si and S.

(i) Trimetaphosphoric acid

(ii) Inosilicate (double chain)

(iii) γ–SO_3

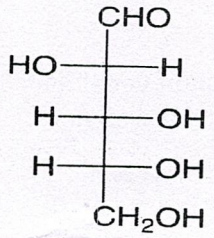
(iv) P_4O_{10}

[20 marks]

SECTION-B

04. Answer **all** parts.

(a) Arabinitol is used in many medical applications and it can be synthesized by monosaccharide arabinose.



Arabinose

(i) Identify whether the above given arabinose is a D/L sugar, an aldose/ketose, based on the number of carbons.

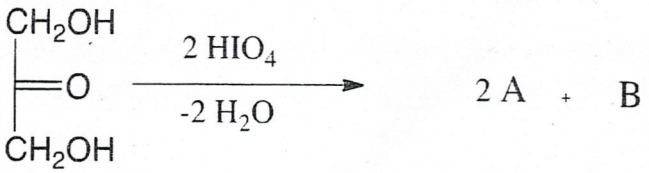
(ii) Propose a synthetic method that can be used to synthesize arabinose from glucose.

(iii) Write down the structure of arabinitol and reaction conditions required for the conversion of arabinose to arabinitol.

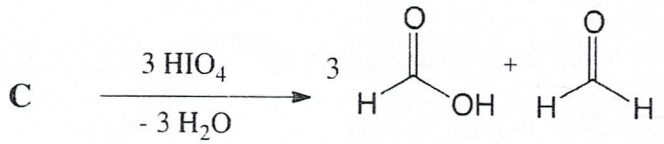
[25 marks]

(b) In the reactions given below, deduce the structures of **A** to **F**, under the given conditions.

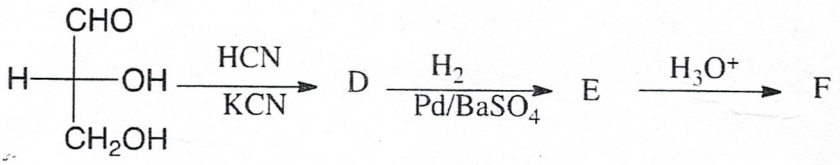
(i)



(ii)



(iii)



[30 marks]

(c) Starch is a polymer of glucose and present in plants as the main energy storage component.

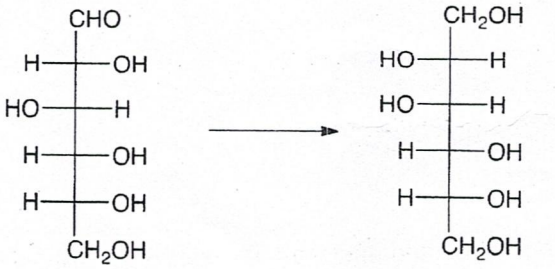
(i) Briefly explain the structure of starch.

(ii) How can starch be identified in the laboratory?

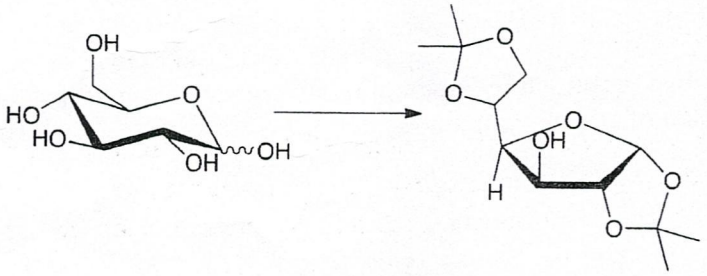
[15 marks]

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

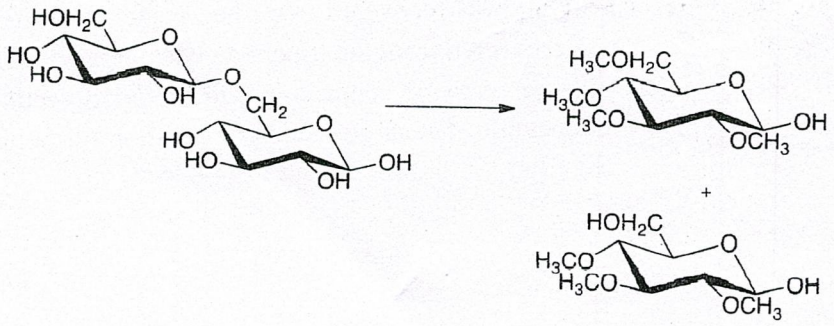
(i)



(ii)



(iii)



[30 marks]

05. Answer **all** parts.

(a) The properties of common α-amino acids differ with their side chains.

(i) Classify the following amino acids into groups of non-polar, polar, acidic or basic.
Met, Cys, Lys, Glu, Asn

[05 marks]

(ii) Draw the chemical structures of **two** of the above amino acids.

[10 marks]

(b) (i) Define the term isoelectric point of amino acids.

[05 marks]

(ii) In gel electrophoresis what direction (none, toward the cathode, toward the anode) does the amino acid Lys, move when placed in an electric field at the following pH values: 1, 3, 5, 7, 9, and 12? (*Isoelectric point of Lys is 9.8*). Explain briefly your answer.

[10 marks]

(c) Answer the following related to protein.

(i) What is meant by primary structure of a peptide/protein?

(ii) What is an α-helix?

(iii) What is a β-sheet?

[20 marks]

(d) (i) Write a short account on enzymatic cleavage of peptides/proteins.

[15 marks]

(ii) A nonapeptide **X** with the amino composition of $(Lys)_2$, $(Gly)_2$, $(Phe)_2$, His, Leu, Met, was treated as described below. Giving reasons derive the amino acid sequence of the peptide **X** by using the given information.

(I) with 1-fluoro-2,4-dinitrobenzene (FDNB) and then hydrolyzed; 2,4-DNP-histidine was identified by HPLC as the product.

(II) with CNBr, an octapeptide and free glycine were recovered.

(III) with trypsin gave a pentapeptide, a tripeptide, and free Lys. 2,4-DNP-histidine was recovered from the pentapeptide, and 2,4-DNP-phenylalanine was recovered from the tripeptide when treated with FDNB.

(IV) with the enzyme pepsin produced a dipeptide, a tripeptide, and a tetrapeptide. The amino acid composition of the tetrapeptide is $(Lys)_2$, Phe, and Gly.

[35 marks]

06. Answer **all** parts.

(a) Briefly explain what enzyme cofactors are.

[10 marks]

(b) What are the **two** models used to explain enzyme–substrate binding? Briefly describe one of these models using a suitable diagram.

[14 marks]

(c) Graphically show the relationship between substrate concentration and the reaction velocity of an enzymetic reaction. Indicate K_m and V_{max} on the graph.

[10 marks]

(d) Explain competitive and non-competitive inhibition of enzyme.

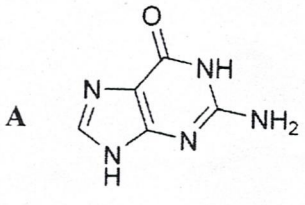
[10 marks]

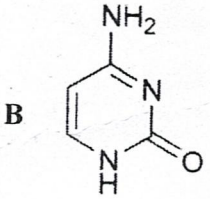
(e) Using a Lineweaver Burk plot show how would the relationship between substrate concentration and the reaction velocity changes in the presence of a competitive and a non-competitive inhibitor.

[22 marks]

(f) (i) Give trivial names of the following two structures.

(ii) Show how base- pairing occurs between these two in a DNA double helix.





[15 marks]

(g) Write down the base sequence of the DNA template leading to replication of a strand of RNA with the following sequence: 5′-AUCGCGUUAA-3′.

[10 marks]

(h) Draw the structure of any RNA nucleotide.

[09 marks)

SECTION-C

07. Answer **all** parts

(a) Using the given data, calculate ΔS^0_{rxn} for the following two reactions. In each case, give reasons for the sign of ΔS^0_{rxn}.

(i) $3\ NO_2(g) + H_2O(l) \longrightarrow 2\ HNO_3(aq) + NO(g)$

(ii) $Cr_2O_3(s) + 3\ CO(g) \longrightarrow 2\ Cr(s) + 3\ CO_2(g)$

Substance	H_2O *(l)*	NO_2 *(g)*	HNO_3 *(aq)*	NO *(g)*	Cr_2O_3 *(s)*	Cr *(s)*	CO *(g)*	CO_2 *(g)*
S^0 J K^{-1} mol^{-1}	70.0	240.1	146.0	210.8	81.2	23.8	197.7	213.8

[20 marks]

(b) (i) State the third law of thermodynamics.

(ii) Using the Boltzmann formula show how the molecular interpretation of entropy, justifies the third law.

[20 marks]

(c) Write expressions to relate Gibbs free energy change of a reaction at temperature T under <u>standard</u> condition to:

(i) its enthalpy and entropy changes

(ii) its equilibrium constant, K

(iii) Combining the above two expressions obtain an equation to show that *ln* K versus 1/T varies linearly.

(iv) An equilibrium reaction was studied at various temperatures. The data was plotted according to the *van't Hoff* equation. The equation of the line that fits to data was found to be $y = 1.0 \times 10^4 \frac{1}{T} + 11.4$.

What is the standard entropy and the enthalpy change forthe reaction?

[40 marks]

(d) A $BaSO_4$ slurry is usually ingested before the gastrointestinal tract is X-rayed. Effect of toxic Ba^{2+} ion is insignificant due to low solubility of $BaSO_4$. If $\Delta G°$ for the dissolution process of $BaSO_4$ in water at body temperature (37 ^{0}C) is 59.1 kJ mol^{-1} what is the Ba^{2+} ion concentration in the intestinal tract? Assume that the only source of SO_4^{2-} is the ingested slurry and neglect the effects of other ions.

[20 marks]

08. Answer **both** parts

(a) (i) Identify the terms in the following equation..

$$\log \gamma \pm = -\frac{A|z_+ z_-|I^{1/2}}{1 + BI^{1/2}}$$

[15 marks]

(ii) When do you use the Extended Debye Huckel Limiting Law? and state the reason/s for using Debye Huckel/Extended Debye Huckel Limiting Laws.

[25 marks]

(b) Consider the following cell at 298 K.

$Zn(s)|ZnCl_2$ (aq) (0.005 $mol\ dm^{-3}$)$|Hg_2Cl_2$ (s)|Hg(l); $E^0 = 1.0304$ V

At 298 K $\left(\frac{\partial E}{\partial T}\right)_p = -4.52 \times 10^{-4}\ V\ K^{-1}$

A and B constants of Extended Debye Huckel Limiting Law are 0.509 and 1.25 respectively

(i) Write down a short description of the above cell.

[10 marks]

(ii) Obtain the cell reaction.

[05 marks]

(iii) Calculate $\Delta G, \Delta S, and\ \Delta H$ for the cell reaction under the given experimental conditions.

[45 marks]

09. Answer **all** parts.

(a) Qualitatively explain what you understand by the *Black Body Radiation*. German physicist Max Planck introduced the phenomenon of *Quantization* in order to explain this observation. Briefly explain what is meant by *Quantization*.

[15 marks]

(b) Comment on the following statement:
"The ejection of electrons from a metallic surface, when irradiated with light is known as the Photoelectric Effect. However there is a threshold frequency characteristic of the metallic surface, below which no electrons are ejected."

[15 marks]

(c) The work function of a certain metal is 4.50 eV and this surface is irradiated with a monochromatic light beam of 190 nm wavelength. Calculate the threshold frequency and kinetic energy of the photoelectrons emitted from this surface.

[20 marks]

(d) 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 explain why the particle is always confined to 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 the particle 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,.....

[The general form of the Schrodinger equation is given by

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

Note: $\int \cos(\alpha x)dx = {}^{1}/_{\alpha} \sin(\alpha x)$; $\quad \cos 2\beta = 1 - 2\sin^2\beta$

[35 marks]