UNIVERSITY OF ESWATINI

MAIN EXAMINATION

ACADEMIC YEAR 2018/2019

TITLE OF PAPER:	**BIO-INORGANIC CHEMISTRY**
COURSE NUMBER:	**CHE633**
TIME ALLOWED:	**THREE (3) HOURS**
INSTRUCTIONS:	**ANSWER ALL FOUR (4) QUESTIONS. EACH QUESTION IS WORTH 25 MARKS.**

A PERIODIC TABLE AND OTHER USEFUL DATA HAVE BEEN PROVIDED WITH THIS EXAMINATION PAPER.

PLEASE DO NOT OPEN THIS PAPER UNTIL AUTHORISED TO DO SO BY THE CHIEF INVIGILATOR.

QUESTION ONE

(a) Discuss the structure of the zinc metalloenzyme *carboxypeptidase* and outline the mechanism of its function. **[5]**

(b) (i) Draw the structure of the porphine ligand. **[2½]**

(ii) Show how the structure of the porphine ligand

(1) has been modified in the chlorophyll molecule. **[2]**

(2) differs from the corrin ring ligand in vitamin B_{12}. **[1½]**

(3) is related to the heme structure. **[1]**

(iii) Eukaryotic cells contain sub-compartments known as *organelles*. Give functions of the following organelles:

(1) Mitochondria **[1]**

(2) Endoplasmic reticulum **[1]**

(3) Peroxisomes **[1]**

(c) When you try to buy a sample of the heart-imaging agent cardiolyte at your local pharmacy, the clerk informs you that he does not carry this compound, because it has no shelf life. Explain. How does this property help make it a good radiopharmaceutical? **[4]**

(d) (i) What is meant by the term *zwitterion*? **[1]**

(ii) Describe what is meant by the term *primary structure of proteins*? **[1]**

(iii) What type of bonding between amino acid residues is most important in holding a protein or polypeptide in a specific secondary configuration? **[1]**

(iv) A globular protein in aqueous surroundings contains the following amino acid residues: methionine, lysine, and alanine. Which amino acid side chains would be directed toward the inside of the protein and which would be directed toward the aqueous surroundings? **[3]**

QUESTION TWO

(a) Describe the characteristics of zinc that make it an important element in Biochemistry. Compare these characteristics to those of the other metals found in biological systems. **[6]**

(b) Uranyl ion (UO_2^{2+}) is commonly used to form heavy-atom derivatives for X-ray diffraction studies. Given that this is a relatively hard ion,

(i) What sorts of functional groups would you expect to be derived? **[2]**

(ii) How does this behaviour compare to that expected for another heavy-metal derivatizing ion, Hg^{2+}? **[2]**

(c) (i) Explain transport, formation and degradation of *hydrogen carbonate*, HCO_3^-, in our body. **[3]**

(ii) Early attempts to synthesise O_2-carrying iron-porphyrin models were prevented by the formation of oxidised porphyrin dimers having a μ–O bridge between the iron atoms. Outline <u>three</u> approaches that have been successfully employed to circumvent this problem. **[3]**

(d) (i) What is the function of the metallo-biomolecule, *nitrogenase*? **[2]**

(ii) Identify the metal(s) that are at the active centres of *nitrogenase*. **[1]**

(iii) Describe the essential features of the structure of *nitrogenase*. **[3]**

(iv) Describe the essential steps in the mechanism of the function of *nitrogenase*. **[3]**

QUESTION THREE

(a) Discuss the roles of the ions of the major elements K^+, Na^+ and Ca^{2+} in metabolic processes. In the discussion, identify which ions are found within and outside the cells and their relative concentrations. **[6]**

(b) Discuss the following topics:

(i) Chelation therapy **[3]**

(ii) Zinc proteins as sensors **[3]**

(c) (i) A novel electron-transport protein has been isolated. Elemental analysis suggests that it contains only zinc. Comment on this observation. **[2]**

(ii) Indicate the oxidation state of the copper ions and of the O_2 ligand in oxyhemocyanin. **[2]**

(d) (i) Outline the mechanism of the catalytic cycle of *cytochrome P-450*. **[6]**

(ii) Your pet lobster (an anthropod) has been sluggish and has been found to be anaemic. Do you think that a good treatment would be to supplement its diet with iron? Suggest an alternative. **[3]**

QUESTION FOUR

(a) (i) Graphically compare the O_2 affinity of hemoglobin and myoglobin. **[3]**

(ii) Show with a picturesque presentation the role of distal imidazole heterocycle for trapping of O_2 by deoxy-hemoglobin. **[3]**

(b) Model complexes for the [2Fe-2S] sites in ferredoxins have been prepared. The most well-characterised models are in the fully oxidised form $[Fe_2S_2(SR)_4]^{2-}$, where both irons are in the +3 oxidation state. One-electron reduction of these complexes produces species of the form $[Fe_2S_2(SR)_4]^{3-}$, which are unstable because two such complexes react to produce one $[Fe_4S_4(SR)_4]^{2-}$ complex.

(i) Write a balanced equation for this reaction. **[1]**

(ii) Why doesn't a similar reaction occur for the oxidised form? **[2]**

(iii) Can you think of a synthetic strategy to decrease the likelihood that this dimerization reaction will occur? **[2]**

(c) (i) What role does Mg play in the functioning of *chlorophyll*? **[2]**

(ii) Which other metal(s) are involved in photosynthesis in the functioning of *chlorophyll*? **[1½]**

(iii) *Chlorophyll* has an absorption maximum at about 660 nm. Calculate the energy available from a photon light at this wavelength. **[1½]**

(iv) What electron transfer systems are used in photosynthesis? **[2]**

(v) Describe the chemical processes that occur during the *photosynthesis* process. **[2]**

(d) (i) What do you understand by 'modelling' of bio-molecules? **[1]**

(ii) Explain how cobalt complexes have provided the best general picture of acting as helpful O_2 binding model systems. **[4]**

PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1.008 **H** 1																	4.003 **He** 2
2	6.941 **Li** 3	9.012 **Be** 4										Atomic mass **Symbol** Atomic No.	10.811 **B** 5	12.011 **C** 6	14.007 **N** 7	15.999 **O** 8	18.998 **F** 9	20.180 **Ne** 10
3	22.990 **Na** 11	24.305 **Mg** 12					TRANSITION ELEMENTS						26.982 **Al** 13	28.086 **Si** 14	30.974 **P** 15	32.06 **S** 16	35.453 **Cl** 17	39.948 **Ar** 18
4	39.098 **K** 19	40.078 **Ca** 20	44.956 **Sc** 21	47.88 **Ti** 22	50.942 **V** 23	51.996 **Cr** 24	54.938 **Mn** 25	55.847 **Fe** 26	58.933 **Co** 27	58.69 **Ni** 28	63.546 **Cu** 29	65.39 **Zn** 30	69.723 **Ga** 31	72.61 **Ge** 32	74.922 **As** 33	78.96 **Se** 34	79.904 **Br** 35	83.80 **Kr** 36
5	85.468 **Rb** 37	87.62 **Sr** 38	88.906 **Y** 39	91.224 **Zr** 40	92.906 **Nb** 41	95.94 **Mo** 42	98.907 **Tc** 43	101.07 **Ru** 44	102.91 **Rh** 45	106.42 **Pd** 46	107.87 **Ag** 47	112.41 **Cd** 48	114.82 **In** 49	118.71 **Sn** 50	121.75 **Sb** 51	127.60 **Te** 52	126.90 **I** 53	131.29 **Xe** 54
6	132.91 **Cs** 55	137.33 **Ba** 56	138.91 ***La** 57	178.49 **Hf** 72	180.95 **Ta** 73	183.85 **W** 74	186.21 **Re** 75	190.2 **Os** 76	192.22 **Ir** 77	195.08 **Pt** 78	196.97 **Au** 79	200.59 **Hg** 80	204.38 **Tl** 81	207.2 **Pb** 82	208.98 **Bi** 83	(209) **Po** 84	(210) **At** 85	(222) **Rn** 86
7	223 **Fr** 87	226.03 **Ra** 88	(227) ****Ac** 89	(261) **Rf** 104	(262) **Ha** 105	(263) **Unh** 106	(262) **Uns** 107	(265) **Uno** 108	(266) **Une** 109	(267) **Uun** 110								

***Lanthanide Series**	140.12 **Ce** 58	140.91 **Pr** 59	144.24 **Nd** 60	(145) **Pm** 61	150.36 **Sm** 62	151.96 **Eu** 63	157.25 **Gd** 64	158.93 **Tb** 65	162.50 **Dy** 66	164.93 **Ho** 67	167.26 **Er** 68	168.93 **Tm** 69	173.04 **Yb** 70	174.97 **Lu** 71
****Actinide Series**	232.04 **Th** 90	231.04 **Pa** 91	238.03 **U** 92	237.05 **Np** 93	(244) **Pu** 94	(243) **Am** 95	(247) **Cm** 96	(247) **Bk** 97	(251) **Cf** 98	(252) **Es** 99	(257) **Fm** 100	(258) **Md** 101	(259) **No** 102	(260) **Lr** 103

( ) indicates the mass number of the isotope with the longest half-life.

General data and fundamental constants

Quantity	Symbol	Value
Speed of light	c	$2.997\,924\,58 \times 10^{8}$ m s^{-1}
Elementary charge	e	$1.602\,177 \times 10^{-19}$ C
Faraday constant	$F = N_Ae$	9.6485×10^{4} C mol^{-1}
Boltzmann constant	k	$1.380\,66 \times 10^{-23}$ J K^{-1}
Gas constant	$R = N_Ak$	$8.314\,51$ J K^{-1} mol^{-1}
		$8.205\,78 \times 10^{-2}$ dm^{3} atm K^{-1} mol^{-1}
		6.2364×10 L Torr K^{-1} mol^{-1}
Planck constant	h	$6.626\,08 \times 10^{-34}$ J s
	$\hbar = h/2\pi$	$1.054\,57 \times 10^{-34}$ J s
Avogadro constant	N_A	$6.022\,14 \times 10^{23}$ mol^{-1}
Atomic mass unit	u	$1.660\,54 \times 10^{-27}$ Kg
Mass		
electron	m_e	$9.109\,39 \times 10^{-31}$ Kg
proton	m_p	$1.672\,62 \times 10^{-27}$ Kg
neutron	m_n	$1.674\,93 \times 10^{-27}$ Kg
Vacuum permittivity	$\varepsilon_o = 1/c^2\mu_o$	$8.854\,19 \times 10^{-12}$ J^{-1} C^{2} m^{-1}
	$4\pi\varepsilon_o$	$1.112\,65 \times 10^{-10}$ J^{-1} C^{2} m^{-1}
Vacuum permeability	μ_o	$4\pi \times 10^{-7}$ J s^{2} C^{-2} m^{-1}
		$4\pi \times 10^{-7}$ T^{2} J^{-1} m^{3}
Magneton		
Bohr	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24}$ J T^{-1}
nuclear	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27}$ J T^{-1}
g value	g_e	2.002 32
Bohr radius	$a_o = 4\pi\varepsilon_o\hbar/m_ee^2$	$5.291\,77 \times 10^{-11}$ m
Fine-structure constant	$\alpha = \mu_oe^2c/2h$	$7.297\,35 \times 10^{-3}$
Rydberg constant	$R_\infty = m_ee^4/8h^3c\varepsilon_o^2$	$1.097\,37 \times 10^{7}$ m^{-1}
Standard acceleration of free fall	g	$9.806\,65$ m s^{-2}
Gravitational constant	G	$6.672\,59 \times 10^{-11}$ N m^{2} Kg^{-2}

Conversion factors

1 cal	=	4.184 joules (J)	1 erg	=	1×10^{-7} J
1 eV	=	$1.602\,2 \times 10^{-19}$ J	1 eV/molecule	=	96 485 kJ mol^{-1}

Prefixes

f	p	n	μ	m	c	d	k	M	G
femto	pico	nano	micro	milli	centi	deci	kilo	mega	giga
10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^{3}	10^{6}	10^{9}