UNIVERSITY OF SWAZILAND

FINAL EXAMINATION

ACADEMIC YEAR 2017/2018

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 HAS 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 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) Imaging agents [3]
(iii) Zinc proteins as sensors [3]

(c) Describe the origin of CO toxicity in mammals, including a consideration of the nature of metal–CO bonding. [2]

(d) (i) Outline the mechanism of the catalytic cycle of cytochrome P-450. [6]
(ii) Why might Copper sensors be 'designed' to bind Cu(I) rather than Cu(II)? [2]

QUESTION TWO

(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) (i) What is the shape and make-up of the manganese complexes utilised in PSII? [2]
(ii) Which features of the manganese suit it to function as a redox centre in PSII, as opposed to metals such as copper or nickel? [2]

(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 THREE

(a) Describe the characteristics of zinc that make it an important element in Biochemistry. Compare these characteristics to those of the other metals (nickel, cadmium, iron, copper, manganese and magnesium) found in biological systems. [6]

(b) The O–O bond lengths in O_2, KO_2 (O_2^-), and BaO_2 (O_2^{2-}) are 1.21, 1.34, and 1.49 Å, respectively. These values provide reference data on the relation between bond length and oxidation state. For the complexes $[Co(CN)_5(O_2)]^{3-}$, $[(NH_3)_5Co(O_2)Co(NH_3)_5]^{4+}$, and $[(NH_3)_5Co(O_2)Co(NH_3)_5]^{5+}$, the O–O bond lengths are 1.24, 1.47, and 1.30 Å, respectively. Comment on the extent of Co to O_2 electron transfer (state number of electrons transferred) in each complex. [3]

(c) 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.

- (i) Suggest a reaction sequence to account for this observation giving products that include oxo-bridged dinuclear Fe(III) porphyrin species. [4]
- (ii) Outline three 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 FOUR

(a) Discuss the uptake of O_2 by myoglobin and haemoglobin and its

- (i) pH dependency [3]
- (ii) cooperative mechanism [3]
- (iii) effect of partial pressure of O_2 [3]

(b) One of the problems that has plagued synthetic Chemists in their attempts to prepare model compounds for cysteine-complexed metal ions in metalloproteins is the easy oxidation of the thiolate anions (RS^-) to RS–SR. Simple complexes with Cu^{2+}–SR and Fe^{3+}–SR bonds that might serve as models for cytochrome P-450 and the ferredoxins are labile because of this reaction. Write balanced equations for the decomposition of $[Cu^{(II)}L_n(SR)]$ and $[Fe^{(III)}L_n(SR)]$. [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

Atomic mass → 10.811; Symbol → B; Atomic No. → 5

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											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.