10

(University of Choice)

MASINDE MULIRO UNIVERSITY OF SCIENCE AND TECHNOLOGY (MMUST)

MAIN CAMPUS

UNIVERSITY EXAMINATIONS

2022/2023 ACADEMIC YEAR

FIRST YEAR FIRST SEMESTER EXAMINATIONS

FOR THE DEGREE OF MASTER OF SCIENCE (CHEMISTRY)

COURSE CODE: SCH 813

COURSE TITLE: ADVANCED COORDINATION CHEMISTRY

DATE: FRIDAY 14TH APRIL 2023 **TIME:** 2:00-5:00 PM

INSTRUCTIONS TO CANDIDATES

Total Marks: 60

Answer all the Questions

TIME: 3 Hours

Question One **(14 Marks)**

a. State and explain THREE factors that favour the formation of complexes with unusual coordination numbers (6 Marks)

b.(i) Activation volume ($\Delta V^{\neq}$) is a complementary parameter to $\Delta H^{\neq}$ and $\Delta S^{\neq}$ in the assignment of the mechanism of a substitution reaction. Show that

$$\ln k_1 = \ln(k_{-1})_0 - \frac{\Delta V^{\neq}}{RT} P \qquad \text{equation (i)}$$

Where, $\Delta V^{\neq}$ the activation volume for the forward reaction, $(k_{-1})_0$ is the compressibility coefficient of the medium, k_1 is the rate constant, R is gas constant, T is reaction temperature and P is pressure (5 marks)

b.(ii) Using equation (i) above explain how you would obtain activation volume and associated parameter for a reaction (3 Marks)

Question Two **(16 Marks)**

a. In an outer-sphere reaction, electron transfer occurs through tunnelling. Using Marcus-Hush equation determine whether the reaction below is consistent with outer-sphere mechanism (4 Marks)

$$[Ru(NH_3)_6]^{2+} + [Co(Phen)_3]^{3+} \longrightarrow [Ru(NH_3)_6]^{3+} + [Co(Phen)_3]^{2+}$$

Given that, the observed rate constant is 1.5×10^4 $dm^3mol^{-1}s^{-1}$ and the equilibrium constant is 2.6×10^5. The rate constants for the self-exchange reactions $[Ru(NH_3)_6]^{2+}/[Ru(NH_3)_6]^{3+}$ and $[Co(Phen)_3]^{2+}/[Co(Phen)_3]^{3+}$ are 8.2×10^2 and 40 dm^3 mol^{-1} s^{-1}, respectively.

b. Metal-organic frameworks (MOFs) a sub-class of coordination polymers represent a porous class of materials that are build up from metal ions or oligonuclear metallic complexes and organic ligands. Briefly explain the following methods that are used in the synthesis of MOFs, highlighting their strengths and limitations (12 Marks)

i. Slow Evaporation and Diffusion Methods

ii. Solvo(Hydro)-Thermal Methods

iii. Mechanochemical Method

iv. Microwave-Assisted Method

Question Three **(14 Marks)**

a. Consider the reaction below is a redox reaction that follows an outer sphere mechanism. Write the mechanism for the reaction (5 Marks)

$$[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} + 5[H_3O]^{+} \longrightarrow [Co(H_2O)_6]^{2+} + [Cr(H_2O)_5Cl]^{2+} + 5[NH_4]^{+}$$

$[Co(NH_3)_5Cl]^{2+}$	$[Cr(H_2O)_6]^{2+}$	$[Co(H_2O)_6]^{2+}$	$[Cr(H_2O)_5Cl]^{2+}$
Low-Spin non-labile	High-Spin labile	High-Spin labile	Low-Spin non-labile

b. Mixed-valent compounds represent an important class of complex compounds that are fundamental for the study of intramolecular electron transfers. The bridging ligand therein play a pivotal role in synthesis of mixed valent compounds. Briefly, explain any THREE types of ligands you would utilize to achieve mixed valent complexes. Use examples where possible (9 Marks)

Question Four **(16 Marks)**

a. Discuss the application of metal complexes in catalysis. Interrogate the successes and challenges in these applications (10 Marks)

b. Are all electronic transition in metal complexes allowed? Explain your answer (6 Marks)

Periodic Table of the Elements

- Metals (main-group)
- Metals (transition)
- Metals (inner transition)
- Metalloids
- Nonmetals

MAIN-GROUP ELEMENTS | TRANSITION ELEMENTS | MAIN-GROUP ELEMENTS

Period	1A (1)	2A (2)	3B (3)	4B (4)	5B (5)	6B (6)	7B (7)	8B (8)	8B (9)	8B (10)	1B (11)	2B (12)	3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	8A (18)
1	1 H 1.008																	2 He 4.003
2	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
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	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
5	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
6	55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	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)
7	87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 (269)	111 (272)	112 (277)						

As of mid-1999, elements 110 through 112 have not yet been named.

INNER TRANSITION ELEMENTS

6	Lanthanides	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
7	Actinides	90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np (237)	94 Pu (242)	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 (260)