JARAMOGI OGINGA ODINGA UNIVERSITY OF SCIENCE AND TECHNOLOGY

SCHOOL OF BIOLOGICAL AND PHYSICAL SCIENCES

UNIVERSITY EXAMINATION FOR THE DEGREE OF BACHELOR OF EDUCATION (SCIENCES)

4th YEAR 1ST SEMESTER 2019/2020 ACADEMIC YEAR

MAIN REGULAR

COURSE CODE: SCH 402

COURSE TITLE: Inorganic Reaction Mechanisms

EXAM VENUE: **STREAM: (BEd. Science)**

DATE:

TIME: **EXAM SESSION:**

INSTRUCTIONS:

1. **Answer question 1 (Compulsory) in section A and ANY other 2 questions in Section B.**
2. **Candidates are advised not to write on the question paper.**
3. **Candidates must hand in their answer booklets to the invigilator while in the examination room.**
4. **Some important information/formulas are found on the last page of this question paper**

SECTION A

Question 1

a) Provide a reaction pathway in a reaction whereby $[CO_3]^{2-}$ ligand is substituted with H_2O. (3 marks)

$[(H_3N)_5Co(OCO_2)]^+ + [H_3O]^+ \longrightarrow$

b) Briefly describe the following terms:

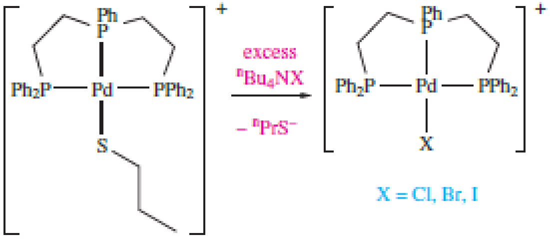
- i. A kinetically labile reaction (2 marks)
- ii. High spin d^5 metal center (2 marks)
- iii. Dissociative interchange (2 marks)
- iv. *Trans-effect* in a square planner (2 marks)
- v. *Nucleophilicity* parameter (2 marks)
- vi. *Marcus–Hush* theory (2 marks)

c) For the reaction:

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

the observed rate constant is 1:5 x 10^4 dm^3 mol-^{1}s^{-1} and the equilibrium constant is 2:6 x10^5. The rate constants for the self-exchange reactions $[Ru(NH_3)_6]^{2+}$ / $[Ru(NH_3)_6]^{3+}$ and $[Co(phen)_3]^{3+}$/ $[Co(phen)_3]^{2+}$ are 8.2x10^2 and 40dm^3 mol^{-1} s^{-1} respectively. Are these data consistent with an outer-sphere mechanism for the cross-reaction? (5 marks)

d) Suggest two experimental methods by which the kinetics of the following reactions might be monitored (4 marks)



a) Suggest products in the following ligand substitution reactions. Where the reaction has two steps, specify a product for each step. Where more than one product could, in theory, be possible, rationalize your choice of preferred product.

$[PtCl_4]^{2-} \xrightarrow{NH_3} \xrightarrow{NH_3}$ (2 Marks)

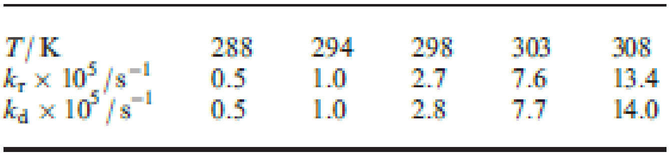
cis-$[Co(en)_2Cl_2]^+ + H_2O \longrightarrow$ (2 Marks)

$[Fe(H_2O)_6]^{2+} + NO \longrightarrow$ (2 Marks)

Section B. Answer any TWO questions

Question 2

a) The rate constants for racemization (k_r) and dissociation (k_d) of $[FeL_3]^{4-}$ at several temperatures, T, are given below.



T / K	288	294	298	303	308
$k_r \times 10^5 / s^{-1}$	0.5	1.0	2.7	7.6	13.4
$k_d \times 10^5 / s^{-1}$	0.5	1.0	2.8	7.7	14.0

[Data from: A. Yamagishi (1986) *Inorg. Chem.*, vol. 25, p. 55.]

i. Determine ΔH and (ΔS), for each reaction. (18 marks)

ii. What can you deduce about the mechanism of racemization? (2marks)

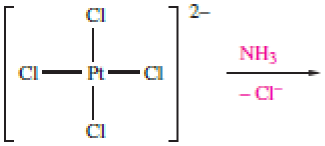
Question 3

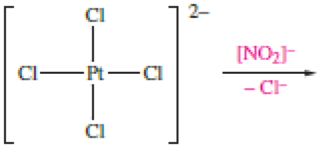
a) Give an example of a reaction that proceeds by an inner sphere mechanism. Sketch reaction profiles for inner sphere electron-transfer reactions in which the rate determining step is (a) bridge formation, (b) electron transfer and (c) bridge cleavage. Which profile is most commonly observed? (12 marks)

b) Discuss, with examples, the differences between inner and outer-sphere mechanisms, and state what is meant by a self-exchange reaction. (8 marks)

Question 4

a) Briefly describe the trans effect by completing the following inorganic reactions: (10 marks)





b) Crystal Field Splitting Energy (CFSE) for the complex ion $[Fe(CN)_6]^{3-}$.

(5 marks)

Question 5

a) Consider the following reaction that takes place in aqueous solution; L, X and Y are general ligands. $Co^{III}L_5X + Y \rightarrow Co^{III}L_5Y + X$. Discuss the possible competing pathways that exist and the factors that favor one pathway over another. (15 marks)

b) Write a rate equation that takes into account the pathways that you discuss. (5 marks)

Periodic table

1
H
1.008

Atomic number, Z
Element symbol
Relative atomic mass, A_r

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** 1.008																	2 **He** 4.00
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.06	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.90	23 **V** 50.94	24 **Cr** 52.01	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.54	30 **Zn** 65.41	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.91	36 **Kr** 83.80
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** 98.91	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.40	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.30
55 **Cs** 132.91	56 **Ba** 137.34	**La–Lu**	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.85	75 **Re** 186.21	76 **Os** 190.23	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.37	82 **Pb** 207.19	83 **Bi** 208.98	84 **Po** 210	85 **At** 210	86 **Rn** 222
87 **Fr** 223	88 **Ra** 226.03	**Ac–Lr**	104 **Rf** [261]	105 **Db** [262]	106 **Sg** [266]	107 **Bh** [264]	108 **Hs** [277]	109 **Mt** [268]	110 **Ds** [271]	111 **Rg** [272]	112 **Uub** [285]						

Lanthanoids	57 **La** 138.91	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** 146.92	62 **Sm** 150.35	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.92	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04	71 **Lu** 174.97
Actinoids	89 **Ac** 227.03	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** 237.05	94 **Pu** 239.05	95 **Am** 241.06	96 **Cm** 244.07	97 **Bk** 249.08	98 **Cf** 252.08	99 **Es** 252.09	100 **Fm** 257.10	101 **Md** 258.10	102 **No** 259	103 **Lr** 262