UNIVERSITY OF ESWATINI

MAIN EXAMINATION 2020/2021

TITLE OF PAPER: PHYSICAL METHODS OF INORGANIC CHEMISTRY

COURSE NUMBER: CHE421

TIME ALLOWED: TWO (2) HOURS

INSTRUCTIONS: THIS PAPER CONTAINS TWO (2) SECTIONS. **ANSWER ALL QUESTIONS FROM SECTION A AND ANY OTHER TWO (2) QUESTIONS FROM SECTION B**. SECTION A IS WORTH 30 MARKS AND EACH QUESTION IN SECTION B IS WORTH 20 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.

SECTION A: ANSWER ALL QUESTIONS

QUESTION 1 COMPULSORY [30 MARKS]

(a) The wavelength of the main line in the sodium atomic spectrum line is 589 nm. What are the frequency and the wavenumber for this line? What is the energy of one photon of this wavelength? [4]

(b) What experimental characterization techniques could be used to:

1. Determine what crystalline components are present in a white powder obtained at a crime scene? [4]
2. Investigate the non-destructive identification of a small amount of an unknown metal oxide in a forensic investigation? [2]

(c) Which of the two chemically different types of protons in $CH_2ClCHCl_2$ resonate at higher frequency? [2]

(d) In the solid state, $[Fe(CO)_5]$ possesses a trigonal bipyramidal structure.

1. How many carbon environments are there?
2. Explain why only one signal is observed in the $^{13}C\{^1H\}$ NMR spectrum of a solution of $[Fe(CO)_5]$, even at low temperature? [6]

(e) Samples of sulfates, $MSO_4.nH_2O$, with M = Cr, Mn, Fe, Co, Ni, and Cu, were found unlabelled in the laboratory. Would it be possible to identify them by their colours alone? [5]

(f) How could IR spectroscopy be used to determine whether the water molecules in $[CrCl_3(H_2O)_3]\ .3H_2O$ are water of crystallisation or coordinated to the metal centre? [2]

(g) Describe how you would determine the following:

1. The amount of the antibiotic drug cefazolin ($C_{14}H_{14}N_8O_4S_3$) that has been incorporated between the layers of the $[Zn(OH)_2]$ in the hybrid inorganic-organic composite $Zn(OH)_2:C_{14}H_{14}N_8O_4S_3$. [3]
2. The silicon to oxygen distance in a silica glass, SiO_2. [2]

SECTION B

ANSWER ANY 2 QUESTIONS FROM THIS SECTION

QUESTION 2 [20 MARKS]

(a) Use your knowledge of features of d-d and charge transfer spectra for octahedral complexes to match each lettered set of the spectral data with the correct complex. Explain your answer. [12]

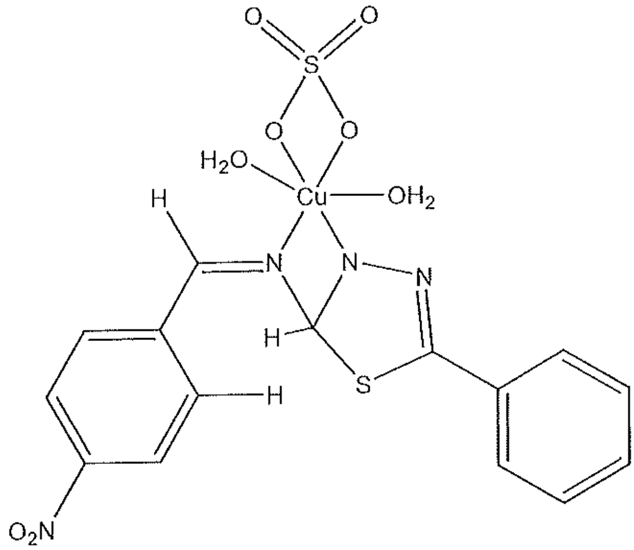
Complex	λ_{max} (in 10^{+3} cm^{-1}) Note: weak means ε = 5-100, strong means $\varepsilon > 10\ 000$
A	22.4 (weak) 25.9 (weak) 36.8 (strong) 41.7 (strong)
B	18.1 (weak) 22.2 (weak) 30.1 (strong) 33.9 (strong)
C	23.9 (weak) 30.1 (weak)
D	32.7 (weak) 39.1 (weak)
E	19.3 (weak) 24.3 (weak) 39.2 (strong)
F	16.6 (weak) 24.9 (weak)
Complexes: $[IrBr_6]^{3-}$, $[Co(H_2O)_6]^{3+}$, $[RhBr_6]^{3-}$, $[Rh(NH_3)_6]^{3+}$, $[RhCl_6]^{3-}$, $[Rh(H_2O)_6]^{3+}$	

(b) The experimental magnetic moment of $[NiCl_4]^{2-}$ in various salts has been measured as 2.85 μB. Use this information to determine whether the $[NiCl_4]^{2-}$ species is tetrahedral or square planar. [4]

(c) The isotropic X-band EPR spectrum of $[Co(CO)_2(Ph_2C_2)(P(OMe)_3)]$ (prepared from the reduction of a dicobalt complex) consists of a sixteen line pattern of approximately equal intensity with g = 2.061, and two hyperfine coupling constants of 45.4 x 10^{-4} cm^{-1} and 166.3 x 10^{-4} cm^{-1}. Explain these observations. (Data from L. V. Casagrande, T. Chen, P. H. Rieger, B. H. Robinson, J. Simpson and S. J. Visco, *Inorg. Chem.* 23 2019 (1984)) [4]

QUESTION 3 [20 MARKS]

The structure of a Cu(II) Schiff base complex is shown. The following data was obtained from the TGA and DTA analysis of the complex:



Step	TGA		DTA	
	Temperature range (°C)	% weight loss	Temperature range (°C)	Peaks
1st	120-160	7	125-165	Endo.
2nd	170-300	23.98	165-290	Exo.
3rd	310-750	37.50	305-740	Exo.

(a) Assign each of the steps to the decomposition intermediate and final decomposition product. [10]

(b) The ESI-mass spectrum of the complex was also measured in order to confirm the composition and the purity of the complex. State the molecular ion peak of the complex. [2]

(c) The spectrum also displayed molecular ion peaks at m/z 487.40, 469.39 and 310.33. Assign the peaks. [8]

QUESTION 4 [20 MARKS]

(a) Predict how many absorption bands there will be (assuming no overlap) in the UV/Vis spectrum of $[Co(NH_3)_6]^{2+}$ and assign the bands. [6]

(b) Use VSEPR theory to predict shape for $XeOF_4$ and hence determine the number of distinct fluorine resonances expected in their ^{19}F NMR spectra. [5]

(c) The two square-planar isomers of $[Pt(PR_3)_2BrCl]$ (where PR_3 is a trialkylphosphine) have different $^{31}P\{^1H\}$ NMR spectra. Isomer **A** shows a single ^{31}P NMR resonance and isomer **B** shows two $^{31}P\{^1H\}$ NMR resonance peaks, each of which is split into a doublet by the second ^{31}P resonance. Which isomer is *cis* and which isomer is *trans*? [4]

(d) When a phosphine, PMe_3, is coordinated to a transition metal a downfield shift is expected in decoupled $^{31}P\{^1H\}$ NMR spectrum. Explain. [3]

(e) A carbonyl compound has a linear OC–M–CO group. How will the CO stretching vibration change (increase, decrease or remain the same) when one CO is replaced by triethylamine $(CH_3CH_2)_3N$? Justify your answer. [2]

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	$F = N_A e$	9.6485×10^{4} C mol^{-1}
Boltzmann constant	k	$1.380\,66 \times 10^{23}$ J K^{-1}
Gas constant	$R = N_A k$	$8.314\,51$ 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} C^{-2} 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	$a_o = 4\pi\varepsilon_o\hbar/m_e e^2$	$5.291\,77 \times 10^{-11}$ m
Fine-structure constant	$\alpha = \mu_o e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Rydberg constant	$R_\infty = m_e e^4/8h^3 c\varepsilon_o^2$	$1.097\,37 \times 10^{7}$ 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}
			23.061 kcal mol^{-1}

f	p	n	μ	m	c	d	k	M	G	Prefixes
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}	

Spectrochemical Series

$I^- < Br^- < S^{2-} < Cl^- < NO_3^- < F^- < OH^- <$ EtOH $< C_2O_4^{2-} < H_2O <$ EDTA $< (NH_3, py) <$ en $<$ dipy $< NO_2^- < CN^- < CO$

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.

TABLE 1. Relative Isotope Abundances of Common Elements.

Elements	Isotope	Relative Abundance	Isotope	Relative Abundance	Isotope	Relative Abundance
Carbon	^{12}C	100	^{13}C	1.11		
Hydrogen	^{1}H	100	^{2}H	0.016		
Nitrogen	^{14}N	100	^{15}N	0.38		
Oxygen	^{16}O	100	^{17}O	0.04	^{18}O	0.2
Fluorine	^{19}F	100				
Silicon	^{28}Si	100	^{29}Si	5.1	^{30}Si	3.35
Phosphorus	^{31}P	100				
Sulfur	^{32}S	100	^{33}S	0.78	^{34}S	4.4
Chlorine	^{35}Cl	100			^{37}Cl	32.5
Bromine	^{79}Br	100			^{81}Br	98
Iodine	^{127}I	100				