UNIVERSITY OF ESWATINI CHEMISTRY DEPARTMENT

FINAL EXAMINATION – November/December 2018

TITLE OF PAPER: PHYSICAL METHODS IN INORGANIC
                           CHEMISTRY

COURSE NUMBER: CHE421

TIME ALLOWED: Three (3) HOURS

INSTRUCTIONS: THERE   ARE   SIX   (6)   QUESTIONS.
                          ANSWER ANY FOUR (4) QUESTIONS.
   EACH QUESTION IS WORTH 25 MARKS.

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

Q.1.

a) Explain why, even though the average atomic mass of silver is 107.9amu, no peak at 108 amu is observed in the mass spectrum of pure silver. What effect does this absence have on form of mass spectra of silver compounds? **[4]**

b) The ^{19}F NMR spectrum of the octahedral ion $[PF_5Me]^-$ shows two signals (δ -45.8 and -57.6 ppm). Why are two signals observed? From these signals, three coupling constants can be measured: J_{PF} = 829 Hz, J_{PF} = 680 Hz and J_{FF} = 35 Hz. Explain the origins of these coupling constants **[6]**

(c) The $^{31}P\{^1H\}$ NMR spectrum of a CDCl3 solution of the square planar rhodium(I) complex, $[RhCl(PPh_3)_3]$, exhibits a doublet of doublets (J = 38 Hz, 145 Hz) and a doublet of triplets (J = 38 Hz, 190 Hz). Rationalize these data. **[6]**

(d) Explain why the ^{19}F NMR spectrum of $[PF_6]^-$ appears as a doublet. **[4]**

(e) The $^{31}P\{^1H\}$ NMR spectrum of trans-$[PtI_2(PEt_3)_2]$ shows a three-line pattern, the lines in which have relative integrals of $\approx$ 1:4:1. What is the origin of this pattern? **[5]**

Q.2.

(a) The figure below shows the single crystal EPR spectrum arising from Cu^{2+} doped into $Ca[Cd(O_2CMe)]_4.6H2O$ for one orientation of the crystal relative to the external magnetic field. The spectrum illustrates the presence of both isotopes of Cu (^{63}Cu and ^{65}Cu), natural abundances 69.2% and 30.8%, respectively, both I=3/2).

   (i) How many peaks do you expect to observe for each isotope? **[2]**

   (ii) Explain why the intensities of the central peaks in the figure are higher than those of the outer peaks. **[4]**

   (iii) The hyperfine coupling constant A(^{65}Cu) is 1.07 times higher than A(^{63}Cu). Which signals in Fig. 4.39 arise from each isotope? Calculate the value of A (in G) for each isotope. **[4]**

   (iv) The EPR spectrum in the figure was measured at 9.75GHz. Calculate the gyromagnetic factor of the copper(II) paramagnetic species. **[2]**

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2800 3000 3200 3400 3600 3800

Magnetic field, B / gauss
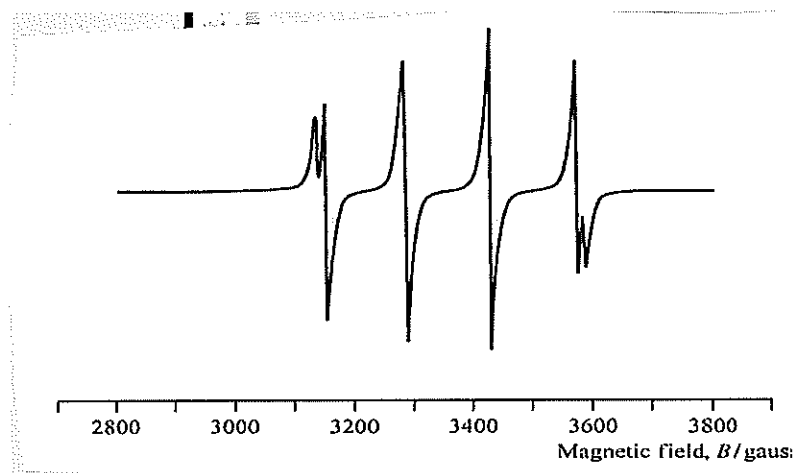
(b)   Vanadium has two isotopes (^{50}V, 0.25%; ^{51}V, 99.75%). The EPR spectrum of an aqueous solution of $[VO(OH_2)_5]^{2+}$ shows an 8-line pattern, and g-values of g_{zz} =1.932, g_{xx} =1.979 and g_{yy} = 1.979 were determined. What can you deduce from the data?   **[6]**

(c)   Predict what you expect to observe in the EPR spectrum of a species in which an unpaired electron interacts with one ^{14}N nucleus (I =1) and one ^1H nucleus (I = 1/2) if the hyperfine coupling constants are (i) $A(^{14}N)$ = $A(^1H)$=30 G; (ii) $A(^{14}N)$ = 30 G, $A(^1H)$ = 10 G.   **[7]**

Q.3.

a)   Why are the reported errors on the N-H bond lengths determined in $(NH_4)_2SeO_4$ by single-crystal X-ray diffraction much larger than the errors on the Se-O bond lengths.   **[2]**

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b) Suggest a suitable experimental technique for each of the following problems.

    i) Single crystal X-ray diffraction data show that acompound crystallizes as a dihydrate. How could you show that the bulk sample was anhydrous? **[2]**

    ii) The single crystal structure of a compound has been determined, and you wish to prepare the same polymorph in bulk in a series of syntheses over a period of several weeks. How can you ensure that the products fulfil this aim? **[2]**

    iii) Changing the conditions under which a compound X crystallizes leads to two batches of crystals with melting points of 97 and 99 ºC, respectively. How can you show that the compounds are polymorphs? **[2]**

c) The EI mass spectrum of lead(II) acetate shows four peak envelopes, each with an isotope pattern characteristic of Pb. The most intense peak in each envelope appears at m/z 326.0, 267.0, 224.0 and 208.0 respectively. (i) By using information provided, sketch the pattern that is exhibited by each envelope. (ii) Assign the peaks. **[10]**

d) The EI mass spectrum of $Cr(CO)_6$ gives a peak corresponding to the molecular ion followed by peak envelopes with spacings equal to mass units of 28. Rationalize the peaks in the spectrum. Illustrate how each fragment is formed. Why is the EI technique suitable for recording the mass spectrum of $Cr(CO)_6$? **[7]**

Q. 4.

a) The interactions, Isomer Shift, Quadrupole Splitting and Magnetic Splitting, alone or in combination are the primary characteristics of many Mössbauer spectra. With the use of suitable diagrams, illustrate how these effects give rise to spectra. **[10]**

b) Using Mossbauer spectroscopy, explain how you would determine whether the compound $Fe_4[Fe(CN)_6]$ contains discrete Fe(II) and Fe(III) sites. **[4]**

c)   Consider the cluster complex $Co_3(CO)_9Se$, where the ligands are
     CO molecules and the Se^{2-} ion.   **[11]**

   (i)   What is the oxidation state of each of the cobalt atoms?

   (ii) Assuming maximum pairing of metal-centered valence
         electrons, how many unpaired electrons are there in the
         cluster?

   (iii) The EPR spectrum of the cluster is shown in the figure below.
         Rationalize the number of peaks and their relative intensities.
         (Note: ^{59}Co, 100% abundant, I=7/2).

Q.5.

(a) A student has prepared a sample of $[Zn(en)_3]Cl_2$ (en = $H_2NCH_2CH_2NH_2$)
     but is worried that the complex appears blue when $[Zn(en)_3]Cl_2$ should be
     colourless. The student wonders if she picked up a bottle of nickel(II)
     chloride instead of zinc(II) chloride. The experimental CHN analysis for
     the complex is C 23.00, H 7.71, N 26.92%.

   (i)   Do the elemental analytical data distinguish between $[Zn(en)_3]Cl_2$
         and $[Ni(en)_3]Cl_2$? Comment on your answer.   **[8]**

   (ii) How would mass spectrometry help you to distinguish between the
         two compounds?   **[3]**

   (iii) Suggest why ^1H NMR spectroscopy might be useful in distinguishing
         between $[Zn(en)_3]Cl_2$ and $[Ni(en)_3]Cl_2$.   **[2]**

   (iv) Suggest why UV-VIS spectroscopy might be useful in distinguishing
         between $[Zn(en)_3]Cl_2$ and $[Ni(en)_3]Cl_2$ **[2]**

(v)   (iv) A single crystal X-ray diffraction study was carried out and confirmed the presence of $[M(en)_3]Cl_2$. Can this technique unambiguously assign M to Zn or Ni? **[2]**

(vi)   Explain why AAS could be used to confirm the identity of the metal

[2]

b) $[Fe(CO)_4]^{2-}$ and $Fe(CO)_5$ have T_d and D_{3h} symmetries respectively. What do you expect to observe in the room temperature ^{13}C NMR spectra of $Na_2[Fe(CO)_4]$ and $Fe(CO)_5$? Rationalize your answer. **[6]**

Commonly Used Physical Constants

Constant	Symbol	Value
acceleration due to gravity	g	9.8 m s^{-2}
atomic mass unit	amu, m$_u$ or u	1.66×10^{-27} kg
Avogadro's Number	**N**	**6.022×10^{23} mol^{-1}**
Bohr radius	a$_0$	0.529×10^{-10} m
Boltzmann constant	k	1.38×10^{-23} J K^{-1}
electron charge to mass ratio	-e/m$_e$	-1.7588×10^{11} C kg^{-1}
electron classical radius	r$_e$	2.818×10^{-15} m
electron mass energy (J)	m$_e$c^2	8.187×10^{-14} J
electron mass energy (MeV)	m$_e$c^2	0.511 MeV
electron rest mass	m$_e$	9.109×10^{-31} kg
Faraday constant	F	9.649×10^4 C mol^{-1}
fine-structure constant	α	7.297×10^{-3}
gas constant	R	8.314 J mol^{-1} K^{-1}
gravitational constant	G	6.67×10^{-11} Nm^{2}kg^{-2}
neutron mass energy (J)	m$_n$c^2	1.505×10^{-10} J
neutron mass energy (MeV)	m$_n$c^2	939.565 MeV
neutron rest mass	m$_n$	1.675×10^{-27} kg
neutron-electron mass ratio	m$_n$/m$_e$	1838.68
neutron-proton mass ratio	m$_n$/m$_p$	1.0014
permeability of a vacuum	μ$_0$	$4\pi \times 10^{-7}$ N A^{-2}
permittivity of a vacuum	ε$_0$	8.854×10^{-12} F m^{-1}
Planck constant	h	6.626×10^{-34} J s
proton mass energy (J)	m$_p$c^2	1.503×10^{-10} J
proton mass energy (MeV)	m$_p$c^2	938.272 MeV
proton rest mass	m$_p$	1.6726×10^{-27} kg
proton-electron mass ratio	m$_p$/m$_e$	1836.15
Rydberg constant	R$_H$	1.0974×10^7 m^{-1}
speed of light in vacuum	C	2.9979×10^8 m/s
Electronic Charge	e	1.602×10^{-19} C

Main isotopes of lead ($_{82}$Pb)

	abundance
^{204}Pb	1.4%
^{206}Pb	24.1%
^{207}Pb	22.1%
^{208}Pb	52.4%

Isotopic abundances vary greatly by sample

Stable isotopes of silver ($_{47}$Ag)

Isotope		
	abundance	
^{107}Ag	51.839%	
^{109}Ag	48.161%	

Standard atomic weight   **107.868**

Periodic Table of the Elements

Main Group Representative Elements

Main Group Representative Elements

Transition metals

☐ Metals ☐ Metalloids ☐ Nonmetals

Group	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 1.00794																	2 He 4.002602
2	3 Li 6.941	4 Be 9.012182											5 B 10.811	6 C 12.0107	7 N 14.0067	8 O 15.9994	9 F 18.998403	10 Ne 20.1797
3	11 Na 22.989770	12 Mg 24.3050											13 Al 26.981538	14 Si 28.0855	15 P 30.973761	16 S 32.065	17 Cl 35.453	18 Ar 39.948
4	19 K 39.0983	20 Ca 40.078	21 Sc 44.955910	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938049	26 Fe 55.845	27 Co 58.933200	28 Ni 58.6934	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.64	33 As 74.92160	34 Se 78.96	35 Br 79.904	36 Kr 83.80
5	37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 Tc [98]	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.90447	54 Xe 131.293
6	55 Cs 132.90545	56 Ba 137.327	71 Lu 174.967	72 Hf 178.49	73 Ta 180.9479	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.078	79 Au 196.96655	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.98038	84 Po [208.98]	85 At [209.99]	86 Rn [222.02]
7	87 Fr [223.02]	88 Ra [226.03]	103 Lr [262.11]	104 Rf [261.11]	105 Db [262.11]	106 Sg [266.12]	107 Bh [264.12]	108 Hs [269.13]	109 Mt [268.14]	110 Ds [281.15]	111 Rg [272.15]	112 Cn [285]	113 [284]	114 Fl [289.2]	115 [288]	116 Lv [299]	117 ** [294]	118 [294]

Lanthanide series	57 La 138.9055	58 Ce 140.116	59 Pr 140.90765	60 Nd 144.24	61 Pm [145]	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.50	67 Ho 164.93032	68 Er 167.259	69 Tm 168.93421	70 Yb 173.04
Actinide series	89 Ac [227.03]	90 Th 232.0381	91 Pa 231.03588	92 U 238.02891	93 Np [237.05]	94 Pu [244.06]	95 Am [243.06]	96 Cm [247.07]	97 Bk [247.07]	98 Cf [251.08]	99 Es [252.08]	100 Fm [257.10]	101 Md [258.10]	102 No [259.10]

[a]The labels on top (1A, 2A, etc.) are common American usage. The labels below these (1, 2, etc.) are those recommended by the International Union of Pure and Applied Chemistry (IUPAC).

Except for elements 114 and 116, the names and symbols for elements above 113 have not yet been decided.

Atomic weights in brackets are the names of the longest-lived or most important isotope of radioactive elements.

Further information is available at http://www.webelements.com

** Discovered in 2010, element 117 is currently under review by IUPAC.