UNIVERSITY OF SWAZILAND

RE-SIT EXAMINATION

ACADEMIC YEAR 2018/2019

TITLE OF PAPER:	COORDINATION AND TRANSITION METAL CHEMISTRY
COURSE NUMBER:	CHE322
TIME ALLOWED:	THREE (3) HOURS
INSTRUCTIONS:	THERE ARE FIVE (5) QUESTIONS. ANSWER ANY FOUR (4) QUESTIONS. EACH QUESTION IS WORTH 25 MARKS.

THE FOLLOWING HAVE BEEN PROVIDED WITH THIS EXAMINATION PAPER:

- **Periodic Table of the Elements**
- **Table of Universal Constants**
- **Tanabe-Sugano diagrams for octahedral complexes**

NON-PROGRAMMABLE ELECTRONIC CALCULATORS MAY BE USED

"Marks will be awarded for method, clearly labelled diagrams, organization and presentation of thoughts in clear and concise language"

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QUESTION 1 [25MARKS]

a) Evaluate the commutator $\left[\frac{d}{dr}, \frac{1}{r}\right]$ [4]

b) The muzzle velocity of a rifle bullet is about 900m/s. if the bullet weighs 30g and the uncertainty in its momentum is 0.10%, how accurate can the position of the bullet be measured? [4]

c) Calculate the probability that a particle in a one-dimensional box of length L is found between 0.31 and 0.35L when it is described by the following wavefunctions.

i. $\sqrt{\frac{2}{L}} sin\frac{\pi x}{L}$ ii. $\sqrt{\frac{2}{L}} sin\frac{3\pi x}{L}$ [7]

d) .

i). Are the eigenfunctions of Ĥ for the particle in a one-dimensional box also eigenfunctions of the position operator, $\hat{x}$? [2]

ii). Calculate the average value of x for n = 3 and n = 5 given the wavefunction to be $\psi(x) = \sqrt{\frac{2}{L}} sin\frac{n\pi x}{L}$, $n = 1,2,3 \ldots..$ [6]

iii). From your results in (ii) suggest an expression for all values of n. [1]

iv). How does your result compare with the prediction based on classical physics? [1]

Useful integrals

$$\int xsin^2axdx = \frac{x^2}{4} - \frac{xsin2ax}{4a} - \frac{cos2ax}{8a^2} + C$$

$$\int Sin^2axdx = \frac{x}{2} - \frac{1}{4a}Sin2ax + C$$

QUESTION 2 [25 MARKS]

a) Explain why Einstein's introduction of quantization accounted for the heat capacities of metals at low temperatures. [5]

b) When lithium is irradiated with light, the kinetic energy of eject6ed electrons is 2.935×10^{-19}J for λ = 300.0nm and 1.28×10^{-19}J for λ = 400.0nm. calculate

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											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											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								

TRANSITION ELEMENTS

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

*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.

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	$\varepsilon_0 = 1/c^2\mu_0$	$8.854\,19 \times 10^{-12}$ J^{-1} C^2 m^{-1}
	$4\pi\varepsilon_0$	$1.112\,65 \times 10^{-10}$ J^{-1} C^2 m^{-1}
Vacuum permeability	μ_0	$4\pi \times 10^{-7}$ J s^2 C^{-2} m^{-1}
		$4\pi \times 10^{-7}$ T^2 J^{-1} 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	$a_0 = 4\pi\varepsilon_0\hbar/m_e e^2$	$5.291\,77 \times 10^{-11}$ m
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Rydberg constant	$R_\infty = m_e e^4/8h^3 c\varepsilon_0^2$	$1.097\,37 \times 10^{7}$ 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}

Prefixes

f	p	n	μ	m	c	d	k	M	G
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}

c) The rotational constant of $^{2}D^{19}F$ determined from microwave spectroscopy is 11.007 cm^{-1}. The atomic masses of ^{19}F and ^{2}D are 18.9984032 u and 2.0141018 u, respectively. Calculate the bond length in $^{2}D^{19}F$ to the maximum number of significant figures consistent with this information. [7]

d) Derive the term symbols for the electron configuration ns^1nd^1. Which of these terms has the lowest energy? [5]

e) The pure rotational Raman spectrum of $^{14}N_2$ shows a spacing of 7.99 cm^{-1} between adjacent rotational lines.

(I) Calculate the value of the rotational constant B. [2]

(II) What is the spacing between the unshifted line ν_{ex} and the pure rotational line closest to ν_{ex}? [2]

(III) If 540.8 nm radiation from an argon laser is used as the exciting radiation, find the wavelength of the two pure rotational Raman lines nearest to the unshifted lines. [4]

QUESTION 3 (25 MARKS)

a) The force constant of $^{79}Br^{79}Br$ is 240 N m^{-1} and the atomic mass of ^{79}Br is 78.9183 u. Calculate

(i) The fundamental vibration frequency $\overline{\nu}$ and [3]

(ii) The zero point energy of $^{79}Br_2$ [3]

b) The fundamental line in the infrared spectrum of $^{12}C^{16}O$ occurs at 2143.0cm $^{-1}$, and the first overtone occurs at 4260.0 cm $^{-1}$. Calculate

(i) The fundamental vibrational frequency, $\overline{\nu}$, and the anharmonicity constant, χ_e [5]

(ii) The exact zero point energy of CO. [3]

c) Given that the fundamental vibrational frequency $\overline{\nu}$ = 4138.32 cm^{-1} and the rotational constant B = 20.956 cm^{-1} for $^{1}H^{19}F$, calculate the first three lines in the P and R branches in the vibration-rotation spectrum of HF. [6]

d) How many normal modes of vibration does the molecule BF_3 have? Sketch two of its bond stretching modes (non-degenerate) and indicate whether they are infrared active or not. [5]

Total Marks **/80/**

UNIVERSITY OF ESATINI

Re-Sit EXAMINATION 2018/2019

TITLE OF PAPER: THEORY OF SPECTROSCOPY

COURSE NUMBER: CHE342

TIME: TWO (2) HOURS

INSTRUCTIONS:

Answer all questions

NB: Each question should start on a new page.

A data sheet and a periodic table are attached

A non-programmable electronic calculator may be used

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QUESTION 1 (25 MARKS)

a) The ionization energies (I) of an electron from the valence orbitals on a carbon and an oxygen atoms are given in the table below:

Atom	Valence orbital	I/MJ mol^{-1}
O	2s	3.116
	2p	1.524
C	2s	1.872
	2p	1.023

(i) Use these data to construct a molecular orbital energy diagram for CO.[5]

(ii) What is the electron configuration of the ground state of CO? [1]

(iii) What is the bond order of CO? [1]

(iv) Is CO paramagnetic or diamagnetic? [1]

b) The highest occupied molecular orbitals for an excited electronic configuration of an oxygen molecule are $(l\pi_g)^1\ (2\sigma_u^*)^1$. Determine the molecular term symbols for oxygen in this electronic configuration. [5]

c) The photoelectron spectrum of NO was obtained using He 58.4 nm (21.22 eV) radiation. It consisted of a strong peak at kinetic energy 4.69 eV and a series of 24 lines starting at 5.56 eV and ending at 2.2 eV. A shorter series of six lines began at 12.0 eV and ended at 10.7 eV. Account for this spectrum. [7]

d) When light of wavelength 440 nm passes through a 3.5 mm of solution of an absorbing substance with a concentration of 0.667 mmol/L, the transmittance is 65.5 %.Calculate the molar absorption coefficient of the solute at this wavelength and express the answer in cm^2mol^{-1}. [5]

QUESTION 2 (30 MARKS)

a) Determine the number of translational, rotational and vibrational degrees of freedom in the following molecules:

(i) CH_3Cl (ii) OCS (iii) C_6H_6 (iv) H_2CO [6]

b) Classify each of the following molecules as spherical , a symmetric or an asymmetric top:

(i) CH_3Cl (ii)CCl_4 (iii) SO_2 (iv) SF_6 [4]