UNIVERSITY OF SWAZILAND

FINAL EXAMINATION 2015/2016

TITLE OF PAPER: **PHYSICAL CHEMISTRY**

COURSE NUMBER: **C302**

TIME: **THREE (3) HOURS**

INSTRUCTIONS:

There are **seven (7)** questions. Each question carries 25 marks. You are required to answer **any four (4) 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) Briefly explain the relationship between the Heisenberg uncertainty principle and the commutation of operators. [5]

(b) Given that $\hat{A}=\frac{d}{dx}$ and $\hat{B}=x^2$ find the commutator $[\hat{A}, \hat{B}]$. [5]

(c) A particle is in a state described by the function $\psi(x) = 0.632e^{2ix} + 0.775e^{-2ix}$. What is the probability that the particle will be found with momentum $2\hbar$? [4]

(d) Consider the function $f(x) = xe^{-x^2/2}$ $\quad -\infty \leq x \leq \infty$

- (i) Normalize f(x) [6]
- (ii) Find the average value of x [5]

QUESTION 2 (25 MARKS)

a) Consider a particle of mass m confined in a cubic box of edge L. The potential energy inside the box is zero and infinity outside the box.

- (i) Write the Hamiltonian for the particle inside the box [1]
- (ii) Write the Schrodinger equation for this system [1]
- (iii) Without doing any calculations, use the solutions of the particle in a one dimensional box (given below) to write the solutions for the above Schrodinger equation and the expression for energy of the system. [4]
- (iv) What is the degeneracy of the energy level $\frac{18h^2}{8mL^2}$? [4]

NB: For a particle in a one dimensional box of length L,

$$\psi(x) = \left(\frac{2}{L}\right)^{\frac{1}{2}} \sin\left(\frac{n\pi x}{L}\right) \text{ where n= 1, 2, 3,... and } E_n = \frac{n^2h^2}{8mL^2}$$

b) The harmonic oscillator may be used for a model for molecular vibrations, considering the masses connected by spring-like bonds. The molecule vibrates like a harmonic oscillator with mass equal to the reduced mass of the atoms of the molecule.

- (i) Calculate the reduced mass of an HBr molecule (atomic masses are 1.0078 u and 79.90 u for H and Br, respectively. [3]

(ii) The vibrational frequency of the HBr molecule is $v = 7.944 \times 10^{13}\ s^{-1}$. Find the bond force constant k_f. [4]

c) Find the most probable value(s) of x for a harmonic oscillator in its ground state, $\psi_0 = Ne^{-ax^2}$, a is a constant. [3]

d) The wavefunction of a particle rotating on a ring is given by $\psi(\phi) = \frac{1}{\sqrt{2\pi}} e^{-im_l\phi}$, $m_l = 0, \pm 1, \pm 2, ...$ Calculate the expectation value of ϕ. [5]

QUESTION 3 (25 MARKS)

Lithium and chlorine both have two naturally occurring isotopes whose abundance and atomic masses are given below:

Isotope	Abundance /%	Atomic mass/u
^{6}Li	8	6.0151
^{7}Li	92	7.0160
^{35}Cl	75	34.9688
^{37}Cl	25	36.9651

Naturally occurring LiCl consists of a mixture of four possible isotopic combinations. A sample of natural LiCl was vaporized at 1500 K and a microwave spectrum obtained. The lowest frequency line was found at 1.24 710 cm^{-1}.

a) Why is the spectrum taken in the gas phase? [1]

b) To which isotopic combination, does the lowest frequency line correspond? [4]

c) Calculate the LiCl bond distance in this compound. [6]

d) Assuming the bond distance is independent of isotopic substitution and rotational state, calculate the frequencies of the next three lines seen in the spectrum. To which isotope does each line correspond? [11]

e) Which of these four lines (i.e. the 1.24 710 cm^{-1} and the three in (d) above should be most intense? The least intense? Explain. [3]

QUESTION 4 (25 MARKS)

a) Describe the fundamental vibrational modes of H_2O and CO_2. For each molecule indicate which modes will show infrared activity and why. [8]

b) Explain the difference between a **"hot band"** and an **"overtone band"** in infrared spectra. How would you distinguish the two experimentally? [5]

c) The anharmonicity constant for $^{35}Cl^{19}F$ is 1.25 x 10^{-2} and the fundamental frequency is 793.3 cm^{-1}. The isotopic masses for ^{35}Cl and ^{19}F are 34.9688 u and 18.9984 u, respectively.

(i) Calculate the energies of the first four vibrational levels. [4]

(ii) Calculate the difference in energy between the v = 25 and v = 26 levels using (1) the harmonic oscillator model and (2) the anharmonic oscillator model. Comment on the difference of your results from the two calculations. [4]

(iii) Calculate the bond force constant in this molecule. [4]

QUESTION 5 (25 MARKS)

a) The energy levels of a hydrogenic atom are given by the following equation:

$E_n = -\frac{R_H hcZ^2}{n^2}$, where R_H is the Rydberg constant, Z is the nuclear charge and n = 1, 2, 3,....

(i) Calculate the wavelength of a photon emitted when an electron goes from n = 3 to n = 2 in the hydrogenic atom He^+ [4]

(ii) What is the wavenumber of the first line in the Lyman series of He^+? (For Lyman series, $n_2 \rightarrow n_l$, with n_l = 1, n_2 = 2, 3...) [3]

b) The wave function for a 2s orbital of a hydrogen atom is

$\psi_{2s} = N(2 - r/a_0)e^{-\frac{r}{2a_0}}$. Determine the normalization constant N. [6]

c) State whether the following transitions are allowed or forbidden in a hydrogen atom. In each case, give a reason for your answer.

(i) 3d → 2s (ii) 3p → 1s [4]

d) What is the lowest term symbol for Ti^{3+} if the first two electrons to be lost are the 4s electrons. [5]

e) Calculate the magnitude of the orbital angular momentum of a 4d electron in a hydrogenic atom [3]

QUESTION 6 (25 MARKS)

(a) Use the molecular orbital theory to explain why the binding energy of N_2^+ is less than that of N_2 whilst that of O_2^+ is greater than that of O_2. [6]

(b) Give the valence bond description of the bonding in ammonia, NH_3. [4]

(c) Use the molecular orbital theory to assign the following bond lengths and binding energies to the following species:

Species: H_2^+, H_2, He_2^+, He_2
Bond lengths (pm): 74, 106, 108, and 6000
Binding energy (kJ/mol) :<<1, 241, 268, 457. [6]

(d) Consider the ions NO^- and C_2^+

- (i) Draw the molecular orbital energy diagram for each of the species [4]
- (ii) Write down the electron configuration and give multiplicity of the ground states. [4]
- (iii) Which ion should have the longer bond length? [1]

QUESTION 7 (25 MARKS)

a) Describe the principles of laser action. Illustrate with an actual example. [10]

b) What features of laser radiation are applied in Chemistry? Discuss two applications of lasers in Chemistry. [10]

c) Photoionization of H_2 by 21 eV electrons produces H_2^+. Explain why the intensity of the $v = 2 \leftarrow 0$ transition is tronger than that of the $0 \leftarrow 0$ transition. [5]

Total marks **/100/**

Useful Integrals

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1. $\int x^2 e^{-x^2} dx = \frac{\sqrt{\pi}}{2}$
2. $\int x^3 e^{-x^2} dx = 0$
3. $\int_0 x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$
4. $\int sin\theta d\theta = -cos\theta + constant$
5. $d\tau = r^2 sin\theta dr d\theta d\phi$
6. $\int x^n dx = \frac{1}{a^{n+1}} \qquad n \neq -1$
7. $\int_0^{2\pi} cos^2\theta sin\theta d\theta = \frac{2}{3}$

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} 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}

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}

PERIODIC TABLE OF ELEMENTS

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

	GROUPS																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
PERIODS	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	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	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.