UNIVERSITY OF SWAZILAND

MAIN EXAMINATION 2017/2018

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) Explain how Einstein's introduction of quantization of energy accounted for the pr operties of heat capacity at low temperatures [4]

b) In an x-ray photoelectron experiment, a photon of wavelength 121 pm ejects an e lectron and it emerges with speed of 5.69×10^7 m/s. calculate the binding energy of the electron. [3]

c) For the following operator and function, show that the function is an eigenfunction of the operator and determine the eigenvalue.

Operator	Eigenfunction	
$\frac{d^2}{dx^2} - 4$	$3\cos 2x$	[3]

d) What is the de Broglie wavelength of an electron accelerated to 100 eV [3]

e) A photon of radiation with a wavelength of 305 nm ejects an electron from a meta l with a kinetic energy of 1.77eV. Calculate the maximum wavelength of radiation capable of ejecting an electron from the metal. [4]

f) By evaluating the commutator, $[x, P_x]$, show whether the operators for position an d momentum commute. [4]

g) Two (unormalised) excited state wavefunctions of the hydrogen atom are

A) $$\psi(r) = \left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}$$

B) $$\psi(r,\theta,\phi) = r\sin\theta\cos\phi e^{-r/2a_0}$$

Show that these two functions are mutually orthogonal. [4]

QUESTION 2 (25 MARKS)

a) 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 $2\hbar$ [3]

b) Consider the energy eigenvalues of a particle in a one dimensional box

$E_n = \frac{h^2n^2}{8mL^2}$, n =1,2,3,...as a function of *n, m* and *L.*

(i) By what factor do you need to change the box length L to decrease the zero point energy by a factor of 400 for a fixed value of *m*? [3]

(ii) By what factor would you have to change ***n*** for fixed values of L and **m** to increase the energy by a factor of 400? [3]

(iii) By what factor would you have to increase L to have the zero point energy of an electron be equal to the zero point energy of a proton? [4]

c) The function $\psi(x) = x\left(1 - \frac{x}{L}\right)$, is an acceptable function for a particle in a one dimensional box of length L and with infinitely high walls.

(i) Normalize $\psi(x)$ [6]

(ii) Calculate the expectation value <x> [6]

QUESTION 3 (25 MARKS)

a) The total energy eigenvalues of the hydrogen atom are given by

$E_n = -\frac{e^2}{8\pi\varepsilon_0 a_0 n^2}$, n = 1, 2, 3,... and the three quantrum numbers associated with the total energy eigenvalues are related by n = 1, 2, 3,...; l = 0, 1, 2,... n – 1; and m_l = 0, ± 1,±2,±3,...,±l. Using the notation ψ_{nlm_l}, list all eigenfunctions that have the following energy eigenvalues and hence give the degeneracy of these energy levels:

(i) $E = -\frac{e^2}{32\pi\varepsilon_0 a_0}$ [3]

(ii) E = $-\dfrac{e^2}{72\pi\varepsilon_0 a_0}$ [3]

b) Calculate the mean value of the radius, <r>, at which you would find an electron if the H atom wave function is $\psi_{210}(r,\theta,\phi) = \dfrac{1}{4\sqrt{2\pi a_0^3}}\dfrac{r}{a_0}e^{-\frac{r}{2a_0}}\cos\theta$ [7]

c) Define the quantum numbers L and S as applied to many electron atoms, indicating the kind of values they may have. State the physical meaning of the two quantum numbers in quantitative terms. Under what conditions are L and S no longer valid as quantum numbers? State the reason in a sentence or two. [7]

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

QUESTION 4 (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 $(1\pi_g)^1\ (2\sigma_u^*)^1$. 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 5 (25 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]

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) 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 v_{ex} and the pure rotational line closest to v_{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]

Useful Integrals

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. $\int_0^{2\pi} cos^2\theta sin\theta d\theta = \frac{2}{3}$

QUESTION 6 (25 MARKS)

a) The force constant of $^{79}Br^{79}Br$ is 240 Nm^{-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]

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 stronger than that of the 0 $\leftarrow$ 0 transition. [5]

Total Marks /100/

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}

PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	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										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.