UNIVERSITY OF ESWATINI

MAIN EXAMINATION 2018/2019

TITLE OF PAPER: PHYSICAL CHEMISTRY

COURSE NUMBER: C302

TIME: THREE (3) HOURS

INSTRUCTIONS:

Attempt any 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) A particle is moving in one dimension between x = α and x = b. the potential is such that the particle cannot be found outside these limits and the wave function in between is $\psi = A/x$

   i). Find the normalization constant [5]

   ii). Calculate the average value of x [5]

b) Which of the following functions below are eigenfunctions of the operator d/dx? For each eigenfunction give the eigenvalue.

   i). $\exp(ikx)$

   ii). $6\cos(4x)$

   iii). $\exp(-\alpha x^2)$

   iv). k [5]

c) The x component of angular momentum of an orbiting electron is $L_x = zp_x - xp_z$.

   i). Find the quantum mechanical operator $\hat{L}_x$ [2]

   ii). Evaluate the following commutator: $[\hat{Y}, \hat{P}_y]$ [3]

d) For a particle in a box whose ends are at x = 0 and x = 0.2000nm, calculate the probability that the particle's x coordinate is between 0.16000 and 0.16001nm if n=1 $\left[\psi = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right)\right]$ [5]

QUESTION 2 [25 MARKS]

Given that a particle in a one dimensional box has the wavefunctionn

$\psi = \left(\frac{2}{L}\right)^{\frac{1}{2}} \sin\left(\frac{\pi x}{L}\right)$, n= 1,2,3... for 0<x<L

a) Derive the expression for the energy of the particle [7]

b) If the particle was now confined in a 3 dimensional cubic box, what would be the energy expression? [4]

c) If now the cubical box has dimensions $L_x = L_y = L_z/2$, what would be the energy when

i). $n_x = 1, n_y = 2, n_z = 2$

ii). $n_x = 1, n_y = 1, n_z = 4$

What can you say about the two energy levels? [7]

d) .

i). Distinguish between the terms "**state**" and "**energy level**" of a system.

ii). For a particle in a cubic box of edge L, how many states have the energies in the range 0 to $13h^2/(8mL^2)$?

iii). How many energy levels lie in this range? [7]

QUESTION 3 [25 MARKS]

a) How did the study of heat capacity of metals consolidate the Plank's hypothesis that energy is quantized? [8]

b) .

i). Write down the expression for a one dimensional harmonic oscillator, defining all terms. [3]

ii). Assuming the vibrations of $^{14}N_2$ molecule are equivalent to those of a harmonic oscillator with a force constant k =2293.8 N/m, what is the zero point energy of the vibrations of this molecule. (the mass of the nitrogen molecule is 14.004u) [7]

c) The rotation of $H^{127}I$ molecule can be pictured as the orbital motion of an H atom at a distance 160 pm from a stationary **iodine** atom. Suppose the molecule rotates only in one plane.

i). Calculate the energy needed to excite the molecule into rotation [4]

ii). What is the minimum non-zero angular momentum of the molecule?

[3]

QUESTION 4 [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 5 [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. [6]

iii). Calculate the bond force constant in this molecule. [2]

QUESTION 6 [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]

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	$\varepsilon_0 = 1/c^2\mu_0$	$8.854\,19 \times 10^{-12}$ 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 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 →
Symbol →
Atomic No. →

*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.