UNIVERSITY OF SWAZILAND

FINAL EXAMINATION 2014/15

TITLE PAPER: PHYSICAL CHEMISTRY

COURSE NUMBER: C302

TIME: THREE (3) HOURS

INSTRUCTIONS:
There are **six (6)** questions. Each question is worth 25 marks. Answer **any four (4)** questions.

A list of integrals, a data sheet, and a periodic table are attached

Non-programmable electronic calculators may be used.

DO NOT OPEN THIS PAPER UNTIL PERMISION TO DO SO HAS BEEN GRANTED BY THE CHIEF INVIGILATOR.

Question 1 (25 marks)

(a) Using wave particle duality, discuss the 'failure' of classical mechanics. [10]

(b) With the aid of a diagram, explain the Ultraviolet catastrophe [5]

(c) The rearranged Schrödinger equation for a free particle in a box is as follows:

$$\frac{d^2\psi(x)}{dx^2}+\frac{2mE}{\hbar}\psi(x)=0 \qquad 0\leq x\leq a$$

And the general solution is

$\psi(x)=A\cos kx+B\sin kx$, where $k=\frac{\sqrt{2mE}}{\hbar}$

Show that the energy of a particle in a box is quantized. [5]

(d) Which of the following functions are eigen functions of $\frac{d^2}{dx^2}$?

(i) lnx, (ii) 5sin3x [4]

(e) In (a) above, list the eigen values of the function where possible? [1]

Question 2 (25 marks)

(a) Normalize the function $\psi=\cos\theta$, $0\leq\theta\leq 2\pi$ [5]

(b) With the aid of a diagram(s), distinguish between bonding and anti-bonding molecular orbitals [10]

(c) When lithium is radiated with light, the kinetic energy (KE) of the ejected electrons is 2.935×10^{-19} J for λ=300.0 nm and 1.280×10^{-19} J for λ=400.0 nm
Calculate the:
(i) Planck's constant, [3]
(ii) the threshold frequency, and [2]
(iii) the work function of lithium from these data. [2]

(d) Classify CCl_4 as spherical, symmetric or asymmetric top [3]

Question 3 (25 marks)

(a) Draw the molecular orbital diagram for NCl and determine the bond order [6]

(b) From (a) above, is NCl paramagnetic or not? Indicate the number of unpaired electrons in each case [2]

(c) Construct the kinetic energy term of the Schrödinger equation. [5]

(d) Which of the following molecules may show infrared absorption spectra?
(i) CH_4 (ii) CH_3F [2]

(e) Explain why the 2s and 2p subshells are degenerate in the hydrogen atom but are not degenerate in many-electron atoms [5]

(f) Explain the origin of spin-orbit coupling and explain how it affects the appearance of a spectrum. [5]

Question 4 (25 marks)

(a) State how classical physics failed in the study of the structure of an atom. [5]

(b) State the ***Heisenberg Uncertainty Principle.*** [4]

(c) The term symbol for a particular state is $^3F_2$.
(i) What are the L, S, and J for this state? [3]
(ii) What is the minimum number of electrons which could give rise to this state? [1]
(iii) Suggest a possible electron configuration [2]

(d) State the general significance of spectroscopy. [4]

(e) Briefly discuss the principles and techniques of Raman spectroscopy. [6]

Question 5 (25 marks)

(a) The term symbol for the ground state of N_2^+ is $^2\Sigma_g^+$.
(i) What is the total spin and orbital angular momentum of the molecule? [2]
(ii) Show that the term symbol agrees with the electron configuration predicted by the building up principle. [4]

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

(c) Distinguish between Fluorescence and Phosphorescence. [4]

(d) Discuss the significance of the **Born-Oppenheimer approximation** in quantum chemistry. [4]

(e) Derive term symbols: $1s^2 2s^2 2p^1 3d^1$ [6]

Question 6 (25 marks)

(a) Suppose that you wish to characterize the normal modes of benzene in the gas phase. Why is it important to obtain both infrared absorption and Raman spectra of your sample? [6]

(b) The force constant of $^1H^{19}F$ molecule is 966 N/m. Note: Isotopic masses are ^1H 1.0078 u and 19F 18.9984 u].

(i) Calculate the zero point vibrational energy for this molecule [5]

(ii) If this amount of energy were converted to translational energy, how fast would the molecule be moving? [3]

(iii) Calculate the frequency of light needed to excite the molecule from the ground state to the first excited [3]

(c) How many normal modes of vibration are there for the following molecules?

(i) C_6H_6, (ii) $C_6H_5CH_3$ (iii) HC≡C–C≡CH [6]

(d) Define degeneracy [2]

THE END...

USEFUL INFORMATION IS GIVEN BELOW

$$\int x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

$$d\tau = r^2 \sin\theta d\theta d\phi dr$$

$$\int x \sin^2 ax dx = \frac{x^2}{4} - \frac{x \sin 2ax}{4a} - \frac{\cos 2ax}{8a}$$

$$\int_0^\pi x \sin x dx = \frac{\pi^2}{2}$$

$$\int \sin^2 x dx = \frac{x}{2} - \frac{1}{4a} \sin 2ax$$

$$\int \sin ax \cos ax dx = \frac{1}{2a} \sin^2 ax$$

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

Atomic mass → / Symbol → / Atomic No. →

TRANSITION ELEMENTS

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								

*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.