UNIVERSITY OF SWAZILAND

SUPPLEMENTARY EXAMINATION 2013/14

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.

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Question 1 (25 marks)

(a) The normalized wavefunction for a particle in a one-dimensional box of length a is;

$$\psi(x) = \sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a}, \quad n= 1, 2, 3...$$

Calculate the probability that a particle in a one-dimensional box of length a is found to be between 0 and $a/2$. [6]

(b) Write down the expression for the energy of a one dimensional harmonic oscillator, defining all terms. [6]

(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 constant, [5]
(ii) the threshold frequency, and [3]
(iii) the work function of lithium from these data. [3]

(d) What is the Zeeman effect? [2]

Question 2 (25 marks)

(a) State the Pauli Exclusion Principle and Hund's rule [4]

(b) Write the electronic configuration of the following atoms [6]
(i) N, (ii) C, (iii) O

(c) Draw the (i) p orbitals [3]
(ii) s orbitals for the first 3 shells [2]

(d) How many nodes are there in a 7s orbital? Support your answer with a diagram [5]

(e) Consider the sulphur dioxide molecule, SO_2. Describe the vibrational modes. [5]

Question 3 (25 marks)

(a) The work function for sodium metal is 1.82 eV.

(i) Explain this statement. [2]

(ii) Calculate the threshold frequency v_0 for sodium [4]

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

(i) *ln*x, (ii) 5sin3x [4]

(c) Describe and account for the variation of first ionization energies along period two of the periodic table. [6]

(d) Calculate the strength of a magnetic field B necessary to produce a Zeeman splitting of 10 cm^{-1} in l=1 state of the hydrogen atom. [4]

(e) Calculate the magnitude of the orbital angular momentum of a 4d electron in a hydrogenic atom. [5]

Question 4 (25 marks)

(a) Which of the following molecules may show infrared absorption spectra?

(i) CH_3CH_3, (ii) O_2 [4]

(b) 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 Rydeberg constant, Z the nuclear charge and n = 1, 2, 3, ...

Calculate the wavelength of a photon emitted when an electron goes from n = 3 to n = 2 in the hydrogenic atom He^+. [5]

(c) 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. [5]

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

(e) From (d) above, is NaCl paramagnetic or not? Indicate the number of unpaired electrons in each case

[3]

Question 5 (25 marks)

(a) The electrons in a vacuum tube are confined in a "box" between the filament and plate which is about 0.1 cm wide.

(i) Compute the spacing between the energy levels in this situation [4]

(ii) Do electrons behave more like waves or golf balls? [2]

(iii) In a simple tube the energy of the electron is about 100 eV. What is the quantum number of the electrons? [4]

(b) Use molecular orbital theory to assign the following bond lengths and binding energies to the following species: [8]

Species: H_2^+, H_2, He_2^+, He_2

Bonde lengths (pm): 74, 106, 108, 6000

Bonding energy (kJ/mol): << 1, 241, 268, 457

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

(d) Define selection rules and state the selection rule for hydrogenic atoms. [3]

Question 6 (25 marks)

(a) Describe the origins of linewidths in the absorption and emission spectra of compounds

[10]

(b) At what speed would a red (660 nm) traffic light appear green (520 nm)? [5]

NOTE: $\nu_{obs} = \nu\left(\frac{1}{1 \pm s/c}\right)$

(c) (i) Calculate the energy levels of the π-electron network in octatetraene, C_8H_{10}, [CH_2=CH-CH=CH-CH=CH-CH=CH_2] using the particle in a box model. Assume the molecule is linear and use the value 140 pm for the C-C conjugated bond-length and add an extra bond length at each end of the molecule. [5]

(ii) What is the wavelength of of light required to induce a transition from ground state to the first excited state? [5]

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	$\varepsilon_o = 1/c^2\mu_o$	$8.854\,19 \times 10^{-12}$ 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

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										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.