UNIVERSITY OF SWAZILAND

SUPPLEMENTARY 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.

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Question 1 (25 marks)

(a) 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

(b) Briefly discuss the Bohr's Model of the Hydrogenic atom [6]

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

(d) Give the valence bond description of the bonding in ammonia, NH_3. [3]

(e) Define degeneracy? [2]

Question 2 (25 marks)

(a) Consider the molecule, sulphur dioxide:

(i) Describe the vibrational modes in SO_2. [10]

(ii) Derive an equation for calculating moment of inertia for each of the structures in (i). [6]

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

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

Question 3 (25 marks)

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

(i) Explain this statement. [3]

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

(b) 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? [7]

(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]

Question 4 (25 marks)

(a) State the Max Born's postulate and explain how it appears to contradict the Heisenberg uncertainty principle. [4]

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

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

(c) 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]

(d) Define selection rules and state the selection rule for hydrogenic atoms. [5]

(e) 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]

Question 5 (25 marks)

(a) The velocity of a riffle bullet is about 900 m/s. If the bullet weighs 30 g, and the uncertainty in its momentum is 0.10%, how accurately can the position be measured? [4]

(d) Derive term symbols: nd^1nf^1 [6]

(e) Calculate the de Broglie wavelength of a neutron moving at 6.0 x 106 cm/s. [5]

(f) 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]

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: $v_{obs} = v\left(\frac{1}{1 \pm s/c}\right)$

(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	$\varepsilon_0 = 1/c^2\mu_0$	$8.854\,19 \times 10^{-12}$ 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

Atomic mass → Symbol → Atomic No. (e.g. 10.811 / B / 5)

TRANSITION ELEMENTS (groups 3–12)

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