UNIVERSITY OF SWAZILAND

SUPPLEMENTARY EXAMINATION 2012/13

TITLE OF PAPER: PHYSICAL CHEMISTRY

COURSE NUMBER: C302

TIME: THREE (3) HOURS

INSTRUCTIONS:

There are **six** questions. Each question is worth 25 marks. Answer **any four** questions.

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) (i) Write down the expression for the energy of a one dimensional harmonic oscillator, defining all the terms. [4]

(ii) Assuming that the vibrations of a $^{14}N_2$ molecule are equivalent to those of a harmonic oscillator with force constant k = 2293.8 Nm^{-1}, what is the zero point energy of vibration of this molecule. (The mass of a ^{14}N atom is 14.0041 u). [4]

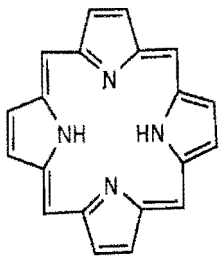
(iii) Calculate the wavelength of a photon needed to excite a transition between neighbouring levels in a nitrogen molecule. [3]

(b) Evaluate the kinetic energy of a particle on a ring that is described by the wavefunction $\Psi = N \cos \varphi$, $0 \leq \varphi \leq 2\pi$ and $\hat{T} = -\frac{\hbar^2}{2I}\frac{d^2}{d\varphi^2}$. [4]

(c) The particle on a ring is a useful model for the motion of electrons around the phorphine ring (see below), the conjugated macrocycle that forms the structural basis of the haem group and chlorophylls. Treat the group as a circular ring of radius 440 pm with 22 electrons in the conjugated system moving along the perimeter of the ring. Assume that in the ground state of the molecule each state is occupied by two electrons.

(i) Calculate the energy of an electron in the highest occupied level [5]

(ii) Calculate the frequency of radiation that can induce a transition between the highest occupied and lowest unoccupied level. [5]



phorphine

Question 2 (25marks)

(a) Use molecular orbital theory to explain why the binding energy of N_2^+ is less than that of N_2 whilst that of O_2^+ is greater than that of O_2. [6]

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

(c) Use molecular orbital theory to assign the following bond lengths and binding energies to the following species.:
Species: H_2^+, H_2, He_2^+, He_2
Bond lengths (pm): 74, 106, 108, 6000
Binding energy (kJ/mol): << 1, 241, 268, 457 [6]

(d) Consider the ions NO^- and C_2^+
(i) Draw the molecular orbital energy diagram for each species [4]
(ii) Write down the electron configuration and give the multiplicity of the ground states. [4]
(iii) Which ion should have the longer bond length? [1]

Question 3 (25 marks)

(a) Briefly explain why the 2s and 2p subshells are degenerate in the hydrogen atom but are not degenerate in an atom with two or more electrons [5]

(b) Locate the radial nodes in the 3p orbital of a hydrogen atom. The radial wavefunction is $R_{3p} = N(4 - \frac{1}{3}\rho)\rho e^{-\rho/6}$, where $\rho = \frac{2Zr}{a_0}$ and N is a normalization constant. [5]

(c) Derive the ground state term symbol for cerium, $[Xe]4f^1 5d^1 6s^2$ [5]

(d) The term symbol for a particular state is $^3F_2$.

(i) What are the values of L, S, and J for this state?
(ii) What is the minimum number of electrons which could give rise to this state?
(iii) Suggest a possible electron configuration. [5]

(e) (i) Explain why the $^2P \rightarrow {}^2S$ transition is split into a doublet in the emission spectrum of potassium and rubidium.
(ii) For which of these elements is the splitting greater? [5]

Question 4 (25 marks)

(a) Consider the sulphur dioxide molecule, SO_2:
- (i) Describe its vibrational modes [3]
- (ii) Indicate the modes which show infrared activity and why [2]
- (iii) Label each mode as parallel or perpendicular. [1]

(b) The wavenumber of the fundamental vibrational transition of $^{79}Br^{80}Br$ is 323.2 cm^{-1}. Calculate the force constant of the bond. [isotopic masses are ^{79}Br 78.9183 u and ^{80}Br 80.9163 u]. [4]

(c) The infrared spectrum of HCN shows strong bands at 721.1 cm^{-1} and 3312.0 cm^{-1}. There is a strong Raman band at 2089.0 cm^{-1}. There are weaker infrared bands at 1412.0 cm^{-1}, 2116.7 cm^{-1}, 2800.3 cm^{-1}, 4004.5 cm^{-1}, 5394 cm^{-1} and 6521.7 cm^{-1}. Identify these bands as fundamental, overtone or combination bands. Give your reasons. [6]

(d) For $^{127}I^{35}Cl$, $\bar{\nu} = 384.3\,cm^{-1}$ and $\bar{\nu}\chi_e = 1.5\,cm^{-1}$.
- (i) Calculate the frequency in wavenumbers of the fundamental band, the first overtone band and the lowest frequency hot band. [6]
- (ii) Calculate the exact zero point energy (in cm^{-1}) [3]

Question 5 (25 marks)

(a) Explain why Einstein's introduction of quantization accounted for the heat capacities of metals at low temperatures. [4]

(b) The work function of platinum is 5.65 eV.
- (i) What is the minimum frequency of light required to observe the photoelectric effect on platinum?
- (ii) If light with a 150-nm wavelength is absorbed by the surface, what is the velocity of the emitted electrons? [6]

(c) What speed does a H_2 molecule have if it has the same momentum as a photon of wavelength 280 nm? [4]

(d) Show that f(x) is an eigenfunction of the operator $\hat{A}$

(i) $f(x) = 3\sin 5x$ $\quad \hat{A} = \frac{d^2}{dx^2}$

(ii) $f(x) = 2y^3e^{3z}$ $\quad \hat{A} = \frac{\partial}{\partial z}$ [6]

(e) Evaluate the commutator $\left[\hat{A}, \hat{B}\right]$ where $\hat{A} = \frac{d}{dx} - x$ and $\hat{B} = \frac{d}{dx} + x$ [5]

Question 6 (25 marks)

The transition J = 3 ← 2 in the rotational spectrum of $^{12}C^{16}O$ is observed at 11.5901 cm^{-1}. The isotopic masses of ^{12}C, ^{13}C and ^{16}O are 12.0000 u, 13.0034 u and 15.9949 u, respectively.

(a) What is the separation between individual lines in the rotational spectrum of $^{12}C^{16}O$? [5]

(b) Calculate the bond length in this molecule. [6]

(c) What is the separation between the first member of the R-branch and the first member of the P-branch in the fundamental absorption band? [3]

(d) Calculate the relative population of the J = 3 and J = 4 energy levels of $^{12}C^{16}O$ at 25 °C. [5]

(e) What is the separation between individual lines in the rotational spectrum of $^{13}C^{16}O$? [6]

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	9 VIIIB	10	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 → 10.811
Symbol → B
Atomic No. → 5

*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.