UNIVERSITY OF SWAZILAND

SUPPLEMENTARY EXAMINATION 2006

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(25marks)

a. With a emphasis on the physical significance, explain precisely what is meant by a normalized wavefunction. [4]

b. When the surface of a piece of pure copper is irradiated with light of wavelength 253.7 nm from a mercury arc, electrons are emitted with energy of 0.24 eV.

(i) What is the binding energy of electrons in copper? [3]

(ii) What is the maximum wavelength of light that will eject electrons from copper? [3]

c. Which of the following functions are eigen-functions of the operator $\frac{d^2}{dx^2}$? For each eigen-function give the eigenvalue.

(i) e^{3x} (ii) e^{-3x^3} (iii) $\sin 2x + \cos 2x$ [5]

d. The normalized ground state wavefunction for a particle in a one dimensional box of length L is $\sqrt{\frac{2}{L}}\sin\frac{\pi x}{L}$.

(i) Calculate the average kinetic energy of the electron in this state. [5]

(ii) What is the probability of finding the electron in the middle third of the box in the ground state? [5]

[Useful intergral: $\int \sin^2 ax dx = \frac{x}{2} - \frac{1}{4a}\sin 2ax$]

Question 2 (25 marks)

a. Calculate the frequency in wavenumbers of the line in the spectrum of Li^{2+} ion that is emitted when the ion makes a transition from the stationary state n = 2 to the ground state. [4]

b. State whether the following transitions are allowed or forbidden. Give reasons for your answers.

(i) $3d \leftarrow 2s$ and $3p \leftarrow 1s$ for the hydrogen atom [3]

(ii) $^1D \leftarrow {}^1S$ and $^3P_1 \leftarrow {}^3P_0$ for the carbon atom [3]

c. The term symbols for the particular states of different atoms are quoted as follows:

(i) $^4S_1$ (ii) $^3D_{7/2}$ (iii) $^0P_1$

Explain why these are wrong. [9]

d. Give the term symbols for the following :

(i) Lithium in its first excited state: $1s^2 2p^1$ [3]

(ii) Ground state scandium: $[Ar]3d^1 4s^2$ [3]

Question 3 (25 marks)

The J = 3 $\leftarrow$ 2 transition in the rotational spectrum of $^{12}C^{16}O$ is observed at 11.5901 cm^{-1}.

a. Calculate the moment of inertia and bond distance in this molecule. The isotopic masses of ^{12}C and ^{16}O are 12.000 and 15.995, respectively. [11]

b. What is the separation between the individual lines in the rotational fine structure of the fundamental IR absorption band of $^{12}C^{16}O$? [2]

c. What is the separation between the first member of the R-branch and the first member of the P-branch in the above band? [2]

d. What is the separation between the individual lines in the rotational Raman spectrum of $^{12}C^{16}O$? [2]

e. Calculate the relative population of the J = 3 and J = 4 levels of $^{12}C^{16}O$ at 25 ^{o}C. [8]

Question 4 (25 marks)

a. State the Born-Openheimer approximation and discuss briefly its practical importance in the theory of molecular structure. [7]

b. For B_2 molecule in its ground state determine
   (i) The molecular orbital electron configuration. [2]
   (ii) The bond order [1]
   (iii) The term symbol [3]

c. Use the electron configurations of NO and N_2 to predict which is likely to have the shorter bond length. [6]

d. Show that the sp^2 hybrid orbital $\sqrt{\frac{1}{3}}\left(s+\sqrt{2}p\right)$ is normalized if s and p are normalized. [6]

Question 5 (25 marks)

a. Describe the factors that contribute to linewidths of spectra of gases. Which if, any of these factors can be eliminated or minimized? [8]

b. The following data are given for $^{1}H^{127}I$: bond length 160.92 pm, bond force constant 313.8 Nm^{-1} and atomic masses ^{1}H 1.0078 u and ^{127}I 126.9045 u. Calculate

(i) The fundamental vibrational frequency $\bar{\nu}_0$ and [4]

(ii) The zero point energy ε_0. [1]

c. The following infrared and Raman data were obtained for a triatomic molecule AB_2

Wavenumber	Infrared contours	Raman
519	Parallel type band	polarized
1151	Parallel type band	polarized
1361	Perpendicular type band	depolarized

The infrared bands do not show simple PR structure.

(i) Deduce the structure of the molecule. Clearly show your reasoning. [4]

(ii) Sketch the vibrational modes of the molecule and assign the above wavenumbers to the various modes. [6]

Question 6 (25 marks)

a. The ground and excited electronic states of homonuclear diatomic halogen anions, X_2^-, have been characterized. These anions have a $^2\Sigma_u^+$ ground state and $^2\Pi_g$, $^2\Pi_u$, $^2\Sigma_g^+$ excited states. To which of the excited states are transitions by absorption of photons allowed? Explain. [5]

b. $[Cr(H_2O)_6]^{3+}$ ions are pale violet but the chromate ion, CrO_4^{2-}, is a stronger yellow. Characterize the origins of the transitions in these two species and account for the relative intensities. [6]

c. The abundance of ozone is typically inferred from measurement of UV absorption and is often expressed in Dobson units (DU): 1 DU is equivalent to a layer of pure ozone 10^{-3} cm thick at 1 atm and 0 °C. Compute the absorbance of UV radiation at (i) 300 nm expected for an ozone abundance of 300 DU (a typical value) and (ii) 100 DU (a value reached during seasonal Antarctic ozone depletion) given the molar absorption coefficient of 476 L mol^{-1} cm^{-1}. [8]

d. The spectrum of O_2 shows vibrational structure which becomes a continuum at 56 876 cm^{-1}. The upper electronic state dissociates into one ground state atom and one excited state atom. The excitation energy of the excited atom as measured from its atomic spectrum is 15 875 cm^{-1}. Estimate the dissociation energy of the ground state O_2 in kJ/mol. [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	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	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								

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.