UNIVERSITY OF SWAZILAND

FINAL EXAMINATION 2008/09

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) For a monatomic gas, one measure of the average speed of the atoms is the root mean square speed, $v_{rms} = <v^2>^{½} = (3kT/m)^{½}$, in which m is the mass of the gas atom and k the Boltzmann constant. Use this formula to calculate the de Broglie wavelength for helium atoms at 100 K and 500 K. [6]

(b) The following data were observed in an experiment on the photoelectric effect from potassium:

Kinetic energy $x10^{19}$ J	4.49	3.09	1.89	1.34	0.700	0.311
Wavelength nm	250	300	350	400	450	500

(i) Plot a graph of kinetic energy against frequency in s^{-1}.
(ii) Use your graph to determine the value of Planck's constant, the work-function and threshold frequency of potassium. [8]

(c) Which of the following functions are eigenfunctions of $\frac{d^2}{dx^2}$? For each eigenfunction give the eigenvalue:

(i) 5Sin3x (ii) $5x^3$ (iii) $5e^{-3x}$ (iv) lnx [6]

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

$$\left[\text{Useful integral} \quad \int \cos^2 \theta d\theta = \frac{\theta}{2} + \frac{1}{4}\sin 2\theta + \text{constant}\right]$$

Question 2 (25 marks)

(a) By substituting in the Schrödinger equation for the harmonic oscillator, show that the wave function, $\psi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$ (where $\alpha = \sqrt{\frac{km}{\hbar^2}}$, k is the force constant and m the mass of the oscillator), is an eigenfunction of the total energy operator, $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$ and determine the eigen value. 10]

(b) The force constant of $^1H^{19}F$ molecule is 966 N m^{-1}. [Isotopic masses are ^1H 1.0078 u and ^{19}F 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) A gas phase $^{1}H^{19}F$ molecule, with a bond length of 91.7 pm, rotates in a three dimensional space. Calculate the smallest quantum of energy that can be absorbed by this molecule in a rotational state. [4]

Question 3(25 marks)

(a) Calculate the frequency (in s^{-1}) of the $J = 3 \leftarrow 2$ transition in the pure rotational spectrum of $^{12}C^{16}O$. The equilibrium bond length is 112.81 pm. [8]

(b) The wavenumber of the incident radiation in a Raman spectrometer is 20 623 cm^{-1}. What is the wavenumber of the scattered Stokes radiation for the $J = 4 \leftarrow 2$ transition of $^{16}O_2$? The equilibrium bond length is120.75 pm. [7]

(c) Which of the following molecules may show a pure rotational microwave absorption spectrum and why?
(i) H_2O, (ii) NH_3, (iii) CH_3Cl, (iv) CH_3CH_3, (v) SF_6 [5]

(d) Which of the following molecules may show a pure rotational Raman spectrum and why:?
(i) CH_4, (ii) SF_6, (iii) H_2O, (iv) O_2, (v) HCl [5]

Question 4(25 marks)

(a) Calculate the radial nodes for the 2s orbital of a C^{5+} ion

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}(2-\rho)e^{-\rho/2}, \qquad \rho = \frac{Zr}{a_0}$$ [3]

(b) The ground state spectroscopic term symbols for some elements are given below:

Element	Term symbol
Nb	$^{6}D_{1/2}$
Mo	$^{7}S_{3}$
Rh	$^{4}F_{9/2}$
W	$^{5}D_{0}$

(i) Write the electron configuration of each atom that is compatible with the spectroscopic term. [8]

(ii) Which of the atoms above are not following the building up principle? [4]

(c) Derive the ground state term symbol for a zirconium atom given that its electron configuration is [Kr]$4d^2 5s^2$. [5]

(d) How many lines will be observed in the fine structure of the transition $^2D \rightarrow {}^2P$? Clearly show your reasons. [5]

Question 5 (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 6(25 marks)

(a) The ground and excited electronic states of homonuclear diatomic halogen anions, X_2^-, have been characterized. The anions have a ground state $^2\Sigma_u^+$ ground state and $^2\Pi_g$, $^2\Pi_u$, $^2\Sigma_g^+$ excited states. To which of these 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 stronger yellow. Characterize the origins of the transitions in the 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 300 nm expected for an ozone abundance of 300 DU (a typical value) and 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 X 10^{8} m s^{-1}
Elementary charge	e	1.602 177 X 10^{-19} C
Faraday constant	$F = N_Ae$	9.6485 X 10^{4} C mol^{-1}
Boltzmann constant	k	1.380 66 X 10^{-23} J K^{-1}
Gas constant	$R = N_Ak$	8.314 51 J K^{-1} mol^{-1}
		8.205 78 X 10^{-2} dm^{3} atm K^{-1} mol^{-1}
		6.2364 X 10 L Torr K^{-1} mol^{-1}
Planck constant	h	6.626 08 X 10^{-34} J s
	$\hbar = h/2\pi$	1.054 57 X 10^{-34} J s
Avogadro constant	N_A	6.022 14 X 10^{23} mol^{-1}
Atomic mass unit	u	1.660 54 X 10^{-27} Kg
Mass		
electron	m_e	9.109 39 X 10^{-31} Kg
proton	m_p	1.672 62 X 10^{-27} Kg
neutron	m_n	1.674 93 X 10^{-27} Kg
Vacuum permittivity	$\varepsilon_o = 1/c^2\mu_o$	8.854 19 X 10^{-12} J^{-1} C^{2} m^{-1}
	$4\pi\varepsilon_o$	1.112 65 X 10^{-10} J^{-1} C^{2} m^{-1}
Vacuum permeability	μ_o	4π X 10^{-7} J s^{2} C^{-2} m^{-1}
		4π X 10^{-7} T^{2} J^{-1} m^{3}
Magneton		
Bohr	$\mu_B = e\hbar/2m_e$	9.274 02 X 10^{-24} J T^{-1}
nuclear	$\mu_N = e\hbar/2m_p$	5.050 79 X 10^{-27} J T^{-1}
g value	g_e	2.002 32
Bohr radius	$a_o = 4\pi\varepsilon_o\hbar/m_ee^2$	5.291 77 X 10^{-11} m
Fine-structure constant	$\alpha = \mu_oe^2c/2h$	7.297 35 X 10^{-3}
Rydberg constant	$R_\infty = m_ee^4/8h^3c\varepsilon_o^2$	1.097 37 X 10^{7} m^{-1}
Standard acceleration of free fall	g	9.806 65 m s^{-2}
Gravitational constant	G	6.672 59 X 10^{-11} N m^{2} Kg^{-2}

Conversion factors

1 cal = 4.184 joules (J)

1 eV = 1.602 2 X 10^{-19} J

1 erg = 1 X 10^{-7} 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

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