UNIVERSITY OF SWAZILAND

FINAL EXAMINATION 2007

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 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)

Lithium and chlorine each have two naturally occurring isotopes whose abundances and atomic masses are given below:

Isotope	Abundance/%	Atomic mass/u
^{6}Li	8	6.0151
^{7}Li	92	7.0160
^{35}Cl	75	34.9688
^{37}Cl	25	36.9651

Naturally occurring LiCl consists of a mixture of four possible isotopic combinations. A sample of natural LiCl was vaporized at 1500 K and a microwave spectrum obtained. The lowest frequency line was found at 1.24 710 cm^{-1}.

a. Why is the spectrum taken in the gas phase? [1]
b. To which isotopic combination, does the lowest frequency line correspond? [4]
c. Calculate the LiCl bond distance in this compound. [6]
d. Assuming the bond distance is independent of isotopic substitution and rotational state, calculate the frequencies of the next three lines seen in the spectrum. To which isotope does each line correspond? [11]
e. Which of these four lines (i.e. the 1.24 710 cm^{-1} and the three in (d) above) should be most intense? The least intense? Explain. [3]

Question 2(25 marks)

a. Describe the fundamental vibrational modes of H_2O and CO_2. For each molecule indicate which modes will show infrared activity and why. [8]

b. Explain the difference between a "**hot band**" and an "**overtone band**" in infrared spectra. How would you distinguish the two experimentally? [5]

c. The anharmonicity constant for $^{35}Cl^{19}F$ is 1.25 x 10^{-2} and the fundamental frequency is 793.2 cm^{-1}. The isotopic masses for ^{35}Cl and ^{19}F are 34.9688 u and 18.9984 u, respectively.
   - (i) Calculate the energies of the first four vibrational levels. [4]
   - (ii) Calculate the difference in energy between the v = 25 and v = 26 levels using (1) the harmonic oscillator model and (2) the anharmonic oscillator model. Comment on the difference of your results from the two calculations. [4]
   - (iii) Calculate the force constant of the bond in this molecule. [4]

Question 3(25marks)

a. Explain how Planck's introduction of quantization of energy accounted for the properties of black body radiation. [3]

b. In an x-ray photoelectron experiment, a photon of wavelength 121 pm ejects an electron and it emerges with a speed of 5.69×10^7 m/s. Calculate the binding energy of the electron. [4]

c. For the following operators and functions show that the function is an eigenfunction of the operator and determine the eigenvalue.

	Operator	Eigenfunction	
(i)	$\frac{d}{dz}$	$3x^2e^{6z}$	[3]
(ii)	$\frac{d^2}{dx^2}-4$	$3\cos 2x$	[3]

d. Evaluate the following commutators:
(i) $[x^2, p_x]$ (ii) $[p_x, p_y]$ [8]

e. What is the de Broglie wavelength of an electron accelerated to 100 eV?
(1 eV = 1.602×10^{-19} J) [4]

Question 4 (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

$R_{3p} = N(4-\frac{1}{3}\rho)\rho e^{-\rho/6}$, $\rho = \frac{2Zr}{a_0}$ 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 given as $^3F_2$. What are the values of L, S and J for this state? What is the minimum number of electrons which could give rise to this? Suggest a possible electron configuration. [5]

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

Question 5 (25 marks)

a. Consider a particle of mass m confined in a cubic box of edge L. The potential energy inside the box is zero and infinity outside the box.

(i) Write down the Hamiltonian for the particle inside the box. [1]

(ii) Write down the Schrödinger equation for this system. [1]

(iii) Without doing any calculations use the solutions of a particle in a one dimensional box (given below) to write down the solutions of the above Schrödinger equation and the expression for the energy of the system. [4]

(iv) What is the degeneracy of the energy level $\frac{18h^2}{8mL^2}$? [4]

(For a particle in a one-dimensional box of length $\psi(x) = \sqrt{\frac{2}{L}} Sin\left(\frac{n\pi x}{L}\right)$; $n = 1, 2, 3, \cdots$ and $E_n = \frac{h^2 n^2}{8mL^2}$)

b. The harmonic oscillator may be used for a model for molecular vibrations, considering the masses connected by spring-like bonds. The molecule vibrates like a harmonic oscillator with mass equal to the reduced mass of the atoms of the molecule.

(i) Calculate the reduced mass of an HBr molecule (atomic masses are 1.0078 u and 79.90 u for H and Br, respectively). [2]

(ii) The vibrational frequency of the HBr molecule is $v = 7.944 \times 10^{13}\ s^{-1}$. Find the bond force constant k. [4]

c. Find the most probable value(s) of x for a harmonic oscillator in its ground state, $\psi_0 = Ne^{-ax^2}$, a is a constant. [4]

d. The wavefunction of a particle rotating on a ring is: $\psi(\varphi) = \frac{1}{\sqrt{2\pi}} e^{-m_l i\varphi}$ $m_l = 0, \pm 1, \pm 2, \ldots$

Calculate the average value of φ. [5]

Question 6 (25 marks)

a. Describe the principles of laser action. Illustrate with an actual example. [10]

b. What features of laser radiation are applied in Chemistry? Discuss two applications of lasers in chemistry. [10]

c. The photoionization of H_2 by 21 eV electrons produces H_2^+. Explain why the intensity of the $v = 2 \leftarrow 0$ transition is stronger than that of the $0 \leftarrow 0$ transition. [5]

The end

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.