UNIVERSITY OF SWAZILAND

FINAL EXAMINATION 2009/10

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(25marks)

(a) 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, ...

(i) Calculate the ionization energy (in kJ/mol) of Li^{2+} when it is in the n =2 state. [3]

(ii) What is the wavenumber of the first line in the Balmer series of Li^{2+}? [3]

(iii) Calculate the difference in energy (in cm^{-1}) between the 1s and 2p levels in a hydrogen atom. [3]

(iv) Calculate the difference in energy between $2p_x$ ($m_l = +1$) and $2p_z$ ($m_l = 0$) in a magnetic field of strength 5 T. [3]

(v) Comment on your results for (iii) and (iv) [1]

(b) The ground state electron configuration of cerium is {Xe}$4f^1 5d^1 6s^2$. What is the lowest energy term symbol for this configuration? [6]

(c) State whether the following transitions are allowed or forbidden in the emission spectrum of helium. In each case give a reason for your answer.

(i) $4^3P_2 \rightarrow 2^3S_1$ (ii) $^3D_1 \rightarrow {}^1P_0$ (iii) $^1D_2 \rightarrow {}^1S_0$ (iv) $^1P_0 \rightarrow {}^1S_0$ [6]

Question 2 (25marks)

(a) A non polar molecule will not show a pure rotational spectrum but may have pure rotational lines in the Raman spectrum. True or false, explain. [3]

(b) Classify the following molecules as spherical, symmetric or asymmetric tops: CH_3Cl, CCl_4, SO_2, PF_3 and benzene (C_6H_6). [5]

(c) The microwave spectrum of $^{39}K^{127}I$ consists of lines whose spacing is almost constant at 3634 MHz. Calculate the bond length of $^{39}K^{127}I$. (atomic mass of ^{39}K is 39.964 u and of ^{127}I is 126.9045 u). [6]

(d) The pure rotational Raman spectrum of $^{14}N_2$ shows a spacing of 7.99 cm^{-1} between adjacent lines.

(i) Calculate the bond length of $^{14}N_2$. (atomic mass of ^{14}N is 14.0031 u). [6]

(ii) If 540.7 nm radiation from an argon laser is used to excite $^{14}N_2$, find the wavelength of the two rotational Raman lines nearest the unshifted line of $^{14}N_2$. [5]

Question 3 (25marks)

(a) An electron is confined in a one dimensional box of length 1.0 nm. The walls of the box are assumed to be infinitely high and as long as the electron remains inside the box its state can be described by $\psi(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$, n = 1, 2, 3, ... where L is the length of the box.

(i) Calculate the average kinetic energy of the electron [5]

(ii) Calculate the probability of finding the electron between 0.38 nm and 0.40 nm when n = 2. [5]

(b) Use the particle in a one dimensional box (whose energy is $E_n = \frac{h^2n^2}{8mL^2}$) as a model for the pi-electrons in 1,3 butadiene, CH_2=CH-CH=CH_2. Assume a carbon-carbon bond length of 140 pm and that the box consists of the three C-C bonds plus an additional length of 140 pm at each end.

(i) Calculate the first three energy levels for pi-electrons in 1,3 butadiene. [5]

(ii) Find the frequency and wavelength of light absorbed if an electron in 1,3 butadiene makes a transition from the highest filled level to the lowest empty level. [4]

(c) A harmonic oscillator consist of a particle of mass 5.16×10^{-26} kg and a force constant 285 N m^{-1}.

(i) Calculate the zero point energy for the oscillator [3]

(ii) Calculate the wavelength of the photon needed to excite a transition between neighboring energy levels. [3]

Question 4 (25marks)

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

(b) Consider the wavefunction $\psi = \frac{1}{x}$, in the range $a \le x \le b$.

(i) Normalize ψ. [5]

(ii) Find the average value of x. [5]

(c) Which of the functions below are eigenfunctions of the operator $\frac{d^2}{dx^2}$?

For each eigenfunction give the eigenvalue.

(i) e^{ikx} (ii) e^{-kx^2} (iii) 6cos 4x (iv) x sin x [6]

(d) Determine the commutator of the operators $\hat{A} = x\frac{d}{dx}$ and $\hat{B} = x^2\frac{d^2}{dx^2}$ [5]

Question 5 (25marks)

Given the following data for the molecule $^1H^{35}Cl$:
Bond length 127.5 pm, bond force constant 516.3 N m^{-1}, atomic masses ^1H: 1.673 x 10^{-27} kg, ^{35}Cl: 58.066 x 10^{-27} kg. Calculate the following, giving your answers in cm^{-1}.

(a) Calculate the fundamental vibrational frequency $\bar{\nu}$ and the zero point energy. [5]

(b) Calculate the rotational constant B. [5]

(c) Calculate the frequency of the first three lines in the P and R branches in the vibration-rotational spectrum of HCl. [6]

(d) Sketch the expected vibration-rotation spectrum of HCl, including the approximate intensity distribution [4]

(e) Suggest two differences you would expect to find between the spectrum you have sketched in (d) and that which is actually observed using a natural sample of HCl, give reasons. [5]

Question 6 (25marks)

(a) Discuss the steps involved in the construction of sp^3 hybrid orbitals. [4]

(b) Consider the following species: NCl, NCl^+, and NCl^-.
 (i) Draw the molecular orbital energy diagram for NCl. [2]
 (ii) Write the valence electron configuration of the three species. [3]
 (iii) Determine the bond order for each species. [3]
 (iv) Determine whether the species is paramagnetic or not; indicate the number of unpaired electrons in each case. [3]

(c) From the ground state electron configuration of B_2 and C_2, predict which molecule should have the greater bond dissociation energy [5].

(d) 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. [3]

USEFUL INTEGRALS

(1) $\int x^n dx = \frac{1}{(n+1)} x^{n+1}, \quad n \neq -1$

(2) $\int \frac{dx}{x} = \ln x + constant$

(3) $\int \sin^2 ax dx = \frac{x}{2} - \frac{1}{4a} \sin 2ax + constant$

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

Atomic mass → Symbol → Atomic No.

TRANSITION ELEMENTS

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											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.