UNIVERSITY OF SWAZILAND

FINAL 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 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)

(a) Distinguish between a bonding and an anti-bonding molecular orbital [6]

(b) Consider the following species: NCl, NCl^+, and NCl^-.
(i) Draw the molecular orbital energy diagram for NCl. [4]
(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) 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. [4]

Question 2 (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 wavelength of a photon emitted when an electron goes from n = 3 to n = 2 in the hydrogenic atom He^+. [4]

(ii) What is the wavenumber of the first line in the Lyman series of He^+? (For Lyman series , $n_2 \rightarrow n_1$, with $n_1 = 1$, and $n_2 = 2, 3, \ldots$) [3]

(b) The wavefunction for a 2s orbital of a hydrogen atom is $\psi_{2s} = N(2 - r/a_0)e^{-r/2a_0}$. Determine the normalization constant N. [6]

(c) State whether the following transitions are allowed or forbidden in a hydrogen atom. In each case give a reason for your answer.
(i) 3d → 2s (ii) 3p → 1s [4]

(d) What is the lowest term symbol for Ti^{3+} if the first two electrons to be lost are the 4s electrons. [5]

(e) Calculate the magnitude of the orbital angular momentum of a 4d electron in a hydrogenic atom. [3]

Question 3 (25 marks)

(a) Suppose that you wish to characterize the normal modes of benzene in the gas phase. Why is it important to obtain both infrared absorption and Raman spectra of your sample? [5]

(b) How many normal modes of vibration are there for the following molecules?
(i) C_6H_6 (ii) $C_6H_5CH_3$ (iii) HC≡C–C≡CH [6]

(c) Which of the following molecules may show infrared absorption spectra?
(i) CH_3CH_3 (ii) CH_4 (iii) CH_3Cl (iv) N_2 [4]

(d) The fundamental and first overtone transitions of $^{14}N^{16}O$ are centred at 1876.06 cm^{-1} and 3724.20 cm^{-1}, respectively. Calculate
(i) the equilibrium vibrational frequency and the anharmonicity constant, [5]
(ii) the exact zero point energy (in cm^{-1}), [2]
(iii) the force constant. [3]

Question 4 (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 eigenvalue. [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 $^1H^{19}F$ 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 5 (25 marks)

(a) Describe how a wavefunction determines the dynamical properties of a system and how those properties may be predicated. [4]

(b) Consider a particle in a one dimensional box defined by $V(x) = 0$ for $0<x<L$ and $V(x) = \infty$ for $x \geq L$, $x \leq 0$. Explain why the following functions are not acceptable as wavefunctions for this system.

(i) $A\cos\frac{n\pi x}{L}$ (ii) $\frac{D}{\sin n\pi x / L}$ [4]

(c) Calculate the probability that a particle in a one dimensional box of length L is found between 0.31L and 0.35L when it is described by the following wavefunctions:

(i) $\sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)$ (ii) $\sqrt{\frac{2}{L}}\sin\left(\frac{3\pi x}{L}\right)$

(iii) What would you expect for a classical particle? Compare your results in the two cases with the classical result. [8]

(d) Are the eigenfunctions of $\hat{H}$ for the particle in a one dimensional box also eigen functions of the position operator, $\hat{x}$? Explain. [2]

(e) Calculate the average value of x for the case when n = 3 i.e. when $\psi = \sqrt{\frac{2}{L}}\sin\left(\frac{3\pi x}{L}\right)$.

Explain your result by comparing it with what you would expect for a classical particle. [7]

Question 6 (25 marks

(a) Classify the following molecules as asymmetric top, spherical top or symmetric top and indicate which will have a rotational spectrum.

(i) C_6H_6 (ii) PH_3 (iii) PCl_5 (iv) H_2O [6]

(b) The rotational spectrum of $^{79}Br^{19}F$ shows a series of equidistant lines 0.71433 cm^{-1} apart. The atomic masses of ^{19}F and ^{79}Br are 18.9984 u and 78.9183 u, respectively.

(i) Calculate the bond length of the molecule. [6]

(ii) Determine the wavenumber of the $J = 9 \rightarrow J = 10$ transition. [3]

(iii) Find which transition gives rise to the most intense spectral line at 300 K. [5]

(iv) Assuming that bond length is unchanged by isotopic substitution, calculate the spacing in the rotational spectrum of $^{81}Br^{19}F$. (Isotopic mass of ^{81}Br is 80.9163 u) [5]

USEFUL INTEGRALS

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

(2) $\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}} \quad a > 0,$ n positive integer

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

(4) $\int \sin\theta d\theta = -\cos\theta + constant$

(5) $\int x \sin^2 ax dx = \frac{x^2}{4} - \frac{x \sin 2ax}{4a} - \frac{\cos 2ax}{8a^2} + constant$

(6) $\int \cos^2 \theta d\theta = \frac{\theta}{2} + \frac{1}{4} \sin 2\theta + constant$

(7) $\int_0^\pi x \sin x dx = \frac{\pi^2}{2}$

(8) $d\tau = r^2 dr \sin\theta d\theta \, d\phi$

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										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	[illegible]97 [illegible]u 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.