UNIVERSITY OF SWAZILAND

FINAL 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. A particle is moving in one dimension between $x = a$ and $x = b$. The potential is such that the particle cannot be outside these limits and that the wavefunction in between is $\psi = \frac{N}{x}$.

(i) Find the normalization constant N. [4]

(ii) Calculate the average value of x. [4]

b. Show whether the following functions are eigenfunctions of the operator $\frac{d}{dx}$? Give the eigenvalue where appropriate.

(i) e^{ikx} (ii) sin kx (iii) k (iv) e^{-kx^2}

(k is a constant) [8]

c. For a particle in a one dimensional box of length L, $\psi = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$, n = 1, 2,... Calculate the probability of finding the particle in the region between $\frac{L}{4}$ and $\frac{3L}{4}$ for n = 1, 2, and 3. [9]

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

Question 2 (25 marks)

a. The hydrogen atom wavefunctions depend on the quantum numbers n. l, m_l. Briefly discuss each of these quantum numbers indicating their possible values and their physical significance. [6]

b. Consider the hydrogenic atom C^{5+}:

(i) Compute its ionization energy in eV. [5]

(ii) Compute the wavelength of the first lines in the Lyman and Balmer series for this ion. [4]

c. Determine the term symbols for (i) $1s^1 2p^1$ (ii) $2p^1 3p^1$. [6]

d. 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) $4^1D_2 \rightarrow 2^1S_0$ [4]

Question 3 (25 marks)

a. 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]

b. Give a brief description of each of the following terms:

(i) Vibronic transition (ii) Franck-Condon principle [6]

c. Why is the intensity of d-d transitions in octahedral complexes much weaker than those in tetrahedral complexes? [4]

d. Why is the fluorescence spectrum displaced to lower frequencies when compared to the corresponding absorption spectrum? Explain with an appropriate diagram. [4]

Question 4 (25 marks)

a. How did the study of heat capacities of metals consolidate Planck's hypothesis that energy is quantized? [8]

b.

- (i) Write down the expression for the energy of a one dimensional harmonic oscillator, defining all the terms. [4]
- (ii) Assuming that the vibrations of a $^{14}N_2$ molecule are equivalent to those of a harmonic oscillator with force constant $k = 2293.8 \text{ Nm}^{-1}$, what is the zero point energy of vibration of this molecule. (The mass of a ^{14}N atom is 14.0041 u). [4]
- (iii) Calculate the wavelength of a photon needed to excite a transition between neighbouring levels in a nitrogen molecule. [3]

c. The rotation of an $^{1}H^{127}I$ molecule can be pictured as the orbital motion of an H atom a distance 160 pm from a stationary I atom. Assume the molecule rotates only in a plane.

- (i) Calculate the energy needed to excite the molecule into rotation. [4]
- (ii) What is the minimum non-zero angular momentum of the molecule? [2]

Question 5 (25 marks)

a. The spacing between two adjacent lines in the rotational spectrum of carbon monoxide is 1.15 x 10^{11} s^{-1}. Calculate

   (i) The moment of inertia of the CO molecule and [5]

   (ii) The internuclear distance [3]

   The atomic masses of C and O are 12.0000 u and 15.9949 u, respectively

b. The rotational constant for $H^{35}Cl$ is observed to be 10.5909 cm^{-1}. What are the values of the rotational constant for $H^{37}Cl$ and $^{2}D^{35}Cl$? The atomic masses are H: 1.0078 u, D: 2.0140 u, ^{35}Cl: 34.9688 u and ^{37}Cl: 36.9651. [8]

c. The fundamental and first overtone of $^{14}N^{16}O$ are centered at 1876.06 cm^{-1} and 3724.20 cm^{-1}, respectively. Evaluate

   (i) The equilibrium vibration frequency and the anharmonicity constant. [4]

   (ii) The exact zero point energy. [2]

   (iii) The force constant of the molecule. [3]

   The atomic masses of ^{14}N and ^{16}O are 14.0031 u and 15.9949 u, respectively.

Question 6 (25 marks)

a. In an experiment, the position of an electron can be measured with an accuracy of ±0.005 nm.

   (i) What will be the accuracy in measuring the momentum of the electron? [3]

   (ii) What will be the accuracy in measuring the speed of the electron? [3]

b. Indicate which of the following functions are "acceptable" as wavefunctions. If one is not give a reason.

   (i) $\psi = x$ (ii) $\psi = x^2$ (iii) $\psi = \sin x$ (iv) $\psi = e^{-x}$

   (v) $\psi = e^{-ax^2}$ $a > 0$ (vi) $\psi = e^{-ax^2}$ $a < 0$. [6]

c. Find the commutator of the operators $\hat{A} = x\frac{d}{dx}$ and $\hat{B} = x^2\frac{d^2}{dx^2}$. [7]

d. A photon powered spacecraft of mass 10.0 kg emits radiation of wavelength 225 nm with a power of 1.50 kW entirely in the backward direction. To what speed will it have been accelerated after 10.0 years if released into free space? [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	$F = N_A e$	9.6485 X 10^{4} C mol^{-1}
Boltzmann constant	k	1.380 66 X 10^{-23} J K^{-1}
Gas constant	$R = N_A k$	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	$a_o = 4\pi\varepsilon_o\hbar/m_e e^2$	5.291 77 X 10^{-11} m
Fine-structure constant	$\alpha = \mu_o e^2 c/2h$	7.297 35 X 10^{-3}
Rydberg constant	$R_\infty = m_e e^4/8h^3 c\varepsilon_o^{\ 2}$	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.