UNIVERSITY OF SWAZILAND

FINAL EXAMINATION 2008

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.

DO NOT OPEN THIS PAPER UNTIL PERMISSION TO DO SO HAS BEEN GRANTED BY THE CHIEF INVIGILATOR.

Question 1(25marks)

a. Why does $\psi^*\psi$ have to be everywhere real, nonnegative, finite and of definite value. [3]

b. What is the standard deviation in the velocity of an electron if the uncertainty in its position is 100 pm? What is the corresponding standard deviation in the kinetic energy of the electron? [5]

c. What speed does a H_2 molecule have if it has the same momentum as a photon of wavelength 280 nm? [3]

d. Evaluate the commutator $[\hat{A},\hat{B}]$ where $\hat{A} = \frac{d}{dx} - x$ and $\hat{B} = \frac{d}{dx} + x$ [5]

e. Determine in each of the following cases if the function in the first column is an eigenfunction of the operator in the second column. If so what is the eigenvalue?

	Functions	**Operator**	
(i)	xy	$x\frac{\partial}{\partial x} + y\frac{\partial}{\partial y}$	[3]
(ii)	$\sin\theta\cos\phi$	$\frac{\partial^2}{\partial \theta^2}$	[3]
(iii)	$e^{-(x^2/2)}$	$\frac{d^2}{dx^2} - x^2$	[3]

Question 2 (25 marks)

a. A particle is in a state described by the function $\psi(x) = 0.632e^{2ix} + 0.775e^{-2ix}$. What is the probability that the particle will be found with momentum $2\hbar$ [3]

b. Consider the energy eigenvalues of a particle in a one dimensional box $E_n = \frac{h^2 n^2}{8mL^2}$, n = 1, 2, 3,..as a function of *n, m* and *L*.

(i) By what factor do you need to change the box length *L* to decrease the zero point energy by a factor of 400 for a fixed value of *m*? [3]

(ii) By what factor would you have to change *n* for fixed values of *L* and m to increase the energy by a factor of 400? [3]

(iii) By what factor would you have to increase *L* to have the zero point energy of an electron be equal tò the zero point energy of a proton? [4]

c. The function $\Psi(x) = x\left(1-\frac{x}{L}\right)$, is an acceptable function for a particle in a one dimensional box of length L and with infinitely high walls.

(i) Normalize $\Psi(x)$ [6]

(ii) Calculate the expectation value <x> [6]

Question 3(25 marks)

a. The total energy eigenvalues of the hydrogen atom are given by $E_n = -\frac{e^2}{8\pi\varepsilon_0 a_0 n^2}$, n = 1, 2, 3,... and the three quantum numbers associated with the total energy eigenfunctions are related by $n = 1, 2, 3,\ldots$; $l = 0, 1, 2,\ldots, n-1$; and $m_l = 0, \pm1, \pm2, \pm3,\ldots, \pm l$. Using the notation ψ_{nlm_l} list all eigenfunctions that have the following energy eigenvalues and hence give the degeneracy of these energy levels:

(i) $E = -\frac{e^2}{32\pi\varepsilon_0 a_0}$ [3]

(ii) $E = -\frac{e^2}{72\pi\varepsilon_0 a_0}$ [3]

b. Calculate the mean value of the radius, <r>, at which you would find an electron if the H atom wave function is $\psi_{210}(r,\theta,\phi) = \frac{1}{4\sqrt{2\pi a_0^3}}\frac{r}{a_0}e^{-r/2a_0}\cos\theta$ [7]

c. Define the quantum numbers L and S as applied to many electron atoms, indicating the kind of values they may have. State the physical meaning of the two quantum numbers in quantitative terms. Under what conditions are L and S no longer valid as quantum numbers? State the reason in a sentence or two. [7]

d. Derive the term symbols for the electron configuration ns^1nd^1. Which of these terms has the lowest energy? [5]

Question 4 (25 marks)

a. The ionization energies (I) of an electron from the valence orbitals on a carbon and an oxygen atom are given in the table below:

Atom	Valence orbital	I/MJ mol^{-1}
O	2s	3.116
	2p	1.524
C	2s	1.872
	2p	1.023

(i) Use these data to construct a molecular orbital energy diagram for CO. [5]
(ii) What is the electron configuration of the ground state of CO? [1]
(iii) What is the bond order of CO? [1]
(iv) Is CO paramagnetic or diamagnetic? [1]

b. The highest occupied molecular orbitals for an excited electronic configuration of an oxygen molecule are $(1\pi_g)^1(2\sigma_u^*)^1$. Determine the molecular term symbols for oxygen in this electronic configuration. [5]

c. The photoelectron spectrum of NO was obtained using He 58.4 nm (21.22 eV) radiation. It consisted of a strong peak at kinetic energy 4.69 eV and a series of 24 lines starting at 5.56 eV and ending at 2.2 eV. A shorter series of six lines began at 12.0 eV and ended at 10.7 eV. Account for this spectrum. [7]

d. When light of wavelength 440 nm passes through 3.5mm of solution of an absorbing substance at a concentration 0.667 mmol L^{-1}, the transmitance is 65.5 %. Calculate the molar absorption coefficient of the solute at this wavelength and express the answer in cm^{2}mol^{-1}. [5]

Question 5(25 marks)

a. Determine the number of translational, rotational and vibrational degrees of freedom in the following molecules:
(i) CH_3Cl (ii) OCS (iiii) C_6H_6 (iv)H_2CO (6)

b. Classify each of the following molecules as a spherical, a symmetric or an asymmetric top:
(i) CH_3Cl (ii) CCl_4 (iii) SO_2 (iv) SF_6 (4)

c. The rotational constant of $^2D^{19}F$ determined from microwave spectroscopy is 11.007 cm^{-1}. The atomic masses of ^{19}F and ^2D are 18.9984032 u and 2.0141018 u, respectively. Calculate the bond length in $^2D^{19}F$ to the maximum number of significant figures consistent with this information. (7)

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

(i) Calculate the value of the rotational constant B. [2]

(ii) What is the spacing between the unshifted line ν_{ex} and the pure rotational line closest to ν_{ex}? [2]

(iii) If 540.8 nm radiation from an argon laser is used as the exciting radiation, find the wavelength of the two pure rotational Raman lines nearest the unshifted lines. [4]

Question 6(25 marks)

a. The force constant of $^1H^{19}F$ molecule is 966 N m^{-1}. Atomic masses of ^1H and ^{19}F are 1.0078 u and 18.9984 u, respectively.

(i) Calculate the zero point energy in kJ/mol for this molecule for a harmonic potential. [5]

(ii) Calculate the light frequency needed to excite this molecule from the ground state to the first excited state. [2]

(iii) Calculate the relative numbers of $^1H^{19}F$ molecules in the ground and first excited states at (i) 298 K and (ii) 1000 K. [6]

b. Calculate the percentage difference in the fundamental vibration wavenumber of $^1H^{35}Cl$ and $^2H^{35}Cl$ on assumption that their force constants are the same. Atomic masses are ^1H 1.0078 u, ^2H 2.0140 u and ^{35}Cl 34.9688. [5]

c. Infrared absorption of $^1H^{127}I$ gives rise to an R branch from v = 0. What is the wavenumber of the line originating from the rotational state J=2. ($\bar{\nu}_0 = 2308.09 cm^{-1}$ and B=6.511 cm^{-1}). [4]

d. Suppose that you wish to characterize the normal modes of benzene in the gas phase. Why is it important to obtain both infrared and Raman spectra of your sample? [3]

Useful Integrals

$$d\tau = r^2 dr \sin\theta d\theta d\phi$$

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

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

$$\int_0^{\pi} \cos^2\theta \sin\theta d\theta = \frac{2}{3}$$

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	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.