UNIVERSITY OF SWAZILAND

SUPPLEMENTARY 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)

a. Show that the average distance of an electron from the nucleus in the ground state of a hydrogen atom is <r> = $\frac{3a_0}{2}$. The ground state wavefunction is:

$$\psi_{1s} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$ [5]

b. Describe and account for the variation of first ionization energies along period two of the periodic table. [6]

c. The electron configuration of one of the excited states of calcium is $[Ar]3d^1 4s^1$.
   (i) Derive the term symbol for the ground state configuration of Ca. [3]
   (ii) Derive the term symbols for this excited state. [3]
   (iii) Discuss the possibility of electronic transitions between the ground state and this excited state. [2]

d. Explain the origin of spin-orbit coupling and how it affects the appearance of a spectrum. [6]

Question 2(25marks)

a. Describe the physical origin of quantization energy for a particle confined to moving inside a one-dimensional box. [5]

b. The normalized wavefunction of a particle in a one-dimensional box of length L is:

$$\psi = \sqrt{\frac{2}{L}} Sin\left(\frac{n\pi x}{L}\right), \text{ where } n = 1, 2, 3, \ldots.$$

   (i) Show that ψ is an eigenfunction of the operator below and give the eigenvalue.

$$\hat{H} = -\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2}$$ [5]

   (ii) Find the average value of the coordinate x when n = 1. [5]

   (iii) Find the average value of the linear momentum p_x when n = 1 [5]

   (iv) What is the probability of finding the particle in the middle third of the box? [5]

Question 3 (25 marks)

a. (i) What is the Zeeman effect? [2]

(ii) How many lines appear in the Zeeman splitting of the n =3, $l = 2$ level of the hydrogen atom? [3]

(iii) Calculate the strength of a magnetic field B necessary to produce a Zeeman splitting of 10 cm^{-1} in the $l = 1$ state of the hydrogen atom. [3]

b. Give the valence bond description of the bonding in ammonia, NH_3. [4]

c. Consider the ions NO^- and C_2^+:

(i) Draw the molecular orbital energy level for each species. [4]

(ii) Write down the ground state electron configuration and give the multiplicity of the ground states of these ions. [3]

(iii) Which ion should have the greater bond dissociation energy? [1]

(iv) Which ion should have the longer bond length? [1]

d. The ground state term symbol for He_2^+ is $^2\Sigma_u^+$. Define and/or explain the four parts comprising this symbol. [4]

Question 4(25 marks)

a. The infrared spectrum of HCN shows strong bands at 712.1 cm^{-1} and 3312.0 cm^{-1}. There is a strong Raman band at 2089.1 cm^{-1}. There are weaker infrared bands at 1412.0 cm^{-1}, 2116.7 cm^{-1}, 2800.3 cm^{-1}, 4004.5 cm^{-1}, 5394 cm^{-1}, and 6521.7 cm^{-1}. Some of the IR bands show PR band contour.

(i) Identify these bands as fundamental, overtone or combination bands [6]

(ii) Suggest the shape of the molecule [1]

(iii) Assign the fundamental frequencies to the vibrational modes. [2]

b. The Vibrational energy levels of NaI lie at the wavenumbers 142.81, 427.31, 710.31 and 991.81 cm^{-1}.

(i) Show that they fit the expression $\varepsilon_v = (v + \frac{1}{2})\bar{\nu} - (v + \frac{1}{2})^2 \chi_e \bar{\nu}$, $v = 0, 1, 2...$ [6]

(ii) Deduce the force constant, zero point energy, and dissociation energy of the molecule. (Atomic masses; Na is 22.99 u and I is 126.90 u) [10]

Question 5 (25 marks)

a. What is the wavelength of an electron moving in a potential difference of 2000 V? How fast (or rather how slow) must a 0.01 kg soccer ball travel to have the same de Broglie wavelength as a 2 000 V electron? (1eV = 1.602×10^{-19} J. [5]

b. 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]

c. Consider the function e^{-ax}.

(i) Is this function an eigenfunction of p_x^2? If it is, what is the eigenvalue? [3]

(ii) Is this function an acceptable function when x varies from $-\infty$ to $+\infty$? Explain [2]

(iii) What conditions should be imposed on the constant a so that it is an acceptable wavefunction in the range $x = 0$ to $x = +\infty$ [1]

d. Find the commutator of the operators $\hat{A} = x\frac{d}{dx}$ and $\hat{B} = x^2\frac{d^2}{dx^2}$. [8]

Question 6 (25 marks)

a. Give the gross and specific selection rules for pure rotational spectroscopy. [4]

b. Which of the following molecules show pure rotational spectra?
H_2 HCl CH_3Cl CH_2Cl_2 H_2O NH_3
Explain your choices. [6]

c. The average spacing between adjacent lines in the rotational spectra of $^{1}H^{19}F$ is 41.912 cm^{-1}. Calculate the bond length of $^{1}H^{19}F$.
(Atomic masses: ^{1}H 1.0078 u, ^{19}F 18.9984) [8]

d. Assuming the bond length is independent of isotopic substitution; calculate the spacing between adjacent lines in the rotational spectra of $^{2}H^{19}F$.
(Atomic mass ^{2}H 2.0140 u) [7]

The end

USEFUL INFORMATION IS GIVEN BELOW

$$\int x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

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

$$\int x \sin^2 ax dx = \frac{x^2}{4} - \frac{x \sin 2ax}{4a} - \frac{\cos 2ax}{8a}$$

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

$$\int \sin^2 x dx = \frac{x}{2} - \frac{1}{4a} \sin 2ax$$

$$\int \sin ax \cos ax dx = \frac{1}{2a} \sin^2 ax$$

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.