UNIVERSITY OF SWAZILAND

FINAL EXAMINATION 2011/12

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) For a monatomic gas, one measure of the average speed of the atoms is the root mean square speed, $v_{rms} = \langle v^2 \rangle^{1/2} = (3kT/m)^{1/2}$, in which m is the mass of the gas atom and k the Boltzmann constant. Use this formula to calculate the de Broglie wavelength for xenon atoms at 100 K and 500 K. [6]

(b) The following data were observed in an experiment on the photoelectric effect from potassium:

Kinetic energy $\times 10^{19}$ J	4.49	3.09	1.89	1.34	0.700	0.311
Wavelength nm	250	300	350	400	450	500

(i) Plot a graph of kinetic energy against frequency in s^{-1}.
(ii) Use your graph to determine the value of Planck's constant, the work-function and threshold frequency of potassium. [8]

(c) Which of the following functions are eigenfunctions of $\frac{d^2}{dx^2}$? For each eigenfunction give the eigenvalue:

(i) 5Sin3x (ii) $5x^3$ (iii) $5e^{-3x}$ (iv) lnx [6]

(d) Normalize the function $\psi = \cos\theta$, $0 \leq \theta \leq 2\pi$ [5]

Question 2 (25 marks)

(a) Consider the following species: $N_2^+, N_2, N_2^-, N_2^{2-}$
(i) Sketch the molecular orbital energy diagram for N_2. [2]
(ii) Write the electron configuration for each of the four species listed above and calculate the bond order for each. [8]
(iii) Arrange the species in order of increasing bond energy [1]
(iv) Arrange the species in order of increasing bond length [1]
(v) Derive the ground state term symbol for each species [8]

(b) Distinguish between bonding and anti-bonding molecular orbitals [5]

Question 3 (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 $^{2}D^{19}F$ determined from microwave spectroscopy is 11.007 cm^{-1}. The atomic masses of ^{19}F and ^{2}D are 18.9984032 u and 2.0141018 u, respectively. Calculate the bond length in $^{2}D^{19}F$ 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 4(25 marks)

(a) Describe the fundamental vibrational modes of H_2O and CO_2. For each molecule indicate which modes will show infrared activity and why. [8]

(b) Explain the difference between a "**hot band**" and an "**overtone band**" in infrared spectra. How would you distinguish the two experimentally? [5]

(c) The anharmonicity constant for $^{35}Cl^{19}F$ is 1.25×10^{-2} and the fundamental frequency is 793.2 cm^{-1}. The isotopic masses for ^{35}Cl and ^{19}F are 34.9688 u and 18.9984 u, respectively.
(i) Calculate the energies of the first four vibrational levels in cm^{-1}. [4]
(ii) Calculate the difference in energy between the $v = 25$ and $v = 26$ levels using (1) the harmonic oscillator model and (2) the anharmonic oscillator model. Comment on the difference of your results from the two calculations. [4]
(iii) Calculate the force constant of the bond in this molecule. [4]

Question 5(25 marks)

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

(b) The ground state normalized wavefunction of a particle in a one-dimensional box of length L is: $\psi = \sqrt{\frac{2}{L}} Sin\left(\frac{\pi x}{L}\right)$

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

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

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

(iii) Find the average value of the linear momentum p_x. [5]

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

Question 6(25marks)

(a) The term symbol of a particular state is quoted as $^4D_{5/2}$. What are the values of L, S and J? What is the minimum number of electrons which could give rise to this? Suggest a possible electronic configuration. [4]

(b) Derive the term symbols for the electron configuration ns^1nd^1 [4]

(c) The term symbol of a particular states of two different atoms are quoted as (i) $^2D_{7/2}$ and (ii) $^0P_1$. Explain why these are erroneous. [4]

(d) What is spin orbit coupling? [3]

(e) Which of the following transitions are allowed and which are forbidden in a hydrogenic atom. Explain.
(i) 2p → 3p (ii) 2p → 5s (iii) 3d → 3s [6]

(f) 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]

USEFUL INTEGRALS

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

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

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

(4) $\int \sin \theta d\theta = -\cos \theta + cons \tan t$

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

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

(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	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.