UNIVERSITY OF SWAZILAND

SUPPLEMENTARY EXAMINATION 2010/11

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 (25 marks)

(a) Distinguish between a bonding and 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 (25 marks)

(a) Briefly explain what is meant by lifetime broadening. Can you minimize this effect and if so how? [6]

(b) Which of the following molecules may show a pure rotational spectrum – justify your answer:

(i) H-C≡C-H	(ii) SF_6	(iii) C_6H_5OH
(iv) NO	(v) NH_3	(vi) H_2S

[6]

(c) The rotational constant for $^{127}I^{79}Br$ determined from microwave spectroscopy is 0.114 619 cm^{-1}. The atomic masses of ^{127}I and ^{79}Br are 126.904473 u and 78.918336 u, respectively. Calculate the bond length in $^{127}I^{79}Br$ to the maximum number of significant figures consistent with the given data. [7]

(d) Calculate the relative population of the J = 3 and J = 4 energy levels of $^{127}I^{79}Br$ at 25 ^oC. [6]

Question 3 (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 4 (25 marks)

(a) (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 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]

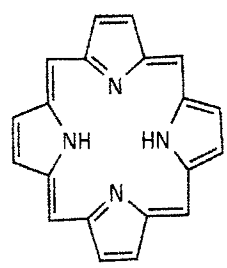
(iii) Calculate the wavelength of a photon needed to excite a transition between neighbouring levels in a nitrogen molecule. [3]

(b) Evaluate the kinetic energy of a particle on a ring that is described by the wavefunction $\Psi = N\cos\varphi$, $0 \le \varphi \le 2\pi$ and $\hat{T} = -\frac{\hbar^2}{2I}\frac{d^2}{d\varphi^2}$. [4]

(c) The particle on a ring is a useful model for the motion of electrons around the phorphine ring (see below), the conjugated macrocycle that forms the structural basis of the haem group and chlorophylls. Treat the group as a circular ring of radius 440 pm with 22 electrons in the conjugated system moving along the perimeter of the ring. Assume that in the ground state of the molecule each state is occupied by two electrons.

(i) Calculate the energy of an electron in the highest occupied level [5]

(ii) Calculate the frequency of radiation that can induce a transition between the highest occupied and lowest unoccupied level. [5]



phorphine

Question 5 (25 marks)

(a) The fundamental and first overtone transitions of $^{12}C^{16}O$ occur at 2143.0 cm^{-1} and 4260.0 cm^{-1}, respectively. Given that the isotopic masses of ^{12}C and ^{16}O are 12 u (exactly) and 15.9949 u, respectively, calculate

(i) The equilibrium vibrational frequency [5]

(ii) The anharmonicity constant [3]

(iii) The exact zero point energy [3]

(iv) The force constant of the molecule [4]

(b) The N_2O molecule has three strong bands in its infrared spectrum at 588.8 cm^{-1}, 1285.0 cm^{-1}, and 2223.5 cm^{-1}. All have been shown to be fundamentals and the molecule has been shown to be linear.

(i) Explain why CO_2, which is also linear, has only two fundamental IR bands while N_2O has three. [5]

(ii) Where would you look for the overtone and combination bands in the IR spectrum of N_2O? [5]

Question 6(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,...; l = 0, 1, 2,..., n-1; and m_l = 0, ±1, ±2, ±3,..., ±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]

USEFUL INFORMATION

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

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

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

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 X 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	$R_\infty = m_e e^4/8h^3c\varepsilon_o^2$	$1.097\,37 \times 10^{7}$ 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.