UNIVERSITY OF SWAZILAND

SUPPLEMENTARY EXAMINATION 2009/10

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) The energy levels of a hydrogenic atom are given by the following equation:

$$E_n = -\frac{R_H hcZ^2}{n^2},$$ where R_H is the Rydeberg constant, Z the nuclear charge and n = 1, 2, 3,...

(i) Calculate the wavelength of a photon emitted when an electron goes from n = 3 to n = 2 in the hydrogenic atom He^+. [4]

(ii) What is the wavenumber of the first line in the Lyman series of He^+? (For Lyman series, $n_2 \rightarrow n_1$, with $n_1 = 1$, and $n_2 = 2, 3, \ldots$) [3]

(b) The wavefunction for a 2s orbital of a hydrogen atom is $\psi_{2s} = N(2 - r/a_0)e^{-r/2a_0}$. Determine the normalization constant N. [6]

(c) State whether the following transitions are allowed or forbidden in a hydrogen atom. In each case give a reason for your answer.

(i) 3d → 2s (ii) 3p → 1s [4]

(d) What is the lowest term symbol for Ti^{3+} if the first two electrons to be lost are the 4s electrons. [5]

(e) Calculate the magnitude of the orbital angular momentum of a 4d electron in a hydrogenic atom. [3]

Question 2 (25marks)

(a) Describe the physical origins of linewidths in the absorption and emission spectra of compounds. [9]

(b) At what speed of approach would a red (660 nm) traffic light appear green (520 nm)? [5]

(c) Estimate the lifetime of a state that gives rise to a line of width of 100 MHz. [5}

(d) In the vibration-rotation spectrum ($v=0 \rightarrow 1$) of HF, the rotational constants are slightly different in the v = 0 and v = 1 states; their values are found to be $B_{v=0} = 20.6\ cm^{-1}$ and $B_{v=1} = 19.8\ cm^{-1}$. Calculate the percentage increase in bond length on going from v = 0 to v = 1. [6]

Useful data

$$\nu_{obs} = \nu\left(\frac{1}{1 \pm s/c}\right), \qquad \delta E = \frac{\hbar}{\tau}, \qquad \delta\bar{\nu} \approx \frac{5.3}{\tau / ps}\ cm^{-1}$$

Question 3 (25 marks)

(a) (i) Given that the energy of a particle of mass m confined in a one dimensional box of length L is $\frac{h^2 n^2}{8mL^2}$, write down the expression for the energy if the particle is now in a three-dimensional cubical box of lengths $L_x = L_y = L_z = L$ [3]

(ii) How many states have energies in the range 0 to $\frac{13h^2}{8mL^2}$? How many energy levels are in this range? [3]

(iii) Suppose the cubical box has the dimensions $L_x = L_y = L_z/2$, what would be the energy when (1) $n_x = 1, n_y = 2, n_z = 2$ (2) $n_x = 1, n_y = 1, n_z = 4$
What can we say about these two energy levels? [4]

(b) (i) Calculate the energy levels of the π-electron network in octatetraene, C_8H_{10}, [CH_2=CH-CH=CH-CH=CH-CH=CH_2], using the particle in a box model. To calculate the box length, assume the molecule is linear and use the value 140 pm for the C-C conjugated bond-length and add an extra bond length at each end of the molecule. [5]

(ii) What is the wavelength of light required to induce a transition from the ground state to the first excited state? [5]

(c) The zero point energy of a particle in a box is not zero. Give a physical reason and a mathematical reason for this observation. [5]

Question 4(25 marks)

(a) Briefly explain the relationship between the Heisenberg uncertainty principle and the commutation of operators. [5]

(b) Given that $\hat{A} = \frac{d}{dx}$ and $\hat{B} = x^2$ find the commutator $[\hat{A}, \hat{B}]$. [5]

(c) 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 $2\hbar$? [4]

(d) Consider the function $f(x) = xe^{-x^2/2}$ $-\infty \le x \le \infty$

(i) Normalize f(x) [6]

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

Question 5 (25marks)

(a) The force constant of $^{79}Br^{79}Br$ is 240 N m^{-1} and the atomic mass of ^{79}Br is 78.9183 u. Calculate

(i) the fundamental vibrational frequency $\bar{\nu}$ and [3]

(ii) the zero point energy of $^{79}Br_2$ [3]

(b) The fundamental line in the infrared spectrum of $^{12}C^{16}O$ occurs at 2143.0 cm^{-1}, and the first overtone occurs at 4260.0 cm^{-1}. Calculate

(i) the fundamental vibrational frequency, $\bar{\nu}$, and the anharmonicity constant, χ_e [5]

(ii) the exact zero point energy of CO. [3]

(c) Given that the fundamental vibrational frequency $\bar{\nu} = 4138.32$ cm^{-1} and the rotational constant B = 20.956 cm^{-1} for $^{1}H^{19}F$, calculate the first three lines in the P and R branches in the vibration-rotational spectrum of HF. [6]

(d) How many normal modes of vibration does the molecule BF_3 have? Sketch two of its bond stretching modes (non-degenerate) and indicate whether they are infrared active or not. [5]

Question 6 (25marks)

(a) Use molecular orbital theory to explain why the binding energy of N_2^+ is less than that of N_2 whilst that of O_2^+ is greater than that of O_2. [6]

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

(c) Use molecular orbital theory to assign the following bond lengths and binding energies to the following species.:

Species: H_2^+, H_2, He_2^+, He_2

Bond lengths (pm): 74, 106, 108, 6000

Binding energy (kJ/mol): << 1, 241, 268, 457 [7]

(a) Consider the ions NO^- and C_2^+

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

(ii) Write down the electron configuration and give the multiplicity of the ground states. [4]

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

USEFUL INTEGRALS

(1) $\int x^2 e^{-x^2} dx = \frac{\sqrt{\pi}}{2}$

(2) $\int x^3 e^{-x^2} dx = 0$

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

(4) $\int \sin\theta d\theta = -\cos\theta + constant$

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

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	$F = N_Ae$	9.6485×10^{4} C mol^{-1}
Boltzmann constant	k	$1.380\,66 \times 10^{-23}$ J K^{-1}
Gas constant	$R = N_Ak$	$8.314\,51$ 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	$a_o = 4\pi\varepsilon_o\hbar/m_ee^2$	$5.291\,77 \times 10^{-11}$ m
Fine-structure constant	$\alpha = \mu_oe^2c/2h$	$7.297\,35 \times 10^{-3}$
Rydberg constant	$R_\infty = m_ee^4/8h^3c\varepsilon_o{}^2$	$1.097\,37 \times 10^{7}$ 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											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											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								

TRANSITION ELEMENTS

Atomic mass → 10.811
Symbol → B
Atomic No. → 5

*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.