UNIVERSITY OF SWAZILAND

FINAL 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 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) Why are molecular orbitals of heteronuclear diatomic molecules not labelled with g and u subscripts? [3]

(b) The ionization energy of CO is greater than that of NO. Explain this difference based on the electron configuration of these two molecules. [5]

(c) Sketch the molecular orbital energy diagram for CO and place the electrons in the levels appropriate for the ground state. The atomic orbital ionization energies are O2s: 32.3 eV, O2p: 15.8 eV, C2s: 19.4 eV and C2p: 10.9 eV. The mo energies follow the sequence (from lowest to highest): 1σ, 2σ, 1π, 3σ, 1π, 4σ. [6]

(d) The bond dissociation energies of the species NO, CF^-, and CF^+ follow the order: $CF^+ > NO > CF^-$. Explain this trend using MO theory. [6]

(e) Show that the sp^2 hybrid orbital, $h = (s + 2^{1/2}p)/3^{1/2}$, is normalized to 1 if the s and p orbitals are normalized to 1. [5]

Question 2 (25 marks)

The transition $J = 3 \leftarrow 2$ in the rotational spectrum of $^{12}C^{16}O$ is observed at 11.5901 cm^{-1}. The isotopic masses of ^{12}C and ^{16}O are 12.000 u and 15.995 u, respectively.

(a) What is the separation between individual lines in the rotational spectrum of $^{12}C^{16}O$? [6]

(b) Calculate the bond length in this molecule. [7]

(c) What is the separation between the first member of the R-branch and the first member of the P-branch in the fundamental absorption band? [3]

(d) What is the separation between individual lines in the rotational Raman spectrum of $^{12}C^{16}O$? [3]

(e) Calculate the relative population of the J = 3 and J = 4 energy levels of $^{12}C^{16}O$ at 25 °C. [6]

Question 3 (25 marks)

(a) Explain why Einstein's introduction of quantization accounted for the heat capacities of metals at low temperatures. [4]

(b) When a clean surface of silver is irradiated with light of wavelength 230 nm, the kinetic energy of the ejected electrons is found to be 0.805 eV. Calculate the work function and the threshold frequency of silver. [6]

(c) Calculate the de Broglie wavelength of an α-particle with kinetic energy 8.00 eV. [4]

(d) Show that f(x) is an eigenfunction of the operator $\hat{A}$ and determine the eigenvalue.

(i) $f(x) = 2\cos 3x$ $\qquad \hat{A} = \frac{d^2}{dx^2}$

(ii) $f(x) = 3x^2 e^{6z}$ $\qquad \hat{A} = \frac{\partial}{\partial z}$ [6]

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

Question 4 (25 marks)

(a) The wavefunction and energy for a particle in a one dimensional box of length L are:

$\psi(x) = \sqrt{\frac{2}{L}} \sin\frac{n\pi x}{L}$ and $E_n = \frac{h^2 n^2}{8mL^2}$ with $n = 1, 2, 3, \ldots$

(i) For a 1.0 x 10^{-26}g particle in a box whose ends are at x =0 and x = 20.00 nm, calculate the probability that the particle is between 16.000 and 16.001 nm if n =1 and n = 2. [4]

(ii) For an electron in a certain one dimensional box, the lowest observed transition frequency is 2.0 x 10^{14} s^{-1}. Find the length of the box. [4]

(b) For a particle in a cubic box of length L,

(iii)How many states have energies in the range 0 to $\frac{16h^2}{8mL^2}$? [3]

(iv)How many energy levels lie in this range? [3]

(c) Verify that $\psi_0 = N_0 e^{-x^2/2\alpha^2}$ where $\alpha = \left(\frac{\hbar^2}{mk}\right)^{1/4}$ is an eigen-function of the harmonic oscillator Hamiltonian, $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$. What is the eigen-value?

[7]

(d) A point mass rotates in a circle with l = 2. Calculate the magnitude of its angular momentum and the possible projections of the angular momentum on an arbitrary axis. [4]

Question 5 (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 6 (25 marks)

(a) One of the excited states of the hydrogen atom is described by the wavefunction

$$\psi = \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$$

(i) Normalize ψ to 1. [6]

(ii) Evaluate the expectation value of r for the hydrogen atom with the above wavefunction. [7]

(b) Specify and account for the selection rules for transitions in hydrogenic atoms. [4]

(c) What atomic terms are possible for the electron configuration ns^1np^1? Which term is likely to lie lowest in energy? [5]

(d) What values of J may occur in the term ^3D. How many states (distinguished by the quantum number M_J) belong to each level? [3]

USEFUL INTEGRALS

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

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

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

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

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

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.