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UNIVERSITY OF SWAZILAND

SUPPLEMENTARY 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 data sheet and a periodic table are attached

Non-programmable electronic calculators may be used.

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Question 1 (25 marks)

(a) Calculate the radial nodes for the 2s orbital of a C^{5+} ion

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}(2-\rho)e^{-\rho/2}, \qquad \rho = \frac{Zr}{a_0}$$ [3]

(b) The ground state spectroscopic term symbols for some elements are given below:

Element	Term symbol
Nb	$^6D_{1/2}$
Mo	$^7S_3$
Rh	$^4F_{9/2}$
W	$^5D_0$

(i) Write the electron configuration of each atom that is compatible with the spectroscopic term. [8]

(ii) Which of the atoms above are not following the building up principle? [4]

(c) Derive the ground state term symbol for a zirconium atom given that its electron configuration is $[Kr]4d^25s^2$. [5]

(d) How many lines will be observed in the fine structure of the transition $^2D \rightarrow {}^2P$? Clearly show your reasons. [5]

Question 2 (25 marks)

(a) Explain why Einstein's introduction of quantization accounted for the heat capacities of metals at low temperatures. [5]

(b) When lithium is irradiated with light, the kinetic energy of ejected electrons is 2.935×10^{-19} J for $\lambda = 300.0$ nm and 1.280×10^{-19} J for $\lambda = 400.0$ nm. Calculate

(i) the Planck constant [4]

(ii) the threshold frequency [2]

(iii) the work function for lithium. [2]

(c) For the following functions and operators show that f(x) is an eigen-function of the operator $\hat{\Omega}$ and determine the eigen-value

(i) $\hat{\Omega} = \frac{\partial}{\partial y}$ $\qquad$ $f(x) = x^2e^{6y}$ [2]

(ii) $\hat{\Omega} = \frac{d^2}{dx^2} + 4\frac{d}{dx} + 3$ $\qquad$ $f(x) = e^{3x}$ [3]

(d) There is an uncertainty principle for energy and time; $\Delta E \Delta t \geq h$. One application of this relationship has to do with the excited state energies and lifetimes of atoms and molecules. If we know that the lifetime of an excited state is 10^{-9}s, then what is the uncertainty in the energy of this state? [3]

(e) Calculate the de Broglie wavelength of a neutron moving at 6.0×10^6 cm/s. [4]

Question 3 (25 marks)

(a). 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 $2\hbar$ [3]

(b). Consider the energy eigenvalues of a particle in a one dimensional box $E_n = \dfrac{h^2 n^2}{8mL^2}$, n = 1, 2, 3,..as a function of *n, m* and *L.*

(i) By what factor do you need to change the box length *L* to decrease the zero point energy by a factor of 400 for a fixed value of *m*? [3]

(ii) By what factor would you have to change *n* for fixed values of *L* and m to increase the energy by a factor of 400? [3]

(iii) By what factor would you have to increase *L* to have the zero point energy of an electron be equal to the zero point energy of a proton? [4]

(c) The function $\Psi(x) = x\left(1-\dfrac{x}{L}\right)$, is an acceptable function for a particle in a one dimensional box of length L and with infinitely high walls.

(i) Normalize $\Psi(x)$ [6]

(ii) Calculate the expectation value <x> [6]

$$\left[\int x^n dx = \frac{1}{(n+1)}x^{n+1}, \quad n \neq -1\right]$$

Question 4 (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]

Question 5 (25 marks)

(a) Give a brief description of the valence bond description of a CCl_4 molecule. [6]

(b) Give the ground state electron configuration of:
(i) NO (ii) CS, (iii) Be_2 (iv) C_2 [6]

(c) Which of the species in (b) would you expect to be stabilized by
(i) the addition of an electron to form AB^-
(ii) the removal of an electron to form AB^+
In each case give the basis of your expectation. [6]

(d) Use the ground state electron configurations of ClF and OF to predict which molecule will have
(i) a greater bond dissociation energy
(ii) a longer bond length [7]

Question 6 (25 marks)

(a) What is the Doppler shift and how can it be minimized? [4]

(b) Which of the following molecules may show infrared absorption spectra? In each case give the basis of your decision
(i) CH_4 (ii) CH_3Cl (iii) CO_2 (iv) Cl_2 [6]

(c) How many normal modes of vibration are there for the following molecules
(i)$HC{\equiv}C{-}C{\equiv}CH$ (ii) C_6H_6 (iii) O_3 [6]

(d) The HCl molecule is well described by the Morse potential with $D_e = 5.33$ eV, $\bar{\nu} = 2989.7$ cm^{-1}, and $\chi_e\bar{\nu} = 52.05$ cm^{-1}. Assuming the potential is unchanged on deuteration, predict the dissociation energies (D_0) of
(i) HCl and
(ii) DCl.
(Isotopic masses are H: 1.0078 u; D: 2.0140 u and ^{35}Cl: 34.9688 u) [9]

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.