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UNIVERSITY OF SWAZILAND

FINAL EXAMINATION 2005

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(25marks)

a. Briefly explain the relationship between the Heisenberg uncertainty principle and the commutation of operators. [4]

b. What is the standard deviation in the velocity of an electron if the uncertainty in its position is 100 pm? What is the corresponding standard deviation in the kinetic energy of the electron? [6]

c. Give the quantum mechanical operator of the following physical quantity
p_y^3 [3]

d. Evaluate the following commutator $[\hat{\frac{1}{x}}, \hat{p}_x]$ [4]

e. For the following functions and operators show that f(x) is an eigen function of the operator and determine the eigenvalue

(i) $\hat{\Omega} = \frac{d^2}{dx^2}$ f(x) = 3 cos4x

(ii) $\hat{\Omega} = \frac{d^2}{dx^2} + 4\frac{d}{dx} - 3$ f(x) = $3e^{ax}$ [8]

Question 2 (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. The ground state wavefunction of a particle confined to a one-dimensional box is

$$\psi = \sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)$$

Suppose the box is 10.0 nm long. Calculate the probability that the particle is in the right half of the box. [6]

c. 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 [6]

d. Calculate the wavelength of a photon needed to excite a transition between neighboring energy levels of a harmonic oscillator of mass equal to that of an oxygen atom (15.9949 u) and force constant 544 N m^{-1}. [4]

Question 3(25 marks)

a. Calculate the wavelength of the photon emitted when an electron goes from the n = 3 to n = 2 level in a hydrogen atom. [3]

b. Calculate the ionization energy of Li^{2+} in kJ/mol. [3]

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

d. Calculate the position of the radial nodes for the 2s orbital of a C^{5+} ion

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

e. 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]

f. Derive the lowest term symbol for $^{22}Ti^{2+}$ if the first two electrons to be lost by the neutral atom are the 4s electrons. [6]

Question 4 (25 marks)

a. Compare the species O_2^+, O_2, and O_2^{2-} in terms of ground state configuration, bond order, stability, bond length and magnetic properties. [12]

b. The photoelectron spectrum of NO was obtained using He 58.4 nm (21.22 eV) radiation. It consisted of a strong peak at kinetic energy 4.69 eV and a series of 24 lines starting at 5.56 eV and ending at 2.2 eV. A shorter series of six lines began at 12.0 eV and ended at 10.7 eV. Account for this spectrum. [8]

c. When light of wavelength 440 nm passes through 3.5mm of solution of an absorbing substance at a concentration 0.667 mmol L^{-1}, the transmission is 65.5 %. Calculate the molar absorption coefficient of the solute at this wavelength and express the answer in $cm^2 mol^{-1}$. [5]

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Question 5(25 marks)

a. Give the vibrational modes of (i) CS_2 (ii) C_2F_2 (iii) CCl_4 [3]

b. Sketch and name the vibrational modes of SO_2. Indicate which are infrared active and which are Raman active. [6]

c. Explain how you can use infrared and Raman spectroscopy to determine the structure of a triatomic, AB_2, molecule. [6]

d. State the selection rules for rotational Raman spectroscopy. [2]

e. 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 6(25 marks)

a. The wavenumber of the fundamental vibrational transition of $^{79}Br^{81}Br$ is 323.2 cm^{-1}. Calculate the force constant of the bond. (Atomic masses are ^{79}Br: 78.9183 u and ^{81}Br: 80.9163 u). [5]

b. Calculate the relative numbers of $^{79}Br^{81}Br$ molecules in the ground and first excited states at (i) 298 K and (ii) 1000 K. (Use data in (a) above. [6]

c. Infrared absorption of $^1H^{127}I$ gives rise to an R branch from v = 0. What is the wavenumber of the line originating from the rotational state J=2. ($\bar{\nu}_0 = 2308.09 cm^{-1}$ and B=6.511 cm^{-1}). [5]

d. The first five vibrational energy levels of HI are at 1144.83, 3374.90, 5525.51, 7596.66 and 9588.35 cm^{-1}. Calculate the dissociation energy of the molecule in reciprocal centimetres and electronvolts [9].

Useful Integrals

$$\int \sin ax \cos ax dx = \frac{1}{2a}\sin^2 ax$$

$$\int \sin^2 ax dx = \frac{x}{2} - \frac{1}{4a}\sin 2ax$$

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

$$\int_{-\infty}^{\infty} x^3 e^{-ax^2} dx = \frac{1}{a}$$

$$\int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{a^3}}$$

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										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.