125

UNIVERSITY OF SWAZILAND

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

b. The work function of Pd is 4.98 eV.
   (i) What is the maximum kinetic energy of photoelectrons ejected from Pd when irradiated with ultraviolet light of 200 nm wavelength?
   (ii) What is the wavelength associated with the electron traveling at this velocity?
   (iii) What is the longest wavelength that will initiate the photoelectric effect in Pd. [8]

c. Calculate the average linear momentum of a particle described by the wavefunction $\psi = e^{5ix}$ [3]

d. Which of the following functions are eigen functions of $\frac{d^2}{dx^2}$. If a function is an eigen function of this operator, what is the eigen value?
   (i) $2\cos 3x$ (ii) $3x^2$ (iii) e^{5x^2} [3]

e. A particle is in a state described by the wavefunction $\psi(x) = (2a)^{1/2}e^{-ax}$, where a is a constant and $0 \leq x \leq \infty$. Determine the expectation value of the commutator of the position and momentum operators, $<[\hat{x}, \hat{p}_x]>$. [7]

Question 2 (25 marks)

a. Discuss the correspondence principle and illustrate it using two examples. [6]

b. Consider a particle confined to a one-dimensional box of length L, and whose wavefunction is $\psi = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$, n = 1, 2, 3, ...

   (i) What are the most likely locations of the particle when n = 3? [6]
   (ii) Calculate the probability that the particle will be found between 0.49L and 0.51L when n =1 and when n =2. [5]

c. A two dimensional oscillator has the potential energy
   $$V = \frac{1}{2}k(x^2 + y^2)$$
   (i) Write down the expression for the Schrödinger equation for this system. [3]

   (ii) The energy levels of a one dimensional oscillator are E = (v + ½)hν, v=0, 1, 2,.... Use this to write an expression for the energy levels of a two dimensional oscillator. [2]

   (iii) What is the degeneracy of the first four energy levels. [3]

Question 3 (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^1nd^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]

Question 4 (25 marks)

a. Distinguish between a bonding and an anti-bonding orbital. [5]

b. 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]

c. Explain or define the following terms

(i) Fluorescence (ii) phosphorescence (iii) vibronic transition [6]

d. Why is the intensity of d-d transitions in octahedral complexes much weaker than those in tetrahedral complexes? [4]

e. Why is the fluorescence spectrum displaced to lower frequencies when compared to the corresponding absorption spectrum? Explain with an appropriate diagram. [4]

128

Question 5(25 marks)

a. write down the expression for the rotational energy levels of a diatomic molecule assumed to be rigid. [3]

b. What is the degeneracy in the above energies? What is the physical interpretation of this degeneracy? [3]

c. Obtain a general expression for the change in energy of the R-branch in HCl in the lowest vibrational state. [4]

d. The high temperature microwave spectrum of $^{39}K^{35}Cl$ vapour shows an absorption at 7687.94 MHz that can be identified with the J=0 to J=1 transition. Calculate the moment of inertia and bond length of KCl. (Atomic masses are ^{39}K: 38.9637 u and ^{35}Cl: 34.9688 u) [15]

Question 6 (25 marks)

a. The fundamental and first overtone transitions of $^{14}N^{16}O$ are centered at 1876.06 cm^{-1} and 3724.20 cm^{-1}, respectively. Given that the isotopic masses of ^{14}N and ^{16}O are 14.0041 u 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]

Useful Integrals and relations

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

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

$\int Sinxdx = -\cos x$

$\int e^{ax} dx = \frac{1}{a}e^{ax}$

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

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

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
PERIODS	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.