UNIVERSITY OF SWAZILAND

SUPPLEMENTARY EXAMINATION 2008

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 how Einstein's introduction of quantization accounted for the heat capacities of metals at low temperatures. [5]

b. The work function of platinum is 5.65 eV.
   (i) What is the minimum frequency of light required to observe the photoelectric effect on Pt? [3]
   (ii) If light with 150 nm wavelength is absorbed by the surface, what is the velocity of the ejected electrons? [3]
   (iii) What is the wavelength associated with the electron traveling at this speed? [3]

c. Show that $f(x) = e^{2x}$ is an eigenfunction of the operator $\hat{\Omega} = \dfrac{d^2}{dx^2} + 2\dfrac{d}{dx} + 3$ and determine the eigen value. [5]

d. Determine the commutator of the operators $\hat{A} = x^2\dfrac{d}{dx}$ and $\hat{B} = \dfrac{d^2}{dx^2}$ [6]

Question 2 (25 marks)

a. Consider the function $\psi(x) = c\sin\pi x/a + d\sin2\pi x/a$.
   (i) Is $\psi(x)$ an acceptable function for the particle in a one dimensional box of length a? [4]
   (ii) Is $\psi(x)$ an eigenfunction of the total energy operator $\hat{H} = -\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2}$? [4]

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

   (i) What are the most likely locations of the particle when n = 3? [5]
   (ii) Calculate the probability that the particle will be found between 0.49L and 0.51L when n =1 and when n =2. [4]

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)hv, 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^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]

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. The ground state of O_2^+ is $^2\Pi_g$ and the next few excited states are $^4\Pi_u$, $^2\Pi_u$, $^4\Sigma_g^-$, $^2\Delta_g$, $^2\Sigma_g^-$, and $^4\Sigma_u^-$. On the basis of the selection rules, which of the excited states can be accessed from the ground state by absorption of UV light?   [6]

d. Predict the number of unpaired electrons and the ground state term of (i) NO and (ii) CO   [8]

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Question 5(25 marks)

a. The following lines were observed in the microwave spectrum of $H^{127}I$ and $D^{127}I$ between 60 cm^{-1} and 90 cm^{-1}:

Molecule	Frequency, cm^{-1}			
$H^{127}I$	64.275	77.130	89.985	
$D^{127}I$	65.070	71.577	78.084	84.591

(i) Calculate the values of B, I, and r_e for each molecule. [12]

(ii) In each case what transition gives rise to the first line above? [4]

(atomic masses are H 1.0078 u, D 2.0140 u and ^{127}I 126.9045 u)

b. Write down the expression for vibrational-rotational energy levels of a diatomic molecule assumed to be rigid. [3]

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

Question 6 (25 marks)

a. The fundamental and first overtone transitions of $^{12}C^{16}O$ occur at 2143.0 cm^{-1} and 4260.0 cm^{-1}, respectively. Given that the isotopic masses of ^{12}C and ^{16}O are 12 u (exactly) 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]

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Useful Integrals and relations

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

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

$$\int Sinx dx = -\cos x$$

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

$2 \sin\theta\cos\theta = \sin 2\theta$

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 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 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								

Legend:
- Atomic mass → 10.811
- Symbol → **B**
- Atomic No. → 5

TRANSITION ELEMENTS

*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.