Birla Institute of Technology & Science, Pilani, Rajasthan 333031

MID-SEMESTER EXAM, 1st Semester 2023-2024

Course Number: CHEM F111 **Date: Friday, 13-10-2023** **Course Title: General Chemistry**

Time: 90 min. **CLOSED BOOK** **Max. marks: 90**

Note: There are **four (4) questions** in all. All questions are compulsory. Answer all parts of each question together. **Do not use pencil**. All symbols carry the usual meaning unless otherwise specified. **Given**: $m_e = 9.11\times10^{-31}$ kg; 1eV = 1.6×10^{-19} J; 1 amu = 1.66×10^{-27} kg; h = 6.626 x 10^{-34} J s; c = 3×10^{8} m s^{-1} ; Wein's constant = 2.9 mm K; At. No. Fe=26, Co=27; 1Å = 10^{-10} m; 1 pm = 10^{-12} m; k_b = 1.38 x 10^{-23} J K^{-1}; $N_A = 6.023\times10^{23}$

Q1.(a) (i) An atom of Gd (At. No. = 64) exhibits a spectral line of frequency 10^{15} s^{-1}. Calculate the energy in joules emitted by it. **(ii)** What is the energy of the light emitted by 1 mole of Gd atoms in (i) above? **(iii)** A time-independent wavefunction has the form $\Psi_{(x)} = C \exp(-x^2/2a^2)$ for a particle free to move along the x-axis. Write down the expression for the normalized wavefunction. [given: $\int_{-\infty}^{+\infty} \exp(-{y^2}/{a^2})dy = a\sqrt{\pi}$] **[1+2+3]**

Q1.(b) The state function of a particle of mass m confined in 1-D box of length *l* is given as: $\Psi = \sqrt{\frac{2}{l}} \sin\frac{3\pi x}{l}$, (where potential=0 inside the box and potential=∞ outside) for $0 \le x \le l$. **(i)** write down the expression for the Hamiltonian operator for this system. **(ii)** Determine the position of the node(s) if any. **(iii)** Determine the magnitude of the momentum of this particle. **[2+2+2]**

Q1.(c) A particle (mass m) is confined to a 3-D cubical box of length L. **(i)** Calculate the energy (in multiples of h^2/mL^2) corresponding to first three excited energy levels. **(ii)** Calculate the degree of degeneracy of the third excited energy level. **[4+1]**

Q1.(d) Consider an electron rotating on a 2-D ring of diameter 2.36 Å. Calculate the energy in Joules corresponding to the transition of the particle from the first excited level to the second excited level. Determine the wavelength of the light source that will result in the above-mentioned transition [Show the major steps of calculation]. **[4+1]**

Q2(a). Given the expressions for a few orbitals of hydrogen atom:

$\psi_a = \frac{r}{a_0}\left(80 - 20\frac{r}{a_0} + \frac{r^2}{a_0^2}\right)e^{-r/4a_0}cos\theta$; $\psi_b = \frac{r^2}{a_0^2}\left(12 - \frac{r}{a_0}\right)e^{-r/4a_0}\, sin^2\theta\, cos2\phi$;

$\psi_c = \frac{r}{a_0}\left(6 - \frac{r}{a_0}\right)e^{-r/3a_0}\, sin\theta\, sin\phi$; Answer the following questions:

(i) Identify the orbitals corresponding to equal number of angular nodes and write the number of angular nodes for the *remaining* one. **[3]**

(ii) Identify the orbitals corresponding to equal number of radial nodes and write the number of radial nodes for the *remaining* one. **[3]**

(iii) For ψ_a, determine the position(s) of the radial node(s), in terms of a_0. **[3]**

(iv) Identify the orbital(s) for which the angular momentum vector lies in xy-plane. **[2]**

(v) Identify the pair(s) of orbitals between which the spectroscopic transition(s) is(are) observable in the electronic spectrum of the hydrogen atom. **[2]**

(vi) Identify all the three orbitals. **[3]**

Q2.(b) The ground state electronic configuration of sulphur atom is $1s^2 2s^2 2p^6 3s^2 3p^4$.

(i) Find the number of all possible states corresponding to this configuration. **[1]**

(ii) Find the ground term and also the degeneracy of the ground term. **[2]**

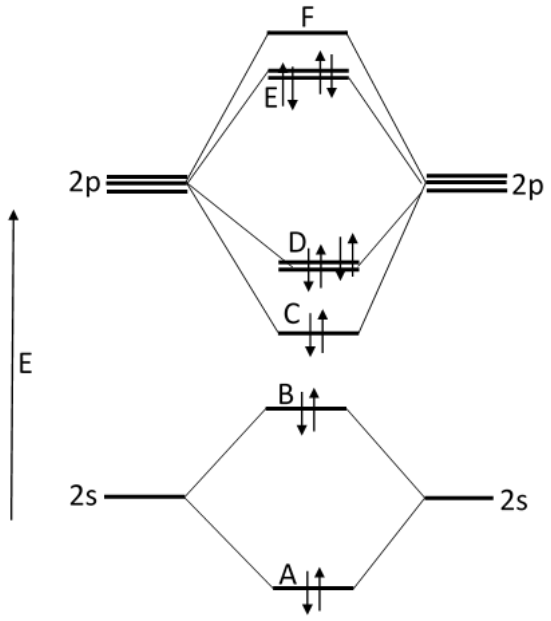
(iii) Find the possible level(s) arising from the ground term (write the term symbol(s)). **[2]**

(iv) Identify the ground level and find the degeneracy of the ground level. **[2]**

Q3.(a) At 298K, the relative intensities of the first two lines in the microwave absorption spectrum of the gas-phase hydrogen fluoride (HF) molecule is 2.451. Calculate the rotational constant (in cm^{-1}) (assume that intensity of the line is directly proportional to the population of the rotational levels). **[6]**

Q3.(b) (i) A diatomic molecule showed rotational Raman spectrum under irradiation with excitation wavelength of 4000 Å. The first Stokes line appeared at a spacing of 350 cm^{-1} from the Rayleigh line. Calculate the frequency (in cm^{-1}) of the first anti-Stokes line. **(ii)** The rotational Raman spectrum of $^{19}F_2$ [m(^{19}F) = 18.9984 amu] shows a series of Stokes line separated by 3.5312 cm^{-1}. Calculate the bond length of the molecule (in pm). **[3+6]**

Q3.(c) Based on the molecular orbital theory, the molecular orbital diagram of a neutral diatomic molecule is shown below:



Referring to the above diagram, answer the following questions:
(i) (a) Which ones (A to F as shown in the diagram) represent the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)? (b) For HOMO and LUMO obtained above, state the type of orbitals they are (σ /π) with appropriate symmetry notations (g/u). (**ii)** Calculate the bond order of the molecular species. **(iii)** Find out the molecular formula of the species from the molecular orbital diagram. **[4+1+2]**

Q4.(a) For $[Fe(H_2O)_6]^{2+}$ complex: **(i)** Calculate EAN of the central metal ion in the given complex. **(ii)** find the ground state term of the central metal ion by showing the steps clearly. **[3]**
(iii) The crystal field stabilization energy (CFSE) of $[CoCl_4]^{2-}$ is 12000 cm^{-1}. What will be the CFSE (**in cm^{-1}**) of $[CoCl_6]^{4-}$ (Assume it is stable, ignore the contribution of pairing energy)? **[6]**

Q4.(b) (i) H_2 molecule has a force constant of 237 Nm^{-1} (atomic mass of **H** is 1.00784 amu). Calculate the reduced mass of the molecule (in kg) and energy difference (in Joules) between two consecutive vibrational energy levels. **[4]**

(ii) Match the following compounds with the corresponding (IR) carbonyl stretching frequencies. **[4]**

Compound name	**Stretching frequency (cm^{-1})**
RCOOEt	1800
RCOCl	1690
RCOOH	1710
$RCONH_2$	1735

Q4.(c) If both 4-hydroxybenzaldehyde and 2-hydroxybenzaldehyde are diluted with CCl_4, in which case the IR absorption band obtained around 3500 cm^{-1} will become sharper? Explain (not more than two lines). **[3]**

Q4.(d) Radiation of wavelength 280 nm was passed through a solution of Tryptophan (0.25 mmol dm^{-3}) kept in cuvette of cell length 2 mm. The intensity of the radiation was reduced to 54 % of its initial value. From this given information determine the Molar absorptivity coefficient of Tryptophan (in $M^{-1}cm^{-1}$). **[3]**

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