Birla Institute of Technology & Science Pilani, Pilani Campus, Rajasthan 333 031

Mid-Semester Examination, First Semester 2022-2023

Course Number: CHEM F111 Course Title: General Chemistry CLOSED BOOK

Maximum Marks: 90 Date: 07 Jan, 2023 Time: 11.00 - 12.30 pm

Given are commonly used data, notations have usual meanings; $m_e = 9.11\times10^{-31}$ kg; $h = 6.626\times10^{-34}$ Js; $R_H = 109677$ cm^{-1}; $c = 3\times10^{8}$ ms^{-1}; *1 amu* = 1.66×10^{-27} kg; $\sigma = 56.7\times10^{-9}$ Wm^{-2}K^{-4}, At. Nos. of Co = 27, Fe = 26, Ti = 22, Cu = 29, Pt = 78, Mn = 25, N = 7. Wien displacement constant: 2.90 mm K. a_0 = 52.9 pm, 1eV = $1.6\times10^{-19} J$, Atomic weight (amu) Co: 58.9, H: 1, N: 14, Cl: 35.5, Ag: 108, O: 16, Boltzmann constant = 1.38×10^{-23} m^2 kg s^{-2} K^{-1}.

Important Instructions

- **There are FOUR questions printed on both sides of the question paper**
- **Answer all questions in the provided answer booklet only**
- **DO NOT use pencils for answering any part**
- **Start answering each question from a fresh page, all sub-sections together**

Q.1. (a) Photoelectrons with a range of wavelengths were ejected from a metal surface when the most intense radiations emitted by a hot filament were suitably filtered and bombarded on the metal surface. If the emittance of the filament were 4.2051×10^{8} Wm^{-2} and the shortest recordable wavelength of the photoelectrons was 1.0 nm, find **(I)** surface temperature (**in Kelvin**) of the filament; **(II)** wavelength (**in nm**) of the most intense radiation emitted by the filament; **(III)** maximum kinetic energy of the photoelectrons; and **(IV)** work-function of the metal; ignoring the relativistic effects. **[2M+2M+4M+4M]**

(b) At 298 K, the standard enthalpy of the reaction, $H_2(g) + D_2(g) \rightarrow 2HD(g)$ is 0.636 *kJ.mol^{-1}*, whereas the standard Gibbs energy change is -2.928 *kJ.mol^{-1}*. Calculate equilibrium constant of the reaction at 298 K and at 310 K. (**Hint**: van't Hoff eqn.) Estimate the standard Gibbs energy of the reaction at 310 K. **[7M]**

(c) The wavefunction of particle of mass m confined to a 1D box defined by potential energy: V=0 for 0≤x≤ 2L; and V=∞ otherwise is given by $\psi_n(x) = A sin\frac{n\pi x}{2L}$. Determine the normalization constant A of the wavefunction. Show mathematically whether the ground state wavefunction is an eigenfunction of kinetic energy operator. If yes, find the eigenvalue. If no, explain your observation in no more than one line. (Given, $\hat{p} = \frac{\hbar}{i}\frac{d}{dx}$) **[4M]**

Q.2. (a) Expressions for two orbitals of hydrogen atom are given below, out of which one is wrong.

$$\psi_a = N_a\left(12 - \frac{r}{a_0}\right)r^2e^{-r/4a_0}sin^2\theta sin2\phi$$

$$\psi_b = N_b re^{-r/3a_0}sin\theta cos\phi$$

Given that N_a and N_b are normalization constants,

(I) Identify the wrong expression with one-line reasoning. **[3M]**

For the correct expression, **(II)** write the name of the orbital and mention the number of radial and angular node(s) if any. **(III)** Find the value(s) of **r** in terms of $\mathbf{a_0}$ where the radial node(s) is/are present.

(IV) Calculate the energy (**in eV**) of the orbital. **[3M+2M+3M]**

(b) Ground state electronic configuration of titanium atom ([Ar]$3d^24s^2$) yields the terms, ^1G, ^3F, ^1D, ^3P and ^1S. **(I)** Identify the ground state term and justify your answer in no more than one line. **(II)** Find the number of states corresponding to the ground state term. **(III)** Upon spin-orbit coupling find the term symbol(s) (include the levels) arising from the ground state term. Identify the lowest level and find the degeneracy of this level. **[2M+1M+5M]**

(c) The π electrons in a cyclic benzene molecule can be approximated as having a 2D rotational motion. If the radius of the electron ring is 1.40 Å, determine the wavelength required for an electronic transition to take place from m = 1 to m = 2. **[4M]**

Q.3. (a) For a heteronuclear diatomic molecule with the reduced mass of 27.44 amu and the bond length of 0.249 nm, calculate the ratio of the number of molecules in the highest populated rotational state to the number of molecules in the ground rotational state at 472 K. **[8M]**

(b) Calculate the vibrational frequency of $^{2}H^{35}Cl$ if the vibrational frequency of $^{1}H^{35}Cl$ is 2880 cm^{-1}, assuming the force constant to be the same for both the molecules. **[5M]**

(c) The wavenumber of the incident radiation in a rotational Raman spectrometer is 20,632 cm^{-1}. What is the wavenumber of the scattered Stokes radiation for the transition $J = 4 \leftarrow 2$ of $^{16}O_2$, if the equilibrium bond length is 120.7 pm.? **[6M]**

(d) Suppose you have prepared a calibration curve by recording the absorbance of five solutions of different concentration of potassium ferrocyanide at 430 nm and plotting them against concentrations. The slope of the curve is 160 L/mol. The cuvette with a path length of 4 cm is used for such measurement. Find out the value of molar absorptivity of the compound. **[3M]**

Q.4. (a) 2.504 g of a complex 'A' (empirical formula $CoH_{15}N_5Cl_3$) reacts with excess $AgNO_3$ and the reaction produces 2.87 g of a white precipitate. Write the formula of the complex 'A' by clearly showing the calculations, and then find out its primary and the secondary valences. Consider all the ligands to be monodentate. **[5M]**

(b) In $CoFe_2O_4$ structure, calculate the CFSE (**in** Δ_o) of both Co^{2+} and Fe^{3+} ions in octahedral and tetrahedral field of O^{2-} ions. Ignore pairing energy for both octahedral and tetrahedral field. Determine whether $CoFe_2O_4$ exhibits normal spinel or inverse spinel structure. Indicate the occupancy of Co^{2+} and Fe^{3+} ions in the tetrahedral and octahedral sites. *Write appropriate answers in the given format in the answer sheet.* **[6M]**

Metal ions	CFSE (**in** Δ_o), Octahedral field	CFSE (**in** Δ_o), Tetrahedral field
Co^{2+}		
Fe^{3+}		

(c) Two isomers are given below.

Complex I: $[Co(H_2O)_6][Co(Cl)_6]$

Complex II: $[Co(H_2O)_4(Cl)_2][Co(H_2O)_2(Cl)_4]$

How would you distinguish *complex I* and *II* based on Werner theory? Justify your answer in brief. Do not use any spectroscopy techniques or X-ray diffraction analysis for the explanation. **[5M]**

(d) The crystal field stabilization energy (CFSE) of $[CoCl_6]^{4-}$ is 18000 cm^{-1}. What will be the CFSE (**in** cm^{-1}) of $[CoCl_4]^{2-}$ (ignore the contribution due to pairing energy while doing calculation)? **[6M]**

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