Civil Services (Main) Examination, 2011

CHEMISTRY

(Paper I)

Time Allowed : Three Hours **Maximum Marks : 300**

QUESTION PAPER SPECIFIC INSTRUCTIONS

(Please read each of the following instructions carefully before attempting questions)

There are EIGHT questions divided in two Sections.
Candidate has to attempt FIVE questions in all.
Question Nos. 1 and 5 are compulsory and out of the remaining, any THREE are to be attempted choosing at least ONE question from each Section.
The number of marks carried by a question/part is indicated against it.
Wherever any assumptions are made for answering a question, they must be clearly indicated.
Word limit in questions, wherever specified, should be adhered to.

SECTION 'A'

1. (a) (i) Show that the function $\psi = N\sin(n\pi x/L)$ satisfies the Schrödinger equation for a particle in a one-dimensional box with a potential function $V(x)$ equal to zero for $0 \le x \le L$ and infinity elsewhere. (ii) What values may the quantum number n take? What are the allowed energy levels? (iii) Why is it important that the wavefunction be normalized? Calculate the normalization constant, N. [Given $\int \sin^2\theta \, d\theta = 1/2(\theta - \sin 2\theta/2)$] **15**

(b) Given the following information: $A+B \rightarrow C+D$ $\Delta H = -10.0$ kJ; $C+D \rightarrow E$ $\Delta H = 15.0$ kJ. Calculate ΔH for each of the following reactions: (i) $C+D \rightarrow A+B$ (ii) $2C+2D \rightarrow 2A+2B$ (iii) $A+B \rightarrow E$ **15**

(c) State the van der Waals equation of state and justify briefly the appearance of the parameters a and b in the equation. Given that for Xe, $a = 4.191$ bar dm^6 mol^{-2}, $b = 5.16 \times 10^{-2}$ dm^3 mol^{-1}, determine the pressure exerted by 1 mol of Xe in a container of volume 20 dm^3 at 300 K. How does the pressure compare with that predicted by the perfect gas law? Explain. ($R = 0.083$ bar dm^3 mol^{-1} K^{-1}) **15**

(d) The nicotine-water system exhibits two critical solution temperatures. What is the effect of external pressure on the system? **15**

2. (a) Draw and label an energy level diagram for molecular orbitals up to $\sigma^* 2p$. Use the diagram to explain why (i) The bond length of Li_2 is much greater than that of B_2. (ii) B_2 is paramagnetic, but C_2 is not. (iii) NO^+ is more stable towards dissociation into its atoms than NO, whereas CO^+ is less stable than CO. **20**

(b) According to the kinetic model of gases, the pressure and volume of a gas are related through the root mean square molecular speed, $c = \langle v^2 \rangle^{1/2}$, by $pV = 1/3nMc^2$ where $M = mN_A$ is the molecule's molar mass, and n is the number of moles of gas present. (i) According to the 'equipartition theorem' of classical mechanics, the average energy per molecule for three-dimensional transitional motion is $3/2k_BT$, where k_B is the Boltzmann's constant. Use this and the above equation to derive the ideal gas law. (ii) Show that the root mean square molecular speed is given by $c = \sqrt{(3RT/M)}$ (iii) Calculate c for O_2 at room temperature (298 K). (iv) Calculate the ratio of c for He to that for O_2 at 298 K. ($R = 8.314$ J K^{-1} mol^{-1}) **25**

(c) Using the Kelvin equation calculate P_s/P at 25°C, where P_s is the vapour pressure for a very small droplet of water of radius $r = 1 \times 10^{-3}$ m and P is that of bulk water. Given that for water at this temperature, $\gamma = 71.97 \times 10^{-3}$ Nm^{-1}, $\rho = 0.9970 \times 10^3$ kg m^{-3} and $R = 8.314$ J K^{-1} mol^{-1}. **15**

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3. (a) The energy levels of the electron in a hydrogen atom are given by $E_n=-R_H/n^2$, n=1,2,3,… where R_H is the Rydberg constant and n is the principal quantum number. (i) Draw a clearly labelled energy level diagram showing the first three energy levels of the electron and all of the quantum states belonging to each energy level. (ii) Give the degeneracies of the first three energy levels, giving the allowed l and m_l values and the orbital rotations. Suggest a simple formula which relates the degeneracy of an energy level to its principal quantum number. (iii) The wavefunction of an electron in a hydrogen 1s orbital is given by: $\psi_{1s}(r) \quad e^{-r/a_0}$ where r is the radial distance from the nucleus, and a_0=52.9 pm is the Bohr radius. Write down an expression for the radial distribution function $4\pi r^2\psi^2$ and explain why this function has a different physical interpretation to ψ^2. Sketch ψ and $4\pi r^2\psi^2$. (iv) Find the most probable radius at which the electron will be found. Justify the statement "the hydrogen atom has a diameter of approximately one Å". **30**

(b) (i) CsCl crystallizes in a cubic structure and has a Cl^- at each corner and a Cs^+ at the centre of the unit cell. Use the ionic radii of Cs^+ (169 pm) and Cl^- (181 pm) to predict the lattice constant a and compare this value with the value of a calculated from the observed density of CsCl, 3.97×10^3 kg m^{-3} (Cs = 132.9, Cl = 35.4). (ii) Calculate the packing efficiency in the primitive unit cell. **30**

4. (a) One mole of $CaCO_3$ was heated in an open vessel at 1 bar pressure to 1000 K when it decomposed into CaO (s) and CO_2 (g). Calculate the work done during the decomposition, assuming that CO_2 may be regarded as an ideal gas. (R=0.083 bar dm^3 mol^{-1} K^{-1}) **15**

(b) (i) The vapour pressure, p, of a liquid varies with temperature, T, according to the Clausius – Clapeyron equation, $d\ln p/dT=\Delta H/RT^2$ where R=8.314 J K^{-1} mol^{-1} is the gas constant and ΔH is the standard enthalpy change of vaporization. Show by integration that this equation can be used to predict the vapour pressure, p_2, at one temperature, T_2, from a known vapour pressure, p_1, at another temperature, T_1. $\ln p_2/p_1=\Delta H/R(1/T_1-1/T_2)$ (ii) What assumption have you made about the temperature dependence of ΔH? (iii) Use the above formula to predict the saturation vapour pressure at 298 K from its value at 373 K. Take ΔH=40.65 kJ mol^{-1}. **25**

(c) (i) Write down the Hamiltonian for the hydrogen molecule ion, H_2^+. (ii) For a trial wavefunction of the form $\phi=c_a\psi_a+c_b\psi_b$ where ψ_i is the normalized atomic orbital on atom i and the c_i are coefficients, show that the normalization constant is $N=(2+2S)^{-1}$ where $S=S_{ab}=S_{ba}$ is the overlap integral. Assume that the c_i's are all equal and that identical normalized hydrogen-like wavefunctions are chosen. (iii) By expanding the probability density, $\phi^*\phi$, qualitatively confirm that $\phi=(2+2S)^{-1/2}(\psi_a+\psi_b)$ represents the wavefunction for a bonding orbital of H_2^+. **20**

SECTION 'B'

5. (a) Draw the shape of 'd' orbitals. On the basis of Crystal Field Theory explain splitting of 'd' orbitals in octahedral and tetrahedral fields. The splitting pattern is different in octahedral and tetrahedral fields. Why? **15**

(b) Discuss the role of sodium and potassium in biological processes. Both alkali metals belong to the same group; even though their function is opposite to each other. Why? **15**

(c) Write BET isotherm equation and define the terms used therein. **15**

(d) Distinguish between homogeneous and heterogeneous catalysis. **15**

6. (a) (i) Complex formation is an acid-base reaction. Explain with suitable example. (ii) Draw the cis and trans structures of complex diamminedichloroplatinum(II). Which form of the complex is used in the treatment of cancer? (iii) Write a note on cytochromes. **20**

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(b) (i) Borazine is a close analogue of benzene. Explain on the basis of preparation, molecular structure and reactions of borazine. (ii) Discuss magnetic and spectral properties of lanthanides. **20**

(c) Write phase rule equation and define the terms used therein. How many phases, components and degrees of freedom are in the following system: NH_4Cl (s)=NH_3 (g)+HCl (g) **20**

7. (a)(i) Give the IUPAC names of the following complexes: (1) $[CoCl(NH_3)_5]\cdot Cl_2$ (2) $K_2[PdCl_4]$ (3) $K_2[OsCl_5N]$ (4) $[Fe(CNCH_3)_6]$ Br_2 (5) $[Co(H_2O)_2(NH_3)_4]\cdot Cl_3$ **10**

(a)(ii) What is EDTA? Give its molecular structure, total number of donor atoms available in it and dentate character. Draw the molecular structure of Zn-EDTA complex. **10**

(b)(i) Give brief account on inter halogen compounds and discuss molecular structure of IF_7. **10**

(b)(ii) Localized accumulation of aluminium in the brain is responsible for Alzheimer's disease. Why? **10**

(c)(i) Derive an expression for the rate constant of a first order reaction. **10**

(c)(ii) Show that the half-life period of a first order reaction is independent of initial concentration. **10**

8. (a) Give electronic configuration of lanthanides and on the basis of this explain lanthanide contraction. **20**

(b) Why does carbon monoxide form metal carbonyls? Give synthesis of metal carbonyls and discuss σ and π bonding in case of $Fe(CO)_5$. **20**

(c) Discuss shape, hybridization, number of unpaired electrons, magnetic moment and their magnetic behaviour in the following: (i) $Ni(CO)_4$ (ii) $[Ni(NH_3)_2]^{2+}$ (iii) $[Pt(CN)_4]^{2+}$ (iv) $[Fe(F)_6]^{3-}$ **20**

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