Civil Services (Main) Examination, 2013

CHEMISTRY

(Paper I)

Time Allowed : Three Hours **Maximum Marks : 250**

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.

Attempts of questions shall be counted in sequential order. Unless struck off, attempt of a question shall be counted even if attempted partly. Any page or portion of the page left blank in the Question-cum-Answer Booklet must be clearly struck off.

SECTION 'A'

1. (a) A particle of mass m is confined in a one-dimensional box of length L. The wavefunctions $\psi_n(x)$ of the particle are given by

$$\psi_n(x)=\sqrt{(2/L)}\ \sin n\pi x/L;\ n=1,2,3,\ldots$$

n is the quantum number, and $0\le x\le L$ is the distance along the length of the box. (i) Sketch the wavefunctions for the states with n = 1, n = 2 and n = 3. (ii) Describe what is meant by the Born interpretation,

$$P_n(x)=\psi_n^{*}(x)\ \psi_n(x)$$

(iii) Sketch the probability of finding the particle within the box for the states with n = 1, n = 2 and n = 3. (iv) What is the average momentum of a particle in a box? **10**

(b) (i) How is entropy defined thermodynamically? (ii) What role does ΔS play in determining the direction of spontaneous change? (iii) At 25 °C, the enthalpy change of the graphite → diamond phase transition is 1.8961 kJ mol^{-1} and the entropy change is 3.2552 J mol^{-1}. Which is the spontaneous direction at 25 °C? Which direction is favoured by a rise in temperature? **10**

(c) Determine expressions for the critical constants (P_c, V_c, T_c) of a Van der Waals gas, defined by the expression

$$P=RT/(V_m-b)-a/V_m^{\ 2}$$

where the symbols have their usual meanings. **10**

(d) Calculate the number of phases, components and degrees of freedom in the following systems: (i) H_2O $(l)\rightleftharpoons H_2O$ (g) (ii) $CaCO_3$ (s)$\rightleftharpoons$CaO (s)+CO_2 (g) (iii) $2H_2$ (g)+O_2 (g)$\rightleftharpoons H_2O$ (g) (iv) H_2O (s)$\rightleftharpoons H_2O$ $(l)\rightleftharpoons H_2O$ (g) (v) NH_4Cl (s)$\rightleftharpoons NH_3$ (g)+HCl (g) **10**

(e) The molar enthalpy of formation of oxygen atoms is 246.5 kJ mol^{-1}. What is the longest wavelength photon which could dissociate O_2? **10**

2. (a)(i) Compare the molecules OF, OF^- and OF^+, discussing molecular orbitals, bond orders, bond lengths, bond energies, and paramagnetism. **15**

(a)(ii) Which of the following pairs is expected to have the larger bond angle and why? (1) H_2O and NH_3 (2) SF_2 and BeF_2 (3) BF_3 and $BF_4^{\ -}$ (4) PH_3 and NH_3 (5) NH_3 and NF_3 **10**

(b) The molecular speeds are distributed according to the Maxwell distribution,

$$f(v)=4\pi(M/2\pi RT)^{3/2}v^2\ e^{-Mv^2/2RT}$$

(i) Sketch f(v) for He and for N_2. (ii) Show that f(v) is normalized, i.e. **15**

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$$\int_0^\infty f(v)\, dv = 1$$

(iii) Show that the most probable molecular speed v_{mp}, is given by

$$v_{mp} = \sqrt{(2RT/M)}$$

(c) The surface tension of water at 20 °C is 72.75×10^{-3} Nm^{-1}. A 33.24 vol% solution of ethanol has $\gamma = 33.24\times10^{-3}$ Nm^{-1} at the same temperature. Given $\rho = 0.9614\times10^{3}$ kg m^{-3} for the solution and 0.9982×10^{3} kg m^{-3} for water. How much less will alcohol solution rise in the same capillary tube? **10**

3. (a)(i) The basic Schrödinger equation for a hydrogenic (1–electron) atom is

$$-\hbar^2/2\mu\nabla^2\psi - (Ze^2/4\pi\varepsilon_0 r)\psi = E\psi$$

(i) Explain what the terms in this equation mean. **5**

(a)(ii) μ is the reduced mass of the electron-nucleus pair. For hydrogen, how does it compare with m_e, the mass of the electron? **5**

(a)(iii) Evaluate the average electron-nucleus separation for the ground state of a hydrogenic atom:

$$\langle r\rangle = \int_0^\infty \psi^*\, r\, \psi\, 4\pi r^2\, dr$$

given that

$$\int_0^\infty r^n e^{-\alpha r}\, dr = n!/(a^{n+1})$$

and the wavefunction is given by

$$\psi(r) = (Z^3/a_0{}^3\,\pi)^{1/2} e^{-Zr/a_0}$$

where Z is the nuclear charge and $a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2 = 52.9$ pm is the Bohr radius. **10**

(a)(iv) Why is this different from the most probable radius (a_0/Z)? **5**

(b) Potassium crystallizes as a body centred cubic lattice having unit cell length a = 520 pm. (i) What is the distance between nearest neighbours? (ii) What is the expected density of crystalline K metal? (Given: At. wt. of K = 39.1) (iii) What is the ionic radius of K^+? **15**

(c) What are the electrode reactions for charging and discharging of the Cd – Ni alkaline battery? What are the advantages of choosing Cd and Ni for the cell? **10**

4. (a) NO_2 gas is a paramagnetic brown gas at room temperature. When a sample of the gas is cooled below 0 °C, its molecular weight increases, and it loses its paramagnetism and colour. (i) Using electron dot structure, write an equation which accounts for these observations. (ii) Based on these observations, predict whether the reaction taking place is endothermic or exothermic. (iii) Use the following data for the pressures of NO_2 and its product at equilibrium to calculate the equilibrium constant for the reaction at 298 K: p_{NO_2} =46 mm Hg, p (product) = 23 mm Hg **15**

(b)(i) What is an ideal solution? **5**

(b)(ii) Show that the entropy of mixing of two liquids to form an ideal solution of mole fractions x_A and x_B is

$$\Delta_{mix}S = -nR\,(x_A \ln x_A + x_B \ln x_B)$$

where $n = n_A + n_B$ is the total amount of solution resulting from n_A moles of liquid A and n_B moles of liquid B. **10**

(b)(iii) What mole fractions give the maximum entropy of mixing? **5**

(c) (i) Construct a trial LCAO – MO wavefunction for the H_2 molecule. (ii) The trial VB wavefunction used by Heitler and London to describe the H_2 molecule in terms of hydrogen-like wavefunctions is

$$\phi = c_1\,\psi_a(1)\,\psi_b(2) + c_2\,\psi_a(2)\,\psi_b(1)$$

Compare with the wavefunction you wrote in (i) and comment on the differences, if any. **15**

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SECTION 'B'

5. **(a)** Show that in the adiabatic reversible expansion of a gas

$$\mu \cdot C_p = -(\partial H/\partial P)_T$$

where μ = Joule – Thomson Coefficient, C_p = Molar specific heat at constant pressure. **10**

(b) Below 18.5 °C triethylamine is miscible with water in any proportion. What is the temperature known as? What is the molecular mechanism for the existence of such a temperature? **10**

(c) ΔG_{298} is found to be −77.8 kJ, for the following reaction

$$H_2\,(g) + 1/2\,O_2\,(g) + H_2O\,(l) \rightarrow 2H^+ + 2OH^-$$

Calculate E_{298} for the following half-reaction

$$1/2\,O_2\,(g) + H_2O\,(l) + 2e^- \rightarrow 2OH^-$$

(Given: 1 Faraday = 96,500 C) **10**

(d) The mechanism of a chemical reaction A → B can be written as follows:

$$A + A \underset{K}{\overset{K_1}{\rightleftharpoons}} A^* + A$$

$$A^* \xrightarrow{K_2^1} B$$

(i) Write expressions for $(-d[A])/dt$ and $d[A^*]/dt$ in terms of [A], [A*] and the rate constants. (ii) Assuming a steady state approximation for A*, express the rate constant for the formation of the product B in terms of [A] and the rate constants. (iii) Under what conditions does the reaction become (1) first order and (2) second order? **10**

(e) How many types of absorption are there on solid adsorbents? Prove that, for chemisorption, the amount of the adsorbed phase m is equal to $AP/(1+KP)$ where P is equal to the pressure of the adsorbent, A and K are some constants of the system. **10**

6. **(a)** R_3SiCl, R_2SiCl_2, $RSiCl_3$, (R = methyl) are used for making silicon polymers. Explain the roles of these compounds in the synthesis. **10**

(b) Explain why (i) The complex $[CuCl_4]^{2-}$ exists, but $[CuI_4]^{2-}$ does not. (ii) $[Co(CN)_6]^{3-}$ is more stable than $[Co(CN)_6]^{4-}$, whereas $[Fe(CN)_6]^{4-}$ is more stable than $[Fe(CN)_6]^{3-}$. (iii) Copper metal dissolves in HCN with evolution of hydrogen gas, but it does not dissolve in sulphuric acid. (iv) The stability constant of $[Cu(en)_2]^{2+}$ is higher than that of $[Cu(NH_3)_4]^{2+}$ (en=$NH_2-CH_2-CH_2-NH_2$). **20**

(c) (i) What is the co-operative effect of haemoglobin during oxygen transport? (ii) Describe the metal site of Cytochrome C and its function. **20**

7. **(a)** A solution of a dye has its maximum wavelength light absorption at 453 nm and maximum fluorescence emission at 508 nm. The quantum efficiency of fluorescence is 40%. What percentage of absorbed light is emitted as fluorescence? **15**

(b) The absorption spectra of lanthanide ions are sharper than those of ions of the first transition series. Explain. **10**

(c) What are the differences between the triple point and boiling point? Illustrate with the help of the phase diagram of water. **10**

(d) Calculate the half-life of N_2O_5 at 25 °C and the fraction decomposed after 10^4 s, given that the rate constant of its decomposition is $k = 6.93 \times 10^{-5}\ s^{-1}$. **15**

8. **(a)** (i) Does the complex $[Co(NH_3)_4Cl_2]^+$ have isomeric forms? If so, draw their structures and identify the type(s) of isomerization. (ii) Write the chemical (IUPAC) name of the complexes. (iii) Do the isomers have identical physical properties and chemical reactivities? **15**

(b) Calculate the values of ΔG, ΔS and ΔH for the reversible condensation of 36 g of water at 0 °C to ice at 0 °C. The latent heat of melting of ice at 0 °C is equal to 335 Jg^{-1}. **15**

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(c) Explain why the eutectic point of a solution between solid A and solid B is invariant. **10**

(d) Calculate the standard potential E of the reaction

$$Hg_2Cl_2 + Cl_2 \rightarrow 2Hg^{2+} + 4Cl^-$$

Given the following reduction potentials: E $(Hg_2Cl_2/Hg)=0.27$ V; E $(Hg^{2+}/Hg_2{}^{2+})=0.92$ V; E $(Hg/Hg^{2+})=0.79$ V; E $(Cl_2/Cl^-)=1.36$ V

Given: Constants for use: $N_A=6.022\times10^{23}$ mol^{-1}; $h=6.626\times10^{-34}$ Js; $K_B=1.38\times10^{-23}$ JK^{-1}; $c=3.0\times10^8$ ms^{-1}; $R=8.314$ JK^{-1} mol^{-1}; $F=96{,}500$ C **10**

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