Civil Services (Main) Examination, 2015

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) The wave functions for a particle in a one-dimensional box (length L) are

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

where n is the quantum number and $0\le x<L$ is the distance along the length of the box. Find expectation values of the momentum $\hat{p}=\hbar/id/dx$ and square of the momentum $p^2=-\hbar^2 d^2/dx^2$ for the $n=1$ state of the particle in the box. Interpret your answer. **10**

(b) The van der Waals equation for real gases is given by

$$P_{obs}=nRT/(V-nb)-a(n/V)^2$$

where P_{obs} is the observed pressure, V is the volume, n is the number of moles, R is the gas constant and T is the temperature. a and b are constants characteristic of a gas. (i) Is P_{obs} greater or less than the pressure expected for an ideal gas? Write a few sentences outlining the reason(s) for your answer. (ii) Consider the halogens F_2 (g), Cl_2 (g) and Br_2 (g). (1) Rank these in order of increasing a. Justify your answer. (2) Rank these in order of increasing b. Justify your ranking. **10**

(c) The standard enthalpy of vapourization, ΔH , for water at 100 °C is around 30.0 kJ mol^{-1} and 1 mol of liquid water is undergoing vapourization at 100 °C and 1 atm pressure. (i) Calculate w. (ii) Calculate Δu. (iii) Under these conditions does the entropy change of the system or the surroundings drive the process? State reasons for your answer. **10**

(d) Buckminsterfullerene (C_{60}) molecules crystallize to form a face-centred cubic unit cell of C_{60} molecules. (i) How many buckminsterfullerene molecules are there in the unit cell of buckminsterfullerene? (ii) How many carbon atoms are there in the unit cell? (iii) What is the mass of carbon atoms in the unit cell? (iv) Given that the radius of a buckminsterfullerene molecule is 502 pm. Calculate the density of buckminsterfullerene in kg m^{-3}. **10**

(e) Construct the MO diagram for the CO molecule. On the basis of the diagram, state whether the bonding in metal carbonyls is of the type M—C or M—O. Explain your reasoning. You may ignore the 1s electrons. **10**

2. (a) The Bohr model for single-electron atoms predicts that the energies of the allowed orbits are given by

$$E_n=-2.18\times10^{-18}\ Z^2/n^2 \text{ joule}$$ **20**

Optional Province · optionalprovince.com

where n=1,2,3,…,∞ and Z is the nuclear charge. (i) The Balmer series corresponds to transitions between which energy levels in the hydrogen atom? Does the Paschen series appear at higher or lower wavelengths than the Balmer series? (ii) Calculate the minimum energy (in J) required to ionize an electron in the n=2 state of hydrogen atom. (iii) Calculate the wavelength (in nm) of the photon emitted by an electron in making the transition from the n=3 to n=1 level of the single-electron ion, Li^{2+}. (iv) Is the photon higher in energy or lower in energy than the transition from n=3 to n=1 in Be^{3+}? Explain your answer.

(b) In terms of the kinetic molecular model of matter, explain why– (i) a liquid in an open container will eventually vapourize even if the temperature is below the boiling point; (ii) the temperature of a pure, boiling liquid substance does not change even though heat is continually flowing into the container. **10**

(c) How high will a liquid rise in a capillary tube of 0.1 mm diameter, if its density is 1.3×10^3 kg m^{-3} and surface tension 0.065 N m^{-1}? Assume $\theta\approx0$. **10**

(d) Copper metal has an f.c.c. unit cell. The accepted value for the metallic radius of copper is 0.128 nm. Calculate the density of copper (at. wt. of Cu = 63.5). **10**

3. (a) A bomb calorimeter has a measured heat capacity of 6.27 kJ/ C. The combustion of 1.84 g of magnesium (at. wt. = 24.3 g mol^{-1}) leads to a temperature change from 21.30 °C to 25.56 °C. The specific heat of water is 4.18 J/ C/g. (i) Calculate the change in internal energy (Δu) per mole of Mg for the reaction

$$Mg\ (s)+1/2O_2\ (g)\rightarrow MgO\ (s)$$

(ii) If the reaction were carried out open to the atmosphere at 25 °C, what would be the enthalpy change (ΔH) of the reaction per mole of Mg? **10**

(b) An important metabolic step is the conversion of fumarate to malate:

$$Fumarate\ (aq)\rightleftharpoons Malate\ (aq)$$

At 25 °C, the equilibrium constant for the reaction, $K=a_m/a_f=4$, where a_f is the activity of fumarate and a_m is the activity of malate. (i) Calculate the standard Gibbs energy change, ΔG , for the above reaction. (ii) Calculate the reaction Gibbs energy, ΔG_r, when at some time during the course of the reaction, the reaction quotient, Q, is 0.01. (iii) What is the difference in chemical potential between the two species when Q=0.01? **15**

(c) Benzene and toluene form a nearly ideal solution. At 80 °C, the vapour pressure of pure benzene (MW = 78.1) is 753 torr and that of pure toluene (MW = 92.1) is 290 torr. The following questions refer to a solution containing equal masses of benzene and toluene: (i) Calculate the partial pressure of each substance in the vapour that would be in equilibrium with the above solution at 80 °C. (ii) At what atmospheric pressure will the solution boil at 80 °C? (iii) Suppose that some of the vapour from the solution is collected and condensed. What will be the composition of the resulting liquid? **15**

(d) The viscosity of gases increases with temperature, but the viscosity of liquids decreases with temperature. Explain. **10**

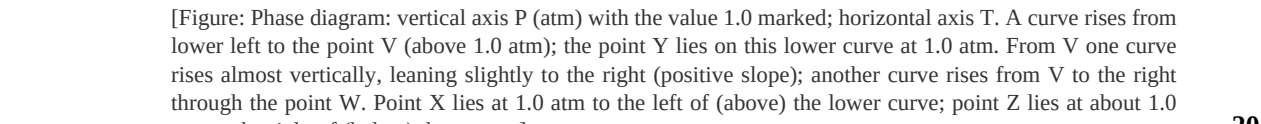
4. (a) The BF molecule is isoelectronic with CO. (i) Construct an MO diagram for the BF molecule. What assumptions can be made in BF which make the MO construction for this molecule much more straightforward than for CO? (ii) Discuss the similarities and differences in the electronic structures of BF and CO in terms of σ and π bonding and non-bonding orbitals. What possible Lewis structures can be drawn for BF and CO, and which of these is most reasonable for each species based on your diagram? **20**

(b)(i) Sodium lauryl sulphate can decrease the surface tension of water, but sodium chloride increases the surface tension. Explain. **5**

(b)(ii) On gradual increase of surfactant from zero concentration to a higher value, there is a sharp change in surface tension after some value. What is the reason for this? **5**

Optional Province · optionalprovince.com

(c) The phase diagram for a pure substance is shown below. Use the diagram to answer the following questions: (i) What does the point *V* represent? What characteristics are specific to the system only at point *V*? (ii) What does each point on the curve between *V* and *W* represent? (iii) Describe the changes that the system undergoes as the temperature slowly increases from *X* to *Y* to *Z* at 1.0 atm. (iv) In a solid-liquid mixture of the substance will the solid float or sink? Explain.



[Figure: Phase diagram: vertical axis P (atm) with the value 1.0 marked; horizontal axis T. A curve rises from lower left to the point V (above 1.0 atm); the point Y lies on this lower curve at 1.0 atm. From V one curve rises almost vertically, leaning slightly to the right (positive slope); another curve rises from V to the right through the point W. Point X lies at 1.0 atm to the left of (above) the lower curve; point Z lies at about 1.0 atm to the right of (below) the curves.]

20

SECTION 'B'

5. (a) Discuss, with the aid of diagrams– (i) why a block of magnesium is attached to a pipeline to reduce corrosion; (ii) what is meant by pitting corrosion and how it occurs. **10**

(b) Explain why– (i) $[Fe(H_2O)_6]^{3+}$ is essentially colourless, while $[Fe(CN)_6]^{3-}$ is highly coloured; (ii) examples of carbonylate anions are more than those of metal carbonyl cations. **10**

(c) Why do lanthanoid ions have similar chemical properties even with variation of atomic number and have higher lifetime in excited states than transition metal ions? **10**

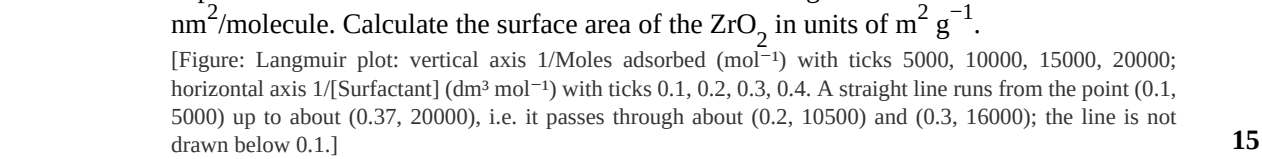
(d)(i) Why is Ca^{2+} more suitable than Mg^{2+} for fast signalling process in cells? **5**

(d)(ii) Which metal ions are responsible for decomposition of H_2O to O_2 during photosynthesis by plants, and what is the nature of this ionic cluster and its ionic state? **5**

(e) In an experiment to measure the quantum efficiency of a photochemical reaction, the absorbing substance was exposed to 490 nm light from a 100 W source for 45 minutes. The intensity of the transmitted light was 40% of the intensity of the incident light. As a result of irradiation, 0.344 mol of the absorbing substance decomposed. Find the quantum efficiency. **10**

6. (a) Photodimerization of a monomer *M* in the presence of a photoinitiator occurs by a chain polymerization process in three steps: Photoinitiation: Rate = I_{abs}; Propagation: Rate = $k_p[M][M^*]$; Termination: Rate = $k_t[M^*]$ where k_p and k_t are the rate constants for the propagation and termination steps, involving the propagating chain radical M^* and I_{abs} is the intensity of absorbed light. Show that the rate of photopolymerization (i.e., the rate of loss of monomer) is proportional to the square root of the light intensity. **15**

(b) The adsorption of a surfactant on colloidal ZrO_2 suspended in water followed a Langmuir isotherm with the results shown below: Given that 10 g of ZrO_2 colloid was used in the experiment and that the cross-sectional area of a single surfactant molecule is 0.25 nm^2/molecule. Calculate the surface area of the ZrO_2 in units of $m^2\ g^{-1}$.



[Figure: Langmuir plot: vertical axis 1/Moles adsorbed (mol⁻¹) with ticks 5000, 10000, 15000, 20000; horizontal axis 1/[Surfactant] (dm³ mol⁻¹) with ticks 0.1, 0.2, 0.3, 0.4. A straight line runs from the point (0.1, 5000) up to about (0.37, 20000), i.e. it passes through about (0.2, 10500) and (0.3, 16000); the line is not drawn below 0.1.]

15

(c) Chlorine trifluoride, ClF_3, is one of the most reactive compounds known. It can be made by heating Cl_2 and F_2 in a closed container. (i) Draw the electron-dot structure of ClF_3. (ii) What is the electron-pair geometry for ClF_3? (iii) Knowing that the molecule is polar, what can you conclude about the molecular geometry? (iv) Calculate the standard enthalpy of formation of gaseous ClF_3, given the following bond energies: F—F: 159 kJ mol^{-1}; Cl—Cl: 243 kJ mol^{-1}; Cl—F: 255 kJ mol^{-1} **20**

7. (a) For the galvanic cell

$$Zn\ (s)\ |\ Zn(NO_3)_2\ (aq)\ (0.5\ M)\ ||\ Cu(NO_3)_2\ (aq)\ (1.0\ M)\ |\ Cu\ (s)$$

15

Optional Province · optionalprovince.com

the standard reduction potentials at 25 °C are the following: $E_{Zn^{2+}/Zn}$ =−0.76 V and $E_{Cu^{2+}/Cu}$ =0.34 V (i) Write down the two spontaneous half-cell reactions based on the convention for electron flow for the cell as written. (ii) Calculate the e.m.f. of this cell based on the concentrations given. In your calculations, use the fact that the mean activity coefficients ($r_{\pm}$) for Zn^{2+} and Cu^{2+} ions under the conditions given are 0.3 and 0.2, respectively.

(b) The hydrolysis of bicarbonate ions in water at a high pH

$$HCO_3^- + \bar{O}H \rightarrow CO_3^{2-} + H_2O$$

follows the rate law Rate = k [HCO_3^-] where k=0.01 s^{-1} at 25 °C. (i) What is the overall order of the reaction? (ii) What is the half-life of HCO_3^-, if the initial concentration of HCO_3^-, $[HCO_3^-]_0$=0.001 *M*? (iii) Is hydroxide ion a catalyst in this reaction? Explain in two lines. (iv) Write down the Arrhenius equation and define each of the terms in this equation. What each term physically relates to? (v) What is the rate constant of the above equation at 350 K, if the activation energy of the reaction is 10.0 kJ mol^{-1}? (vi) The hydrolysis reaction is exothermic. Draw a curve of the reaction showing how the energy of the system changes in going from reactants to products. Mark in the activation energy for the forward and back activation steps, and show the overall change in energy of the reaction. **25**

(c)(i) Arrange the following ligands in order of increasing Δ and justify your arrangement: NH_3, NF_3 and NCl_3 **5**

(c)(ii) The complex $[Mn(CN)_6]^{4-}$ is less paramagnetic than $[Mn(H_2O)_6]^{2+}$. Explain. **5**

8. (a) Account for the following observations: (i) Although $NH_2-CH(NH_2)-CH_2-NH_2$ has three basic sites, it functions as a bidentate ligand when the ligand is in excess. (ii) Copper(I) iodide is a stable species, while copper(II) iodide does not exist. **10**

(b) For the complex reaction

$$[Ni(en)_2(H_2O)_2]^{2+}(aq) + tren(aq) \rightarrow [Ni(tren)(H_2O)_2]^{2+}_{(A)}(aq) + 2en(aq)$$

the logβ value is 1.88. Explain the value, giving the structure of *A*. [tren=$N(CH_2CH_2NH_2)_3$] **10**

(c) (i) What property/properties of lanthanide β-diketone complexes make(s) them useful as shift reagents in NMR spectroscopy? (ii) What change in the position of iron in haemoglobin occurs in binding to oxygen and why? **10**

(d) Silicates produce a large number of silicate frameworks like $Al_2(OH)_4Si_2O_5$ (*A*) $Al_2(OH)_2Si_4O_{10}$ (*B*) $Mg_3(OH)_2Si_4O_{10}$ (*C*) $KAl_2(OH)_2Si_3AlO_{10}$ (*D*) $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot xH_2O$ (*E*) Name the compounds *A*, *B*, *C*, *D* and *E*. **10**

(e) State whether the following statements are true or false, and if false, correct them: (i) It is possible to change the rate constant for a reaction by changing the temperature. (ii) The reaction rate remains constant as a first-order reaction proceeds at a constant temperature. Useful Constants and Integrals (printed on page 15 of Paper I): N_A=6.02×10^{23} mol^{-1}; h=6.63×10^{-34} J s; k_B=1.38×10^{-23} J K^{-1}; c=3.00×10^8 m s^{-1}; R=8.31 J K^{-1} mol^{-1}; 1 F=96500 C; g=9.8 m s^{-1}; At 25 °C, 2.3RT/F=59 mV, RT/F=25.7 mV; $\int_0^L \sin\pi x/L \cos\pi x/L\, dx=0$; $\int_0^L \sin\pi x/L \sin\pi x/L\, dx=L/2$ **10**

Optional Province · optionalprovince.com