CC/M/EXAM.
2020

CHEMISTRY

PAPER—I

Time : 3 hours]

[Full Marks : 250

Note : 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.

SECTION—A

1. Answer *any* **five** of the following questions :   10×5=50

   (a) Define work and internal energy. A litre of ideal gas at 27 °C and 10 atm pressure is held in a cylinder fitted with a frictionless piston. Calculate the work done when the gas is expanded to a final pressure of 1 atm—

   (i) isothermally and reversibly;

   (ii) in one step, against a constant opposing pressure of 1 atm.

   (b) It is not possible to deduce the nature of the gases from the measured properties alone. Therefore, it becomes necessary to look for a model to account for the observed facts and to make some assumptions. State the five assumptions of kinetic theory of gases.

   (c) What is galvanic cell? With the help of a neat diagram, explain the working of a Daniell cell. Show the different half-cells and cell reactions involved.

   (d) Answer *any* **two** of the following questions :

   (i) Predict the wave number and wavelength of the second line in the Paschen series.

   (ii) Which ion would be more polarisable, an F^- ion or an I^- ion? Give justification to your answer.

   (iii) How many radial nodes does a $5s$ orbital have?

   (iv) Among $3p$ and $3d$ orbitals, in which one an electron has the greater probability of being found close to the nucleus? Give justification to your answer.

   (v) The ionization energies of Cl^-, Cl and Cl^+ are 349, 1251 and 2300 kJ/mol, respectively. Explain this trend.

(e) Prepare a molecular orbital energy level diagram for NO, showing clearly how the atomic orbitals interact to form MOs. Answer any *one* of the following questions :

  (i) How does your diagram illustrate the difference in electronegativity between N and O?

  (ii) Predict the bond order and the number of unpaired electrons.

  (iii) Compare the bond orders of NO^+ and NO^- ions with the bond order of NO. Which of the three would you predict to have the shortest bond? Why?

(f) Suggest the probable unit cells structure of any *two* of the following :

		Cationic radius	Anionic radius
(i)	RbBr	1·48 Å	1·95 Å
(ii)	MgTe	0·65 Å	2·21 Å
(iii)	MgO	0·65 Å	1·40 Å
(iv)	BaO	1·35 Å	1·40 Å

(g) Give chemical names/structures for any *two* of the following :

  (i) $Rb[AgF_4]$

  (ii) $[Ir(CO)Cl(PPh_3)_2]$ (*two* isomers)

  (iii) μ-oxo-bis[pentaamminechromium(III)] ion.

  (iv) Diaquadiiododinitrito Pd(IV) (all isomers).

2. Answer the following questions :

(a) Starting with $[PtCl_4]^{2-}$, show the sequence of reactions to get Pt(II) complexes with (i) four different ligands—py, NH_3, NO_2^- and CH_3NH_2; (ii) with two different sets of trans ligands.   20

(b) Draw the Jablonski diagram to show different paths for the decay of excited state electrons.   15

(c) Essential condition for liquefaction of gases was discovered by Andrews. Explain Andrews isotherm for liquefaction of CO_2 gas emphasizing on critical temperature and pressure.   15

3. Answer the following questions :

(a) Explain the following :   20

  (i) Drop of water assumes spherical shape

  (ii) Soap can be used as detergent to remove dirt

  (iii) Liquid rises in a capillary tube

  (iv) Surface tension of a liquid decreases with rise in temperature

(b) Write and explain the consequence of Kelvin equation which relates vapour pressure of a liquid with its surface tension. 15

(c) Answer *any* **one** of the following questions : 15

(i) Estimate the reaction enthalpy for the production of SF_6 (g) from SF_4 (g), given that the mean bond enthalpies of F_2, SF_4 and SF_6 are 158, 343 and 327 kJmol^{-1}, respectively, at 25 °C. Explain how electronegativity can be used for estimating bond enthalpies.

(ii) Match the molecules/ions in Column—A with the correct structures in Column—B in the table below :

Column—A	Column—B
B_4H_8	Closo
$B_6H_6^{2-}$	Arachno
B_5H_{11}	Nido

4. Answer the following questions :

(a) Borazine is isostructural and isoelectronic with benzene.

(i) Draw a molecular orbital energy level diagram for the π-orbitals (only) in borazine.

(ii) Draw the π-molecular orbitals of borazine. 20

(b) Answer *any* **three** of the following questions : 15

(i) What is the most common oxidation state for lanthanides? Mention any two lanthanide ions in oxidation states other than the common oxidation state of lanthanides.

(ii) In the electronic absorption spectra, broadening of *f-f* transition in lanthanide cations is less as compared to *d-d* transition in transition metals. Explain why.

(iii) Why spin only formula for calculation of magnetic moment is not suitable in case of actinides?

(iv) Discuss how the size of lanthanides varies along the period and its influence in separation of lanthanides.

(c) Derive Nernst equation to show the effect of electrolyte concentration on electrode potential. What is standard electrode potential? 15
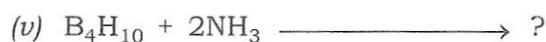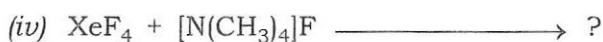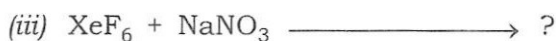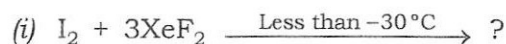
SECTION—B

5. Answer *any* **five** of the following questions : 10×5=50

(a) Match the functions of the metal ions in Column–A to the correct biological importance in Column–B in the following table :

Column–A	Column–B
Zn^{2+}	Used in cell walls, bones and some shells as structural component
Fe^{2+}	Stabilizes coiled ribosome
Mg^{2+}	Major cation in intercellular fluid in animals
K^+	Electron transfer
Ca^{2+}	Present in chlorophylls

(b) Identify the products of any *two* of the following reactions :

   (i) $I_2 + 3XeF_2 \xrightarrow{\text{Less than} -30\,°C} ?$

   (ii) $V(CO)_6 + NO \longrightarrow ?$

   (iii) $XeF_6 + NaNO_3 \longrightarrow ?$

   (iv) $XeF_4 + [N(CH_3)_4]F \longrightarrow ?$

   (v) $B_4H_{10} + 2NH_3 \longrightarrow ?$

(c) The solution of the Schrödinger equation for an electron in the ground state of the hydrogen atom is $\Psi_{1s} = \dfrac{1}{\sqrt{\pi a_0^3}} e^{\frac{-r}{a_0}}$, where r is the distance from the nucleus and a_0 is 0.529×10^{-8} cm. Find the maximum probability of finding the electron in $1s$ orbital of hydrogen.

(d) Distinguish between molecularity and order of a reaction with example. Nitrogen pentoxide decomposes to nitrogen dioxide and oxygen. Balance the equation and write the rate law. For a certain reaction, it takes 5 minutes for initial concentration of 0.5 molL^{-1} to become 0.25 molL^{-1}. What is the specific rate constant of the reaction?

(e) Derive Clausius-Clapeyron equation. Draw and explain the phase diagram of a pure substance.

(f) What is the difference between an isothermal process and an adiabatic process? Prove that $C_P - C_V = 2$ calories for 1 mole of an ideal gas.

(g) In a cell, one electrode is made of platinum over which hydrogen gas at 1 atm is bubbled and dipped in a solution of unkonwn pH, whereas the other electrode is made of silver metal immersed in 0.01 M solution of silver ion. What is the pH of the solution if the cell potential is 1.04 V?

6. Answer the following questions :

   (a) Answer the following questions : 20

      (i) What is Joule-Thomson effect? Prove that

      $$\mu_{J-T} = -\frac{\left(\partial H \big/ \partial P\right)}{C_P}$$

      (ii) Calculate the free energy change (ΔG) which occurs when $0 \cdot 5$ mole of an ideal gas expands reversibly and isothermally at $310\,K$ from an initial volume $50\,L$ to $909\,L$.

      (iii) Prove that maximum work obtained from a system other than that due to change in volume at constant temperature and pressure is decrease of free energy.

      (iv) Explain the importance of the following relation :

      $$\Delta S_{sys} + \Delta S_{sur} \geq 0$$

   (b) The d^2 ions CrO_4^{4-}, MnO_4^{3-}, FeO_4^{2-} and RuO_4^{2-} have been reported. 15

      (i) Which of these has the largest value of Δ_t ? Which has the smallest? Explain briefly.

      (ii) Of the first three, which ion has the shortest metal—oxygen bond distance? Explain briefly.

      (iii) The charge-transfer transitions for the first three complexes occur at $43,000$, $33,000$ and $21,000\ cm^{-1}$, respectively. Are these more likely to be ligand-to-metal or metal-to-ligand charge-transfer transitions? Explain briefly.

   (c) What are (i) critical solution temperature and (ii) partial molar quantities? Explain their significance. 15
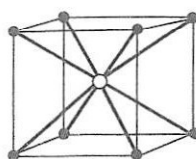
7. Answer the following questions :

   (a) Using the diagrams of unit cells shown below, count the number of atoms at each type of positions (corner, edge, face, internal) and each atom's fraction in the unit cell to determine the formulas $(M_m X_n)$ of the compounds represented. Open circles represent cations and closed circles represent anions. 20
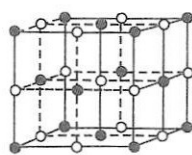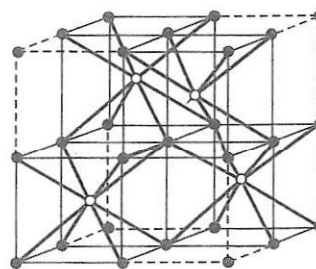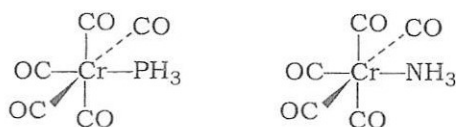

(i)   (ii)

(b) Discuss the working of an electrode concentration cell. What is fuel cell? Explain the principle of H_2–O_2 fuel cell.   15

(c) Explain the kinetics of chain reactions taking example of formation of HBr.   15

8. Answer the following questions :

(a) Describe the biological functions of hemoglobin and myoglobin.   20

(b) Certain changes occur when the following compounds are oxidized by one electron :

$$\begin{array}{cc}
\underset{\displaystyle\overset{|}{\underset{OC}{OC-Cr-PH_3}}}{\overset{CO\,.CO}{\diagup\diagup}} \qquad\qquad & \underset{\displaystyle\overset{|}{\underset{OC}{OC-Cr-NH_3}}}{\overset{CO\,.CO}{\diagup\diagup}}
\end{array}$$

  (i) When these compounds are oxidized, what is the effect on the C—O distance? Explain.

  (ii) When these compounds are oxidized, what are the effects on the Cr—P distance and the Cr—N distance? Explain.   15

(c) Mention the assumptions involved in derivation of Langmuir isotherm. Prove that $\theta = \dfrac{K_{pA}}{1 + K_{pA}}$ (symbols signify their usual meanings). What is the limitation of Langmuir's adsorption isotherm?   15

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