Indian Forest Services (Main)
Examination-2025

DJSM–U–CHMY

CHEMISTRY

PAPER—I

Time Allowed : Three Hours	Maximum Marks : 200

QUESTION PAPER SPECIFIC INSTRUCTIONS

Please read each of the following instructions carefully before attempting questions

There are EIGHT questions in all, out of which FIVE are to be attempted.

Question Nos. **1** and **5** are compulsory. Out of the remaining SIX questions, THREE are to be attempted selecting at least ONE question from each of the two Sections A and B.

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.

All questions carry equal marks. The number of marks carried by a question/part is indicated against it.

Unless otherwise mentioned, symbols and notations have their usual standard meanings.

Assume suitable data, if necessary, and indicate the same clearly.

Neat sketches may be drawn, wherever required.

Answers must be written in ENGLISH only.

Useful Constants :

$h = 6 \cdot 626 \times 10^{-34}$ J s

$k_B = 1 \cdot 38 \times 10^{-23}$ J K^{-1}

$R = 8 \cdot 314$ J K^{-1} mol^{-1}

$\pi = 3 \cdot 14$

$c = 3 \times 10^{8}$ m s^{-1}

$F = 96500$ C mol^{-1}

$N_A = 6 \cdot 023 \times 10^{23}$ mol^{-1}

1 atm = 101325 Pa

$m_e = 9 \cdot 1 \times 10^{-31}$ kg

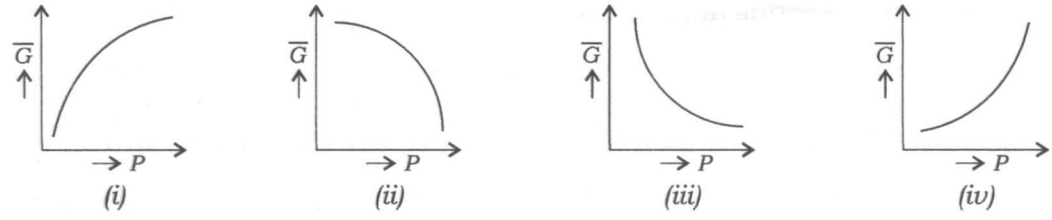
SECTION—A

1. *(a)* The observed nitrogen-oxygen bond length in nitrate ion is 1·21 Å. However, the calculated bond lengths for N—O and N = O bonds are 1·36 Å and 1·15 Å respectively. Account for this with requisite structures. 8

(b) In a cubic close-packed structure of a mixed oxide, the lattice is made up of oxide ions (O^{2-}), one-eighth of tetrahedral voids are occupied by divalent ions (A^{2+}), while one-half of octahedral voids are occupied by trivalent ions (B^{3+}). What is the formula of the oxide? 8

(c) The equilibrium pressure of $H_2(g)$ over solid uranium and uranium hydride, UH_3, at 500 K is very low and its value is 139 Pa. Calculate the standard Gibbs energy of formation of $UH_3(s)$ at 500 K and 1 atm. 8

(d) Select the figure below that illustrates the correct dependence of the molar Gibbs free energy, $\overline{G}$, on pressure P at constant temperature for a single solid component. Explain your choice :



8

(e) Draw and explain the shapes of steady-state current potential curves of the following systems with the same open-circuit potential and same diffusion limiting currents :

(i) A fast system

(ii) A slow system 8

2. *(a)* *(i)* Write down the time-independent Schrödinger equation for stationary states of hydrogen atom in spherical polar coordinates (r, θ, ϕ) considering origin at the nucleus of the atom and the proton to be stationary. Show pictorially the interrelation between the Cartesian and spherical polar coordinates. How are r, θ and ϕ called? 10

(ii) When a particle of mass $9 \cdot 1 \times 10^{-28}$ gram in a certain one-dimensional box goes from $n = 5$ level to $n = 2$ level, it emits a photon of frequency $6 \cdot 0 \times 10^{14}$ s^{-1}. Find the length of the box. [Given : $h = 6 \cdot 626 \times 10^{-27}$ erg s] 5

(b) (i) The average time gap between the excitation of an atom and consequent emission of a photon is 10^{-8} s. Calculate the uncertainty in the (1) energy measurement and (2) frequency determination. [Given : $h = 6 \cdot 626 \times 10^{-34}$ J s] 5

(ii) The energies (in kJ mol^{-1}) necessary to dissociate one O atom from different dioxygen species are reported as 642, 494, 394 and 210. Correlate these values with the species O_2^{2-}, O_2^{1-}, O_2 and O_2^{1+}. Explain in the light of molecular orbital theory. 10

(c) (i) Arrange the following molecules in the increasing order of their dipole moment values. Justify your answer : 5

$$NH_3, \quad NF_3, \quad H_2O$$

(ii) "B_2 has a bond order of one and it is paramagnetic." Substantiate the statement. 5

3. (a) (i) A certain solid crystallizes in the body-centered cubic lattice. The first-order X-ray ($\lambda = 0 \cdot 154$ nm) reflection maximum from a set of (2 0 0) planes was observed at 16·1°. Calculate the edge length of the unit cell.

[Given : $\sin 16 \cdot 1° = 0 \cdot 2773$] 5

(ii) Describe the unit cell structure of NaCl. Calculate the value of the Avogadro's constant from the following data :

Density of NaCl $= 2 \cdot 165$ gm cm^{-3}

Distance between Na^+ and Cl^- ions in NaCl = 281 picometre (pm)

Molar mass of NaCl $= 58 \cdot 5$ gm mol^{-1} 10

(b) (i) A balloon is filled with H_2 and O_2. Both the gases leak through pores in the balloon. If 45% of H_2 leaks, what is the ratio of O_2 / H_2 left in the balloon? 5

(ii) Calculate the change in entropy of n moles of an ideal gas that undergoes quasi-static processes a and b from an initial state (T_0, P_0, V_0) to final state (T_0, P_1, V_1). Then redo the calculation for n moles of gas making the change via process c.

a. Isobaric quasi-static expansion, (T_0, P_0, V_0) to (T_1, P_0, V_1)

b. Isochoric quasi-static heating, (T_1, P_0, V_1) to (T_0, P_1, V_1)

c. Isothermal expansion, (T_0, P_0, V_0) to (T_0, P_1, V_1)

What conclusion can you draw from your answer? 10

(c) A nitrogen nucleus spin can adopt any of three orientations in a magnetic field, and its energies are 0, $\pm \gamma_N \hbar B$, where γ_N is a magnetogyric ratio of the nucleus. Deduce an expression for partition function and mean energy of the nucleus, and sketch the variation of the functions with B. Calculate the relative populations of the spin states at 298 K, when $B = 20 \cdot 0$ T.

[Given : $\gamma_N \hbar = 2 \cdot 04 \times 10^{-27}$ J T^{-1}] 10

4. (a) (i) For water, $\Delta H_{\text{vaporization}}$ is 40·65 kJ mol^{-1} and the normal boiling point is 373·15 K. Calculate the boiling point for water on the top of a mountain of height 5500 m, where normal barometric pressure is 380 torr. 5

(ii) By what amount does the chemical potential of water exceed that of ice at –5·00 °C and 1 atm pressure?

[Given : $S^\circ_{H_2O,\, s} = 48 \cdot 0$ J mol^{-1} K^{-1} and $S^\circ_{H_2O,\, l} = 70 \cdot 0$ J mol^{-1} K^{-1}] 5

(b) (i) Draw the phase diagrams for the following types of systems :

(1) Two-component, temperature-composition, solid-liquid diagram, one compound of formula AB_2 that melts incongruently, negligible solid-solid solubility

(2) Two-component, constant temperature-composition, liquid-vapour diagram, formation of an azeotrope at $X_B = 0 \cdot 333$, complete miscibility

Label the regions and intersections of the diagrams, stating what materials (possibly compounds or azeotropes) are present and whether they are solid, liquid or gas. 5

(ii) An electrochemical cell is represented by

$$\text{Ag(s), AgBr(s)} \,|\, \text{KBr(aq)} \,||\, \text{Cd(NO}_3\text{)}_2 \text{ (aq., 0·01 } M\text{)} \,|\, \text{Cd(s)}$$

The standard potentials on the hydrogen scale of the pairs $Cd^{2+}|Cd$ and $AgBr|Ag$ are –0·40 V and +0·07 V respectively. At 25 °C, the potential of the cell is –0·62 V. Show that

$$\gamma_{C\pm,\, KBr} = \frac{0 \cdot 035}{C_{KBr}} \quad (\gamma_{C\pm} = \text{mean activity coefficient})$$

when the Debye-Hückel ion cloud model holds good. 10

(c) (i) Describe the functioning of (1) hydrogen-oxygen and (2) propane-oxygen fuel cells. What type of fuel cells is used in manned space flights? 10

(ii) The standard potential of $Zn^{2+}|Zn$ electrode is –0·76 V at 25 °C. The exchange current density for H^+ discharge at platinum is 0·79 mA cm^{-2}. Can Zn be plated on platinum at that temperature?

[Take unit activities and assume transfer coefficient, $\alpha = 0 \cdot 50$] 5

SECTION—B

5. *(a)* The following gas-phase reaction was studied at 290 °C by observing the change in pressure as a function of time in a constant volume vessel :

$$ClCO_2CCl_3(g) \longrightarrow 2COCl_2(g)$$

Determine the order of the reaction and rate constant based on the following data :

Time (s)	*P* (mmHg)
0	15·76
181	18·88
513	22·79
1164	27·08

where *P* is the total pressure.

[Use graph sheets] 8

(b) State the assumptions on which Langmuir's adsorption isotherm is based. Derive Langmuir's isotherm, $\theta = \frac{KP}{1+KP}$, where θ is the fraction of the total surface covered by the adsorbed molecules, *P* is the pressure of the gas and *K* is the adsorption coefficient. 8

(c) Discuss the bonding in $[Cr(NH_3)_6]Cl_3$ with the help of valence bond theory. What is the magnetic nature of the complex? 8

(d) Write the structure of $Co_2(CO)_8$. Explain how to differentiate between the terminal CO and bridging CO using IR spectrum. 8

(e) Predict the product(s) in the following reactions :

(i) $PbI_2 + KNH_2 \xrightarrow{\text{liq. } NH_3}$

(ii) $NaClO_4 + TlF \xrightarrow{\text{anhy. HF}}$

(iii) $C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4}$

(iv) $2KI + SOCl_2 \xrightarrow{\text{liq. } SO_2}$ 8

6. *(a)* *(i)* The decomposition of ozone, $2O_3(g) \rightarrow 3O_2(g)$, occurs by the reaction mechanism

$$M(g) + O_3(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2(g) + O(g) + M(g)$$

$$O(g) + O_3(g) \xrightarrow{k_2} 2O_2(g)$$

where M is a molecule that can exchange energy with the reacting ozone molecule through a collision but M itself does not react. Using this mechanism, derive the rate law expression for $\frac{d[O_3]}{dt}$ assuming that the intermediate, O(g), concentration can be treated by the steady-state approximation. 10

(ii) Distinguish between fluorescence and phosphorescence. Both fluorescent and phosphorescent radiations are of shorter frequencies than the exciting light. Why? 5

(b) *(i)* A first-order reaction has an activation energy of 104500 J mol^{-1} and the pre-exponential factor, A, in the Arrhenius equation has a value of $5 \cdot 0 \times 10^{13}$ s^{-1}. At what temperature will the reaction have a half-life of 1 minute?

[Given : $R = 8 \cdot 314$ J K^{-1} mol^{-1}] 10

(ii) What is heterogeneous catalysis? Explain giving one example. 5

(c) The photochemical reaction, $H_2(g) + Br_2(g) \xrightarrow{h\nu} 2HBr(g)$, follows the following mechanisms :

(i) $Br_2 + h\nu \xrightarrow{k_1} 2Br$

(ii) $Br + H_2 \xrightarrow{k_2} HBr + H$

(iii) $H + Br_2 \xrightarrow{k_3} HBr + Br$

(iv) $H + HBr \xrightarrow{k_4} H_2 + Br$

(v) $2Br \xrightarrow{k_5} Br_2$

Applying steady-state approximation to [Br] and [H], derive the expression for the rate of formation of HBr.

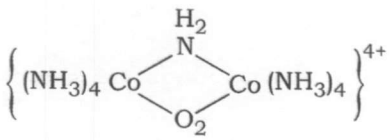
[Given : I_a is the intensity of the absorbed radiation.]

The quantum yield for this reaction is only 0·01. Why is the value so low? 10

7. *(a)* Explain the major steps involved in photosynthesis. List the significant role of Mg^{2+} in the above process. 15

(b) Write the IUPAC names of the following complexes :

(i) $[PtCl_2(NH_3)_4]\,[PtCl_4]$

(ii) 

(iii) $[Cr(PPh_3)(CO)_5]$

(iv) $[CoCl(ONO)(en)_2]^+$

(v) $[PtCl_4(NH_3)_2]$ 10

(c) *(i)* The low-spin $[Fe(CN)_6]^{4-}$ and the high-spin $[Fe(H_2O)_6]^{2+}$ are colourless. Justify your answer. 5

(ii) Draw the structure of geometrical isomers of the complex ion $[CrCl_2(ox)_2]^{3-}$. Can it exhibit optical isomerism? Justify your answer. 10

8. *(a)* *(i)* In $[Co_2(CO)_6\,(PhC{\equiv}CPh)]$, the acetylenic linkage (C — C) group lies above and right angles to the (Co — Co) vector. Write the structure and justify the bonding. 10

(ii) Alkene insertion is common for M—H bond but less common for M—R bond. Justify your answer. 5

(b) *(i)* Explain how the lanthanides are separated using valency change method. 5

(ii) The atomic (covalent) radii of the pairs of elements Zr–Hf, Nb–Ta, Mo–W, Ru–Os, Rh–Ir and Pd–Pt are almost same. Justify your answer. 10

(c) Justify the following :

(i) The conductivity of the solution decreases with increasing alkali metal concentration in liquid ammonia. 5

(ii) The colour of the alkali metal in liquid ammonia is independent of the metal involved. 5

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