Indian Forest Service (Main)
Examination, 2024

JBNV-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.*

*Questions No. **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.*

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

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

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

$\pi = 3{\cdot}14$

$c = 3 \times 10^{8}$ ms^{-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

Q1. (a) For a free particle, show how the time-independent Schrodinger equation gives a solution to explain de Broglie relation. *8*

(b) For a reaction *8*

$$H_2\,(g) + \frac{1}{2}\,O_2\,(g) \longrightarrow H_2O\,(g)$$

calculate standard entropy change of the reaction at 373 K, using data as below :

Given : S°_{298} for H_2O (g) = 188·825 J/K/mol

O_2 (g) = 205·138 J/K/mol

H_2 (g) = 130·684 J/K/mol

Molar heat capacities at constant pressure of

H_2O (g) = 33·58 J/K/mol

O_2 (g) = 29·37 J/K/mol

H_2 (g) = 28·84 J/K/mol

(c) An absorbing substance is exposed to a light of wavelength 400 nm using a 100 mW laser source for 50 minutes. The intensity of the transmitted light is 40% that of incident light. As a result, 0·4 mmol of the absorbing substance is decomposed. Determine the primary quantum yield of this photochemical reaction. *8*

(d) Equivalent quantities of NH_3 and HCl form a one-component system, but when slight excess of NH_3 or HCl is added, it becomes a two-component system. Explain. *8*

(e) In a galvanic cell, if $E^\circ_{Al^{3+}/Al}$ and $E^\circ_{Mg^{2+}/Mg}$ are – 1·66 and – 2·37 V respectively, calculate the standard free energy change for the cell reaction and also calculate the equilibrium constant for the cell reaction. *8*

Q2. (a) Determine the most probable radius at which electron will be found when it occupies 1s orbital of Li^{2+} ion. *10*

(b) Derive an expression to calculate the number of vacancies per mole of metal atoms at a given temperature. *15*

Assume the following :

(i) Contribution to entropy by vibration of atoms is small and can be neglected.

(ii) Use E_v as the energy required to create one mole of vacancy.

(c) The rate constant for the first-order decomposition of ethylene oxide into CH_4 and CO follows the equation :

$$\log k \text{ (in } s^{-1}) = 14{\cdot}34 - (1{\cdot}25 \times 10^4 \text{ K}) / T$$

Calculate :

(i) the activation energy of the reaction.

(ii) the rate constant at 700 K.

(iii) the frequency factor, A. *10*

(d) A metal M_1 can displace hydrogen but another metal M_2 can not. Metal M_2 can displace another metal M_3 from its salt solution. Arrange the metals M_1, M_2, M_3 in decreasing order of the E° values. Justify. *5*

Q3. (a) Explain the thermodynamic formulation of the activated complex theory for a simple bimolecular reaction. Draw energy profile diagram for an exothermic and an endothermic reaction. *15*

(b) Consider an atomic crystal where N atoms are situated at lattice sites. Assume all lattice sites are identical and each atom is vibrating with same frequency, as a three-dimensional harmonic oscillator.

The partition function that satisfies this model is given as :

$$Q = e^{-\beta U_0} \left(\frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} \right)^{3N}$$

$\nu \rightarrow$ characteristic frequency of vibration of the atoms

$U_0 \rightarrow$ Sublimation energy at 0 K.

$\beta \rightarrow \dfrac{1}{k_B T}$ where k_B is Boltzmann constant

Calculate the molar heat capacity of this atomic crystal from the given partition function at higher temperature. (Assume constant volume) *10*

(c) Consider a molecule 'A' in a solution undergoes the following steps when it absorbs UV light of intensity I_{abs}.

(i) $A + h\nu \xrightarrow{I_{abs}} A^*$

(ii) $A^* + A \xrightarrow{k_2} A_2$ (dimerization)

(iii) $A^* \xrightarrow{k_3} A + h\nu'$ (fluorescence)

(iv) $A_2 \xrightarrow{k_4} 2A$ (thermal decomposition)

Derive an expression for determining the concentration of A_2 at equilibrium, when the concentration of A is large. *10*

(d) Consider 'A' and 'B' are two metals with cubic unit cell. The powder XRD pattern of 'A' gives XRD lines corresponding to (110), (200), (220), (311), (400) and (331) planes, while the powder XRD pattern of 'B' gives XRD lines corresponding to the planes of (110), (200), (211), (220), (301) and (222). Comment on the type of space lattice in 'A' and 'B', and justify. What fraction of space in the unit cell of 'A' is available for tightest possible packing of its atoms ? *5*

Q4. (a) Draw the phase diagram of lead-silver system. Explain its significance in desilverization of lead. *15*

(b) Calculate the mean ionic activity coefficient $\gamma_{\pm}$ of (i) NaCl at a molality of 0·01, and (ii) Na_2SO_4 at a molality of 0·001 in aqueous solution at 25°C. *15*

(c) What is the meaning of isotherm ? Write BET equation and explain how specific surface area of a solid is determined. *10*

SECTION B

Q5. (a) Explain why LiF is less soluble than LiI in water. Using your explanation, state, between CsF and CsI, which one would be more soluble in water. *8*

(b) Draw the structures of possible diastereoisomers of

$[Co(NH_3)_2\ (H_2O)_2\ Cl_2]Cl$. Among these isomer(s), which is/are optically active ? *8*

(c) Predict the structure of $Co(CO)_8$ with the help of 18-electron rule. What differences do you expect in the C = O stretching frequency(ies) between $Co(CO)_8$ and $Mn(CO)_{10}$? Explain.
[Atomic number of Mn = 25; Co = 27] *8*

(d) Explain how 'Relativistic effect' contributes in 'Lanthanide contraction'. *8*

(e) Write down the chemical equation for nitrogen fixation by nitrogenase enzyme. Discussing the thermodynamic and kinetic aspects of the reduction of N_2, state why nitrogen fixation requires an enzyme. *8*

Q6. (a) (i) Showing the crystal field splitting, calculate the spin only magnetic moment of $[CoCl_4]^{2-}$ and $[Co(H_2O)_6]^{2+}$.

(ii) The experimentally observed magnetic moment of which of these two species would deviate more from the calculated spin only value ? Explain your answer.

(iii) Colour of which of these two species would be less intense ? Explain your answer. *5+5+5=15*

(b) (i) State the changes that occur in Hemoglobin molecule on oxygenation.

(ii) What is 'blue baby syndrome' ? Why does it occur ?

(iii) What do you understand by 'Haldane effect' in relation to oxygen-uptake proteins ? *7+4+4=15*

(c) Predict the product(s) in the following reactions : *5×2=10*

(i) $RCO_2H + HF \text{ (liquid)} \longrightarrow$

(ii) $BF_3 + HF \text{ (liquid)} \longrightarrow$

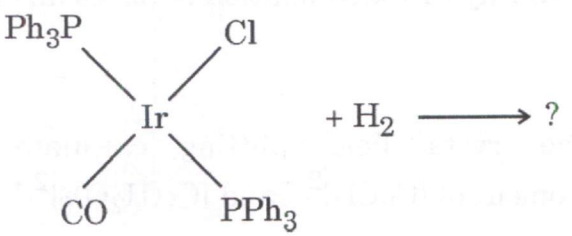
(iii) $[Pt(NH_3)_4]^{2+} + Na \xrightarrow{\text{in liquid } NH_3}$

(iv) $SO_3 + H_2SO_4 \text{ (liquid)} \longrightarrow$

(v) $Cl_2 + NH_3 \text{ (liquid)} \longrightarrow$

Q7. (a) N_2 and CO are isoelectronic but their Molecular Orbitals (MOs) are different from each other. Drawing the MOs of both the molecules, state with reasons the differences of these two MOs and their coordinating ability. *15*

(b) (i) Write the product of the following reaction :



Explain the 'coordinative unsaturation' and 'oxidative addition' in the above reaction. *5*

(ii) Explain how the fluxional behaviour of the molecule

$[(\eta^1 - C_5H_5)_2 (\eta^5 - C_5H_5)_2 Ti]$ can be characterised. *10*

(c) Explain why 2+ oxidation state is stabilized in Eu (At. No. 63). With the help of your explanation, predict among Ce (At. No. 58), Tb (At. No. 65) and Sm (At. No. 62), which one is most likely to show 2+ oxidation state. *10*

Q8. (a) Calculate the temperature at which the average velocity of oxygen equals to that of hydrogen at 20 K. *10*

(b) Using critical constants P_c , V_c and T_c for a real gas that satisfies van der Waals equation, find the critical compression factor of the gas near critical point. *10*

(c) Among Ne and Ar, under similar conditions, whose standard molar entropy is larger ? Explain.
Assume both Ne and Ar are perfect gases. *10*

(d) Why is yellow colour observed, when sodium chloride is heated in sodium vapour ? *10*