Indian Forest Service
(Main) Exam, 2020

JKLO–U–CHM

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.

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.

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.

Answers must be written in ENGLISH only.

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

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

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

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

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

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

$\pi = 3{\cdot}14$

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

1 atm = 101325 Pa

SECTION—A

1. *(a)* *(i)* Why is crystallization of solute a spontaneous process?

(ii) Consider a 1·00 kg block of iron at 99 °C placed in contact with a 1·00 kg block of iron at 25 °C. Find the final temperature of the blocks and the amount of heat transferred. For iron, $C_p = 444$ J/K/kg 8

(b) The O—O bond distances in O_2, O_2^- and O_2^{2-} are found respectively to be 1·21 Å, 1·28 Å and 1·49 Å. Justify in the light of molecular orbital energy level diagram. 8

(c) Cesium chloride (CsCl) crystal has a cubic structure in which Cs^+ ions occupy the centre position of a unit cell and its corner positions are occupied by all Cl^- ions. If the ionic radii of Cs^+ ion and Cl^- ion are 0·169 nm and 0·181 nm, respectively, compute the lattice parameter, a. 8

(d) State the factors contributing to liquid junction potential. Suggest ways to minimize it. 8

(e) How is the smoke in horror films made? Explain it with the help of phase diagram also. 8

2. *(a)* Astronomers have suggested that intergalactic space contains hydrogen atoms at a temperature of $7{\cdot}8\times10^5$ K, with about 1 atom per 100 dm^3.

(i) Calculate the mean free path of a hydrogen atom in the intergalactic space.

(ii) Calculate the approximate average time in years, between collisions of an atom.

Assume that the collision diameter of a hydrogen atom is 200 pm. 15

(b) Obtain an expression of wave function for the ground state and first excited state for a particle confined in a one-dimensional box of length L with infinitely hard walls between $x = -\frac{L}{2}$ to $x = +\frac{L}{2}$. 15

(c) Discuss concisely the types of electrokinetic phenomena. 10

3. *(a)* Calculate q, w and ΔU at 1·00 bar for the phase transition between two crystalline forms, s-I and s-II of Li_2SO_4

$$Li_2SO_4 \text{ (s-II)} \rightarrow Li_2SO_4 \text{ (s-I)}$$

which takes place at 859 K. The enthalpy change is 27·2 kJ for this reaction. The densities of Li_2SO_4 (s-II) and Li_2SO_4 (s-I) are $2{\cdot}221\times10^3$ kg m^{-3} and $2{\cdot}07\times10^3$ kg m^{-3}, respectively. Given, the molecular weight of Li_2SO_4 = 110 g/mol. 15

(b) (i) Why does deflating the tyres on a car improve its road-holding on ice? 5

(ii) Compare the phase diagrams in Figure 1 and Figure 2, and comment briefly :

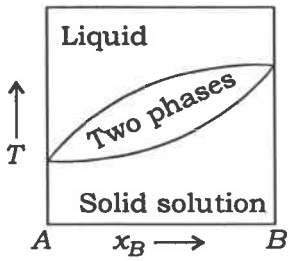

Figure 1

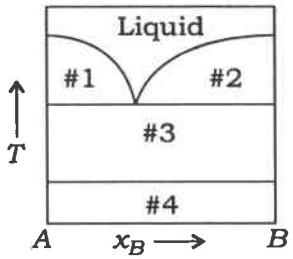

Figure 2

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(c) For an unknown cubic metal, the diffracting angles (θ), obtained with Cu K_α radiation ($\lambda = 1{\cdot}541$ Å) are 20·1°, 29·2°, 36·6°, 43·5°, 50·2°, 57·4°, 65·5°. Identify whether the metal is simple cubic, body centred or face centred. Determine the lattice constant a for this metal. Given—

$\sin(20{\cdot}1°) = 0{\cdot}344$
$\sin(29{\cdot}2°) = 0{\cdot}488$
$\sin(36{\cdot}6°) = 0{\cdot}596$
$\sin(43{\cdot}5°) = 0{\cdot}688$
$\sin(50{\cdot}2°) = 0{\cdot}768$
$\sin(57{\cdot}4°) = 0{\cdot}842$
$\sin(65{\cdot}5°) = 0{\cdot}910$

15

4. (a) Assume that impure copper contains only iron, silver and gold as impurities. After passage of 140 A of current for 482·5 seconds, the mass of the anode decreases by 22·260 g and the cathode increased in mass by 22·011 g. Estimate the iron and copper originally present in percentage. 10

(b) What is the Born-Haber cycle? Construct the Born-Haber cycle of NaCl mentioning the names of the various parameters involved in it. 15

(c) (i) The total energy eigenvalues for the hydrogen atom are given by

$$E_n = \frac{-e^2}{8\pi\varepsilon_0 a_0 n^2}$$

List all the eigenfunctions that have the following total energy eigenvalue :

$$E = \frac{-e^2}{72\pi\varepsilon_0 a_0}$$

What is the degeneracy of energy level? 10

(ii) An atom exists in an excited state for about $\Delta t = 10^{-8}$ second. Estimate the uncertainty, Δf in the frequency of emitted photons when an atom makes a transition from an excited state with the emission of photon. 5

SECTION—B

5. *(a)* Considering the reaction $AB + CD \rightarrow AC + BD$, determine the rate expression for the following condition :

A plot of $[AB]$ versus time is a straight line whenever $[CD]$ is held very high and nearly constant. A plot of $\frac{1}{[CD]}$ versus time is a straight line. 8

(b) What is Zeise's salt? Discuss its structure. 8

(c) The absorption spectral bands of trivalent lanthanide ions are very sharp and are not affected by complexing agents appreciably. Explain why. 8

(d) What is a nitrogenase? Show the mechanism of nitrogen fixation pathway catalyzed by nitrogenase. 8

(e) Provide the steps involved in fluid-phase reactions on a solid and identify the rate-determining step. 8

6. *(a)* The rate constant for a certain second-order reaction is $8{\cdot}00 \times 10^{-5}\ M^{-1}\ min^{-1}$. How long will it take a 1·00 M solution to be reduced to 0·500 M in reactant? How long will it take from that point until the solution is 0·250 M in reactant? Explain why half-life is not used often for second-order reactions. 15

(b) What are ferredoxins? Draw the active site structures of 2Fe–2S and 4Fe–4S ferredoxins. Mention their functions. 15

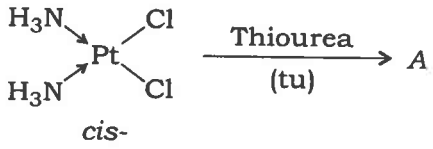
(c) Electrical conductivity of solutions of alkali metals in liquid ammonia initially decreases with increase in concentration of the metal but again increases at higher concentration. Explain why. 10

7. *(a)* Discuss the formation of $[CoF_6]^{3-}$ and $[Co(CN)_6]^{3-}$ complex ions. Comment on their magnetic moment. [Z for Co = 27] 15

(b) Mention the important oxidation states of lanthanides. How would you account for them? 15

(c) When propionaldehyde is irradiated with light λ of 3020 Å, it decomposes to form carbon monoxide. The quantum yield for the reaction is 0·54. The light energy absorbed is 15000 erg mol^{-1} in a given time. Find the amount of carbon monoxide formed in moles in the same time. 10

8. *(a)* *(i)*



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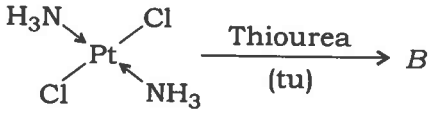

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Identify *A* and *B*, and explain your answer. 8

(ii) Show all the possible isomers of $[Co(en)_2Cl_2]Cl$ and mention their categories of isomerism. [en ≡ ethylenediamine] 7

(b) Addition of K_2SO_3 to a solution of $AlCl_3$ in liquid SO_2 forms a white precipitate which dissolves in excess K_2SO_3. The precipitate reappears on adding $SOCl_2$. Elucidate the results with necessary equations. 10

(c) *(i)* What is the basis of collision model describing the kinetics of chemical reactions? How is the rate affected by each of the following?

(1) Activation energy

(2) Temperature

(3) Frequency of collisions

(4) Orientation of collisions 10

(ii) Among the following reactions, which one will proceed at a faster rate at room temperature? Justify your answer :

$$2Ce^{4+}(aq) + Hg_2^{2+}(aq) \rightarrow 2Ce^{3+}(aq) + 2Hg^{2+}(aq)$$

$$H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l)$$ 5

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