

INDIAN FOREST SERVICE EXAMINATION
UPSC - INDIAN FOREST SERVICE - 2014

C-HENT-N-BGDLA

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 chronological 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 Answer Book must be clearly struck off.

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

Answers must be written in **ENGLISH** only.

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.

SECTION—A

$$(h = 6.626 \times 10^{-34} \text{ JS}; k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}; R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}; \pi = 3.14;$$
$$R_H = 10973731.6 \text{ m}^{-1}; c = 3 \times 10^8 \text{ ms}^{-1})$$

Q. 1. Answer briefly all the parts :

10×4=40

Q. 1(a) A Phase Rule can be written as $F = C - P + 2$, where F is the number of degrees of freedom, P is the number of phases and C is the number of components.

(i) Define the terms *degree of freedom*, *phase* and *component*.

(ii) Use the Phase Rule to show why, when plotting a phase diagram of a 2-component system, it is necessary to fix a variable (usually volume). 6,4

Q. 1(b) What is meant by the lattice energy of an ionic compound ? What quantities need to be determined and how are they used to calculate the lattice energy of an ionic compound ?

10

Q. 1(c) The BF molecule is isoelectronic with carbon monoxide.

- (i) Construct an MO diagram for the BF molecule. What assumption can be made in BF which makes 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 bonds and nonbonding orbitals. What possible Lewis structures can be drawn for BF and CO and which is the most reasonable for each species based on your diagrams ?

5,5

Q. 1(d) Explain the following observations on the basis of the kinetic theory of gases :

- (i) When NH_3 gas is introduced at one end of a long tube while HCl gas is introduced simultaneously at the other end, a ring of white ammonium chloride is observed to form in the tube after a few minutes. This ring is closer to the HCl end of the tube than the NH_3 end.
- (ii) "Nitrogen gas gets cooled on expansion at room-temperature whereas hydrogen gas gets warmer." Explain.

5,5

Q. 2(a) Heisenberg's Uncertainty Principle (HUP), as applied to the position, x , and momentum, p , of a particle can be given mathematically as :

$$\Delta x \Delta p \geq h/4\pi$$

- (i) Define the symbols Δx and Δp .
- (ii) Give an alternative non-mathematical statement of HUP.
- (iii) For a particle trapped in a one-dimensional box of length L , the maximum value of Δx is L . Calculate the minimum value of Δp for an electron trapped in a linear molecule of length $L = 3 \times 10^{-9}$ m, and clearly state the units.
- (iv) Starting from the de Broglie relation, $\lambda = h/p$, show that the propagation of errors implies that

$$\Delta \lambda = h \Delta p / p^2 = \lambda^2 \Delta p / h,$$

and hence calculate the uncertainty in the wavelength of the electron in (iv) assuming that the wavelength $\lambda = 2L$. Comment on your answer.

4,4,6,6

Q. 2(b) A certain line in the spectrum of atomic hydrogen is associated with the electronic transition of the H atom from the sixth energy level ($n = 6$) to the second energy level ($n = 2$).

- (i) Indicate whether the H atom emits energy or absorbs energy during the transition. Justify your answer.
- (ii) Calculate the wavelength, in nm, of the radiation associated with the spectral line.
- (iii) Account for the observation that the amount of energy associated with the same electronic transition ($n = 6$ to $n = 2$) in the He^+ ion is greater than that associated with the corresponding transition in the H atom.

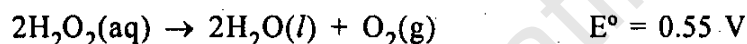
5,10,5

Q. 3(a) Match the following rotational temperatures $\Theta_{\text{rot}} = 0.164 \text{ K}, 0.082 \text{ K}, 9.12 \text{ K}, 0.0154 \text{ K}$ to the four molecules ICl, HI, I₂ and IBr. Assign the order of increasing rotational partition function for the four molecules at 100 K. Explain your reasoning. 20

Q. 3(b) Five identical balloons are each filled to the same volume at 25°C and 1.0 atmosphere pressure with the pure gases CO₂, O₂, He, N₂ and CH₄.

- Which balloon contains the greatest mass of gas? Explain.
- Compare the average kinetic energies of the gas molecules in the balloons. Explain.
- Which balloon contains the gas that would be expected to deviate most from the behaviour of an ideal gas? Explain.
- Twelve hours after being filled, all the balloons have decreased in size. Predict which balloon will be the smallest. Explain your reasoning. 5,5,5,5

Q. 4(a) At 25°C, H₂O₂ decomposes according to the following equation :



- What is meant by the standard electrode potential and how is it measured?
- Determine the value of the standard Gibbs energy change, ΔG° , for the reaction at 25°C.
- Determine the value of the equilibrium constant, K_{eq} , for the reaction at 25°C.
- The standard reduction potential, E° , for the half reaction $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$ has a value of 1.23 V. Using this information in addition to the information given above, determine the value of the standard reduction potential, E° , for the half reaction below :



Q. 4(b) (i) Why is it usually a poor approximation to equate activities and concentrations for ionic solutions?

- Outline the Debye-Hückel theory of dilute ionic solutions. Why is the central result of this theory described as a *limiting law*?
- When and why can Debye-Hückel theory fail to describe the behaviour of ionic solutions accurately? 5,10,5

SECTION—B

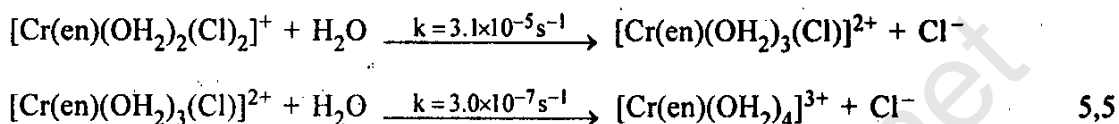
Q. 5(a) Account for each of the following observations :

- The complex $[\text{NiCl}_4]^{2-}$ is attracted towards a magnetic field.
- $[\text{PtCl}_2(\text{NH}_3)_2]$ has two isomers. 5,5

Q. 5(b) In the reaction $[\text{CoCl}_2(\text{NH}_3)_4]^+ + \text{Cl}^- \rightarrow [\text{CoCl}_3(\text{NH}_3)_3] + \text{NH}_3$, only one isomer of the complex product is obtained. Is the initial complex *cis* or *trans*? Explain your answer.

10

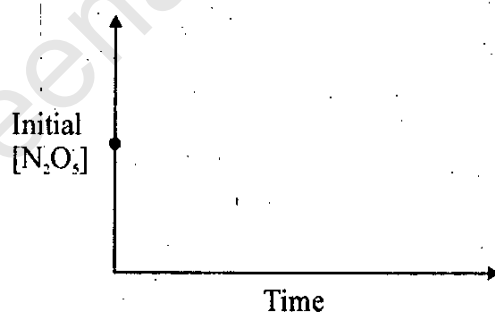
Q. 5(c) Based on the rate constants given, indicate if the stepwise substitution reaction shown below proceeds *via* an associative or dissociative mechanism. Explain your answer.



Q. 5(d) Explain why f-f transitions in the electronic spectra of lanthanide complexes are weaker than d-d transitions in the corresponding spectra of transition metal complexes. 10

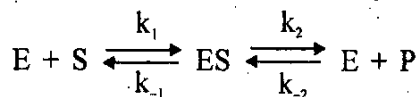
Q. 6(a) The reaction $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ is first order with respect to N_2O_5 .

- Using the axes below, complete the graph that represents the change in $[\text{N}_2\text{O}_5]$ over time as the reaction proceeds.
- Describe how the graph in part (i) could be used to find the reaction rate at a given time, t .
- Considering the rate law and the graph in part (i), describe how the value of the rate constant, k , could be determined.
- If more N_2O_5 were added to the reaction mixture at constant temperature, what would be the effect on the rate constant, k ? Explain.



5,5,5,5

Q. 6(b) The reaction catalyzed by an enzyme recently purified from *E. coli* is shown below :



- Derive the *Steady State* rate equation for the above reaction in the forward direction. Assume initial rate conditions (i.e. $[\text{P}]_{t=0} = 0$). Show all of your work and the necessary assumptions and equations.
- Under what circumstances the kinetics are :
 - First-order in substrate concentration
 - Zero-order in substrate concentration ?

10,10

Q. 7(a) For the complex $[\text{CoCl}_4]^{2-}$:

- (i) Draw a diagram to show the energy splitting of the 3d orbitals, indicating appropriate symmetry labels for the orbitals, the occupancy of the orbitals with electrons, and the crystal field splitting parameter. 15,5
- (ii) Calculate the crystal-field stabilization energy in multiples of the crystal-field splitting parameter. 15,5

Q. 7(b) (i) Give reasons why complexes of second and third row transition metals typically show a larger ligand field splitting than complexes of first row transition metals.

- (ii) Explain the ways in which increased ligand-field splitting for second and third row transition metals affects the geometry of four-coordinate Pt(II) complexes compared with the geometry of four-coordinate Ni(II) complexes. 10,10

Q. 8(a) Write brief notes on the following :

- (i) Ferredoxins
- (ii) Super-acids. 10,10

Q. 8(b) (i) Compare the solvent behaviour of water and liquid ammonia. How does ammonium hydroxide behave in liquid ammonia ?

- (ii) The relaxation-time for a reversible first-order reaction is 1×10^{-5} s, and the equilibrium constant is 1×10^3 . Find K_1 and K_{-1} . 10,10