Combined Geo-Scientist
(Main) Exam,2021

SDT-F-CHE

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 **ELEVEN** questions divided under **SIX** sections.*

*Candidate has to attempt **SIX** questions in all.*

*The **ONLY** question in Section **A** is **compulsory**.*

*Out of the remaining **TEN** questions, the candidate has to attempt **FIVE,** choosing **ONE** from each of the other Sections **B, C, D, E** and **F**.*

The number of marks carried by a question / part is indicated against it.

Neat sketches are to be drawn to illustrate answers, wherever required. These shall be drawn in the space provided for answering the question itself.

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

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

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.*

SECTION A

Answer all of the following : *5×10=50*

Q1. (a) Explain why aluminophosphate forms quartz-like structure. *5*

(b) The stepwise formation constants for the complexes of NH_3 with $\left[Cu(OH_2)_6\right]^{2+}_{(aq)}$ are log K_{f_1} = 4·15, log K_{f_2} = 3·50, log K_{f_3} = 2·89, log K_{f_4} = 2·13, and log K_{f_5} = – 0·52. Why is K_{f_5} so different ? *5*

(c) Both H^- and $P(C_6H_5)_3$ are ligands of similar field strength, high in spectrochemical series. Discuss the orbital factors that account for the field strength of each ligand. *5*

(d) Why is methyl orange not a suitable indicator for titration of a strong base against a weak acid ? *5*

(e) Explain how post-precipitation differs from co-precipitation. *5*

(f) Explain the role of $HgCl_2$ in the volumetric determination of iron using potassium dichromate. *5*

(g) Explain the role of chelating agents in complexometric titrations. *5*

(h) Arrange the following metal carbonyls in the increasing order of their increasing C – O bond strength giving reason : *5*

$[Cr(CO)_6]$

$[Mn(CO)_6]^+$

$[V(CO)_6]^-$

(i) Complete the following nuclear reactions by giving the value of X : *5*

(i) $^{14}_{7}N + {}^{4}_{2}He \longrightarrow X + {}^{1}_{1}H$

(ii) $X + {}^{4}_{2}He \longrightarrow {}^{30}_{15}P + {}^{1}_{0}n$

(iii) $^{23}_{11}Na + X \longrightarrow {}^{23}_{12}Mg + {}^{1}_{0}n$

(iv) $^{113}_{48}Cd + X \longrightarrow {}^{114}_{48}Cd + \text{energy}$

(v) $X \longrightarrow {}^{0}_{-1}e + {}^{232}_{91}Pa$

(j) Why does the μ_{eff} value for transition metal ions with ground state term S agree well with $\mu_{s.o.}$ value while it differs with metal ions having ground state term as D or F ? Explain with reason. *5*

SECTION B

Attempt any *one* question :

Q2. (a) Sketch the unit cell of ReO_3 and determine (i) the coordination number of Re and O, and (ii) the identity of the structure type that would be generated if a cation is inserted in the centre of each ReO_3 unit cell. *10*

(b) Would gallium arsenide be a suitable compound for a semiconductor ? How could n- and p-type semiconductors be designed from it ? *10*

(c) (i) The compound Fe_xO generally has $x < 1$. Describe the probable metal ion defect that leads to x being less than 1. *5*

(ii) Identify the product of the following : *5*

(I) $BaCO_3\,(s) + TiO_2\,(s) \xrightarrow{1000°C}$

(II) $ZrO_2\,(s) + 2H_3PO_4\,(l) \longrightarrow$

(III) $3KF\,(aq) + MnBr_2\,(aq) \longrightarrow$

Q3. (a) Explain the magnetic properties of the following coordination compounds using Crystal Field Theory : *5*

(i) $[Co(NH_3)_6]^{3+}$

(ii) $[Co(en)_3]^{3+}$

(iii) $[Co(NO_2)_6]^{3-}$

(iv) $[CoF_6]^{3-}$

(v) $[Co(H_2O)_3F_3]^{3-}$

(b) Why are the chemical properties of d-block elements seemingly erratic and irregular as compared to homogeneous chemical properties of lanthanides ? *10*

(c) Why are the electronic spectra of lanthanides sharper as compared to transition metal complexes ? Explain by giving suitable reason(s). *15*

SECTION C

Attempt any *one* question :

Q4. (a) An approximately 'octahedral' complex of Co(III) with ammine and chlorido ligands gives two bands with ε_{max} between 60 and 80 $dm^3\ mol^{-1}\ cm^{-1}$, one weak peak with $\varepsilon_{max} = 2\ dm^3\ mol^{-1}\ cm^{-1}$ and a strong band at higher energy with $\varepsilon_{max} = 2 \times 10^4\ dm^3\ mol^{-1}\ cm^{-1}$. What do you suggest for the origin of these transitions ? *15*

(b) (i) Given that only the split between the top two energy levels of a square planar field can give rise to high and low-spin states, what number of d electrons, d^n, would have both possibilities ? Explain your answer. *10*

(ii) Consider the following cyanide complexes :

$[Ni(CN)_4]^{2-}$, $[Mn(CN)_6]^{3-}$, $[Cr(CN)_6]^{3-}$

Write the order of their lability. Justify your answer. *5*

Q5. (a) Bearing in mind the Jahn-Teller effect, predict the structure of $[Cr(H_2O)_6]^{2+}$. *10*

(b) Predict the product and explain its formation in the following reactions : *10*

(i) $[Pt(PR_3)_4]^{2+} + 2Cl^- \longrightarrow$

(ii) $[PtCl_4]^{2-} + 2PR_3 \longrightarrow$

(iii) *cis* – $[Pt(NH_3)_2(py)_2]^{2+} + 2Cl^- \longrightarrow$

(c) The equilibrium constants for the successive reactions of 1,2-diaminoethane with Co^{2+}, Ni^{2+} and Cu^{2+} are as follows :

$[M(OH_2)_6]^{2+} + en \rightleftharpoons [M(en)(OH_2)_4]^{2+} + 2H_2O \quad K_1$

$[M(en)(OH_2)_4]^{2+} + en \rightleftharpoons [M(en)_2(OH_2)_2]^{2+} + 2H_2O \quad K_2$

$[M(en)_2(OH_2)_2]^{2+} + en \rightleftharpoons [M(en)_3]^{2+} + 2H_2O \quad K_3$

Ion	$\log K_1$	$\log K_2$	$\log K_3$
Co^{2+}	5·89	4·83	3·10
Ni^{2+}	7·52	6·28	4·26
Cu^{2+}	10·72	9·31	– 1·0

(i) What does the above data inform about successive formation constants ?

(ii) How do you account for very low value of K_3 for Cu^{2+} ? *10*

SECTION D

Attempt any *one* question :

Q6. (a) Find out the volume in mL of 0·1 N HCl solution required to react completely with 1·0 g of a mixture of Na_2CO_3 and $NaHCO_3$ containing equimolar amounts of two components. *10*

(b) Methyl red has $K_a = 10^{-5}$. The acid form HIn is red and its conjugate base, $In^{\ominus}$ is yellow. Complete the following table : *10*

pH	3	5	7
$[In^{\ominus}] / [HIn]$	–	–	–
Colour	–	–	–

(c) Sketch the general appearance of the curve for the titration of a weak diprotic base with strong acid. Explain different regions of the curve. *10*

Q7. (a) What are redox titrations ? Explain the various types of redox titrations with examples. *15*

(b) Give reasons for the following : *15*

(i) Starch solution is added near the end point in iodometry titrations.

(ii) Why is hot solution titrated against $KMnO_4$ solution ?

(iii) Potassium iodide is added in iodometric titration.

SECTION E

Attempt any *one* question :

Q8. (a) Explain the complexometric titration curve for the titration of EDTA vs. M^{n+} ion solution. *15*

(b) Explain the principle in the determination of Mn-Mg-Zn mixture using complexometric titration. *15*

Q9. (a) (i) What peculiarities does the Wilkinson's catalyst have that it behaves as a catalyst ? *5*

(ii) Explain the mechanism for hydrogenation of alkene by Wilkinson's catalyst. *10*

(b) How would you account for metal-metal bonding in $[Re_2Cl_8]^{2-}$ with the help of MO approach ? *15*

SECTION F

Attempt any *one* question :

Q10. (a) What are the common possible nuclear fission reactions in case of $^{235}_{92}U$ when a slow neutron enters the uranium nucleus ? *5*

(b) What is radioactive displacement law ? Illustrate the radioactive displacements by referring to the four radioactive decay series. *15*

(c) What do you understand by Alpha Decay ? Explain by giving suitable examples. *10*

Q11. (a) Explain the general methods to avoid the supersaturation during precipitation in gravimetric estimation. *10*

(b) Explain the term peptisation with suitable example. *10*

(c) A very large excess of the precipitating agent is avoided in quantitative analysis. Justify. *5*

(d) Explain the effect of temperature on the solubility of a precipitate in gravimetric estimation. *5*

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SDT-S-CHE

CHEMISTRY

Paper – II

*Time Allowed : **Three** Hours*

*Maximum Marks : **200***

Question Paper Specific Instructions

Please read each of the following instructions carefully before attempting questions :

*There are **FIFTEEN** questions divided under **THREE** sections.*

*Candidate has to attempt **TEN** questions in all.*

*The **ONLY** question in Section **A** is **compulsory**. In Section **B**, **SIX** out of **NINE** questions are to be attempted. In Section **C**, **THREE** out of **FIVE** questions are to be attempted.*

The number of marks carried by a question / part is indicated against it.

Neat sketches are to be drawn to illustrate answers, wherever required. These shall be drawn in the space provided for answering the question itself.

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Some useful fundamental constants and conversion factors

$N_A = 6{\cdot}022 \times 10^{23}\ \text{mol}^{-1}$

Rydberg constant $= 2{\cdot}178 \times 10^{-18}$ J

$c = 2{\cdot}998 \times 10^{8}\ \text{ms}^{-1}$

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

$e = 1{\cdot}602 \times 10^{-19}$ C

$m_e = 9{\cdot}109 \times 10^{-31}$ kg

$F = 96485\ \text{C mol}^{-1}$

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

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

$\pi = 3{\cdot}142$

1 amu $= 1{\cdot}66 \times 10^{-27}$ kg

1 cal $= 4{\cdot}184$ J

$1\ \text{J} = 1\ \text{kg m}^2\ \text{s}^{-2}$

1 Å $= 10^{-8}$ cm $= 10^{-10}$ m $= 0{\cdot}1$ nm $= 100$ pm

1 atm $= 760$ torr $= 1{\cdot}01325 \times 10^{5}$ Pa

1 bar $= 1 \times 10^{5}$ Pa $= 0{\cdot}9869$ atm

1 eV $= 1{\cdot}602 \times 10^{-19}$ J

1 L atm $= 101{\cdot}34$ J

1 eV $= 23060$ cal

SECTION A

Q1. Answer all of the following questions : *5×16=80*

(a) Explain the conditions under which real gases show the ideal behaviour. *5*

(b) Define compressibility factor (Z). Describe Z vs. P plots with a suitable example. *5*

(c) A compound formed by elements X and Y crystallizes in the cubic structure. X atoms are situated at the corners and Y atoms are at the centre of faces. What is the formula of the compound ? *5*

(d) The data on the unit cell are given below. Identify the crystal system in each case. *5*

(i) $a = b \neq c$ $\alpha = \beta = \gamma = 90°$

(ii) $a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$

(iii) $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90°$

(iv) $a = b \neq c$ $\alpha = \beta = 90°, \gamma = 120°$

(v) $a = b = c$ $\alpha = \beta = \gamma = 90°$

(e) Explain the electrophoretic effect in Debye-Hückel-Onsager theory of strong electrolytes. *5*

(f) Explain the terms : activity and activity coefficient. Write their units and magnitudes. *5*

(g) Why is a finely powdered substance a more effective adsorbent ? *5*

(h) Show that the half-life period of a first order reaction is independent of initial concentration of the reactant. *5*

(i) What is the role of phosphoric acid in the volumetric titration of Fe^{2+} ions and $Cr_2O_7^{2-}$ ions when diphenylamine is used as internal indicator ? *5*

(j) Why can a voltmeter not be used for determining the EMF of a galvanic cell ? *5*

(k) What are well-behaved functions ? Which of the following functions are well-behaved ? 5

(i) $\phi(x) = e^{-\alpha x}$ $(\alpha > 0)$ $0 < x < \alpha$

(ii) $\phi(x) = \dfrac{1}{4 - x}$ $1 < x < 10$

(l) Suppose that the uncertainty in determining the position of an electron in an atom is 0·4 Å. What will be the uncertainty in its velocity ? 5

(m) Which of the following molecules are microwave active ? Why ? 5

C_2H_2, CH_3Cl, C_6H_6, CO_2

(n) Which of the following molecules has the highest fundamental frequency of vibration ? Explain. 5

H_2, D_2, HD

(o) What are photosensitized reactions ? Explain with examples. 5

(p) Calculate the energy in ergs, calories and electron volts in ultraviolet light of wavelength 2500 Å absorbed per mole. 5

SECTION B

Attempt any *six* questions : ***10×6=60***

Q2. What is the virial equation of state ? Derive the expression for the second virial coefficient from Van der Waals equation. *10*

Q3. The first order reflections from the 100, 110 and 111 planes of a given cubic crystal were found to occur at angles 5·9°, 8·4° and 5·2° respectively. Determine the type of crystal lattice to which the crystal belongs. *10*

Q4. For a component in a homogeneous mixture, the chemical potential is given as

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{\substack{T,P,n_{js} \\ j\neq i}}$$

Show that μ_i may be expressed in the following equivalent terms : *10*

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{\substack{T,P,n_{js} \\ j\neq i}} = \left(\frac{\partial A}{\partial n_i}\right)_{\substack{T,V,n_{js} \\ j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{\substack{S,P,n_{js} \\ j\neq i}} = \left(\frac{\partial U}{\partial n_i}\right)_{\substack{S,V,n_{js} \\ j\neq i}}$$

Q5. Outline the collision theory of bimolecular gaseous reactions. Show that it leads to the rate expression

$$r = P\left\{\pi\,\sigma_{AB}^2\left(\frac{8KT}{\pi\mu}\right)^{\frac{1}{2}} N_A^*\, N_B^*\right\}\exp\left(\frac{-E_o}{RT}\right). \qquad 10$$

Q6. For the following cell

$$Pb\,|\,PbCl_2\,(s)\,|\,PbCl_2\,(soln)\,|\,AgCl\,(s)\,|\,Ag,$$

the potential at 298 K is 0·490 V and the variation of emf with temperature is given by

$$E = a - (1{\cdot}86 \times 10^{-4}\ V/K)\,(T - 25\ K)$$

Calculate ΔG, ΔH and ΔS for the reaction at 298 K. *10*

Q7. What is the probability of locating a particle in one-dimensional box between $\frac{L}{4}$ and $\frac{3L}{4}$ where L is the length of the box ? Assume the particle to be in the lowest energy state. *10*

Q8. (a) Sketch qualitatively the Raman spectrum showing Rayleigh, Stokes and anti-Stokes lines. Why are Stokes lines more intense than the anti-Stokes lines ? *7*

(b) State and illustrate the rule of mutual exclusion. Comment on the converse of this. *3*

Q9. Describe the changes observed in the vibrational quantum number in an electronic transition using Franck-Condon principle. *10*

Q10. (a) From the following reduction reactions and E° values :

$$Fe^{3+}(aq) + e \rightarrow Fe^{2+}(aq) \quad E_1^\circ = 0{\cdot}772\ V$$

$$Fe^{3+}(aq) + 3e \rightarrow Fe\ (s) \quad E_2^\circ = -0{\cdot}036\ V$$

Calculate E_3° for the half-cell reaction

$$Fe^{2+}(aq) + 2e \rightarrow Fe\ (s).$$ *5*

(b) Calculate the molecular diameter (d) of helium if its Van der Waals constant b is $23{\cdot}70\ cm^3\ mol^{-1}$. *5*

SECTION C

Attempt any *three* questions : ***20×3=60***

Q11. (a) What is Boyle temperature ? Give its significance for the gases H_2, He, N_2 and NH_3. *10*

(b) Classify the solid state of the following substances as ionic / covalent / molecular / metallic crystals and explain. *5*

SiC, S_4, KBr, LiCl, Mg

(c) How does the temperature dependence of electrical conduction in an aqueous solution compare with that in metal ? *5*

Q12. (a) Derive the Gibbs-Duhem equation in the term $\sum_i n_i(d\bar{Y}_i) = 0$ at constant temperature and pressure where $\bar{Y}_i$ is an extensive property of a solution. Describe the physical significance of the above equation. *10*

(b) For the first order reaction

$$2N_2O_5\,(g) \rightarrow 4NO_2\,(g) + O_2\,(g)$$

A is $4{\cdot}3 \times 10^{13}\ s^{-1}$ and K is $4{\cdot}329 \times 10^{-5}\ s^{-1}$, calculate the energy of activation at 300 K. *10*

Q13. (a) How is the pH of a solution determined using hydrogen electrode ? *10*

(b) What are the steps involved in the mechanism of photochemical decomposition of hydrogen-iodide reaction ? *10*

Q14. (a) What is degeneracy ? Illustrate with the cubic box of length L. How many eigenstates are there with energy equal to $\frac{101\,h^2}{8\,mL^2}$? *10*

(b) Consider a particle moving in a three-dimensional box with sides a, b and c. Assuming n_1, n_2 and n_3 as quantum numbers for the motions along x, y and z directions, write down the wavefunction and energy for this system. State whether the pair of Laplacian operator and this wavefunction satisfy the eigenvalue equation. If yes, what is the eigenvalue ? *10*

Q15. (a) The $J = 3 \rightarrow 4$ transition for a diatomic molecule occurs at 0·50 cm^{-1}. What is the wave number for the $J = 6 \rightarrow 7$ transition for this molecule ? Assume the molecule is a rigid rotor. *10*

(b) Sketch the fundamental vibration modes of CS_2 and OCS. Which of these are IR active ? *5*

(c) Why is a saturated solution of KCl or NH_4NO_3 used in the salt bridge ? *5*