TDP (Honours) 3rd Semester Exam., 2020

(Held in 2021)

CHEMISTRY

(Honours)

THIRD PAPER (A)

Full Marks : 48

Time : 2 hours

The figures in the margin indicate full marks for the questions

Answer **four** questions, taking **two** from each Unit

Use separate answer-script for each Unit

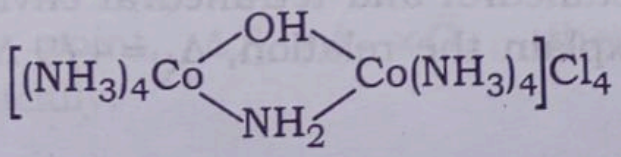
UNIT—I

(Inorganic Chemistry)

1. *(a)* Write the salient features of Werner's coordination theory.

(b) Write the IUPAC name of the following coordination compounds (any *three*) :

(i) $Na[Pt(Cl)(Br)(NO_2)(H_2O)]$

(ii) 

(iii) $K[PtCl_3(C_2H_4)]$

(iv) $[Cr(en)_2(H_2O)_2]Br_3$

(c) Draw and explain the possible optical isomer for the complex $[Co(en)_2Cl_2]Cl$. (en = ethylenediamine)

(d) Define linkage isomerism. Give an example of linkage isomerism in coordination compound.

3+(1×3)+(2+1)+3=12

2. (a) Explain pink coloured $[Co(H_2O)_6]^{2+}$ turns into blue $[Co(H_2O)_4]^{2+}$ on dehydration.

(b) Define magnetic susceptibility. Write about Curie law of magnetic susceptibility.

(c) Magnetic moment of $[Fe(H_2O)_6]^{3+}$ is 5·92 BM and that of $[Fe(CN)_6]^{3-}$ ion is 1·73 BM. Explain.

(d) What are major limitations of valence bond theory in explaining the properties of coordination compound? 2+4+3+3=12

3. (a) Draw the splitting pattern of *d*-orbital in octahedral and tetrahedral environment. Explain the relation, $\Delta_t = 4/9\,\Delta_0$.

(b) What is nephelauxetic effect?

(c) Why is the adjusted crystal field theory introduced?

(d) Explain why tetrahedral complexes are usually high spin. (2+3)+2+3+2=12

UNIT—II

(Physical Chemistry)

4. (a) Derive an expression for work done in isothermal reversible expansion of an ideal gas.

(b) Using Arrhenius equation, derive

$$\log\frac{k_2}{k_1} = \frac{E_a}{2\cdot303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

(c) Why is enthalpy of neutralization of all strong acids with strong base almost identical?

(d) 2 mole of an ideal gas at 27 °C and 5 atm pressure expands isothermally and reversibly till the final pressure is 2 atm. Calculate w, dq, ΔU and ΔH. 3+3+2+4=12

5. (a) Derive an expression of elevation of boiling point, $\Delta T_b = k_b \times C_m$, thermodynamically.

(b) State and explain Henry's law.

(c) What is the effect of temperature on surface tension of a liquid?

(d) Find the osmotic pressure of an aqueous solution of $BaCl_2$ at 288 K containing 0·39 gm per 60 ml. The salt dissociated 60%. (M_{Ba} =137, M_{Cl} =35·5) 4+2+2+4=12

6. (a) Explain the terms 'induced polarization' and 'orientation polarization'.

(b) BF_3 has a planar and NH_3 has a pyramidal structure. Explain.

(c) What do you mean by circular dichroism (CD)? Mention its application in determining the structure of molecule.

(d) Two optically active substances *A* and *B* have specific rotations of +50° and –30° respectively. A mixture containing 6 gm of *A* and 4 gm of *B* is dissolved in water and the solution is made up to 50 cc. Find the angle of rotation for the solution kept in a 5 cm polarimeter tube.

(e) What do you mean by optical exaltation? 2+2+3+3+2=12

★★★

TDP (Honours) 3rd Semester Exam., 2019

CHEMISTRY
(Honours)

THIRD (A) PAPER

Full Marks : 48

Time : 2 hours

The figures in the margin indicate full marks for the questions

Answer **four** questions, taking **two** from each Unit

Use separate answer-script for each Unit

UNIT—I

(Inorganic Chemistry)

1. *(a)* Define the following with suitable examples :

(i) Ambidentate ligand

(ii) Bridging ligand

(b) Write the IUPAC name of the following coordination compounds :

(i) $[Fe(H_2O)_5 NO] SO_4$

(ii) $[Cr(en)_3][Co(CN)_6]$

(iii) $LiAlH_4$

(c) How many stereoisomers are possible for $[Fe(C_2O_4)_3]^{3-}$ ion? Also draw the structures of all the plausible stereo-isomers.

(d) Discuss the application of coordination compounds in animal world.

(1½×2)+(1×3)+3+3=12

2. (a) What do you mean by chelate effect? Explain why it is called an entropy effect.

(b) Give the structure of dimethyl-glyoximatonickel(II). What type of complex is it? Indicate the different types of bond in this compound.

(c) Calculate CFSE value for the following :

(i) d^4 high-spin octahedral complex

(ii) d^5 strong field octahedral

(iii) d^6 tetrahedral complex

(iv) d^9 tetrahedral complex

(d) Explain why tetrahedral complexes show intense colour compared to octahedral complexes. (2+1)+(1+1+1)+4+2=12

3. (a) Explain, why—

(i) $K_2[NiCl_4]$ is paramagnetic whereas $K_2[PtCl_4]$ is diamagnetic although both Ni(II) and Pt(II) are d^8 ions;

(ii) aq. solution of Mn(II) sulfate is almost colourless, whereas aq. solution of Cu(II) sulfate is blue;

(iii) $[NiCl_4]^{2-}$ is paramagnetic but $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral;

(iv) the ion $[FeF_6]^{3-}$ is colourless whereas $[CoF_6]^{3-}$ is coloured.

(b) What is charge-transfer transition? Give one example of each type of CT transition. (2×4)+(2+2)=12

UNIT—II

(Physical Chemistry)

4. (a) Give a mathematical expression for the first law of thermodynamics for a closed system and apply it in case of adiabatic process.

(b) "Hess's law is a corollary to the first law of thermodynamics." Justify the statement.

(c) Compare collision theory and transition state theory for reaction rates.

(d) 10 litres of a monoatomic gas expands adiabatically from 5 atm to 1 atm. Final volume is 23·6 litres. Calculate the adiabatic work. (2+1)+2+4+3=12

5. *(a)* Derive an expression for rate constant of a second-order reaction with two reactants having same initial concentration.

(b) Derive an expression of lowering of vapour pressure thermodynamically.

(c) How is the phenomenon of viscosity in gases different from the viscosity in liquids?

(d) Which one is expected to be higher between K_f and K_b?

(e) 2 gm of KCl is dissolved in 100 gm water. If dissociation occurs to the extent of 90%, calculate its freezing point.

2+3+2+2+3=12

6. *(a)* Define rheochor and molar refractions.

(b) *(i)* The polarizability of CCl_4 is independent of temperature while that of $CHCl_3$ changes with temperature. Explain.

(ii) *p*-hydroxy benzene is a polar molecule. Justify.

(c) What do you mean by diamagnetism and paramagnetism?

(Continued)

(d) The refractive index of CCl_4 for the sodium *D* line at 20 °C is 1·457 and its density is 1·595 gm/cc. Calculate the molar refraction. If the atomic refraction of carbon is 2·42, calculate the atomic refraction of chlorine.

(1½+1½)+(2+1)+2+4=12

★★★

TDP (Honours) 3rd Semester Exam., 2017

CHEMISTRY
(Honours)

THIRD (A) PAPER

Full Marks : 48

Time : 2 hours

The figures in the margin indicate full marks for the questions

Answer **four** questions, taking **two** from each Unit

Answer each Unit in separate answer script

UNIT—I

(Inorganic Chemistry)

(*Marks* : 24)

1. *(a)* Discuss the differences between high-spin and low-spin complexes.

(b) Draw the structure of all the possible isomers of $[Cr(en)_2Cl_2]Cl$.

(c) Explain thermodynamically chelated complexes are 10^{10} time more stable than those of non-chelated complexes.

(Turn Over)

(d) Mention some roles of metal chelates in living system.

(e) Why are tetrahedral complexes unable to exhibit geometrical isomerism?

2+3+3+2+2=12

2. (a) Determine the oxidaton state and type of hybridisation of metal atom present in the complex compound corresponding to the brown ring in nitrate test. Given that, magnetic moment value of the complex is 3·89 BM.

(b) Draw energy-level diagram and indicate the number of electrons in each energy level for the complex $[Co(CN)_6]^{3-}$ ($\Delta_0 > P$).

(c) The crystal field splitting parameter (Δ_0) of $[IrCl_6]^{3-}$ is 27600 cm^{-1}. Convert this wave number to nm. What is your prediction about the magnetic properties of $[IrCl_6]^{3-}$ ion?

(d) A light pink-coloured cobalt(II) chloride becomes deep blue on addition of excess of HCl. Give reason.

(Continued)

(e) For $[Cr(H_2O)_6]^{2+}$ ion, the mean pairing energy (P) is found to be equal to 23500 cm^{-1}. The magnitude of Δ_0 is 13900 cm^{-1}.

Calculate the CFSE for this complex ion corresponding to HS and LS state. Which state is more stable? 3+2+2+2+3=12

3. (a) What is magnetic susceptibility and how does it vary with temperature?

(b) Define Curie temperature and Neel temperature.

(c) Calculate the magnetic moment value of the following complexes :

(i) Square planar $K_2[Ni(CN)_4]$

(ii) Octahedral $[Mn(H_2O)_6]Cl_2$

(d) Explain the origin of the purple colour of MnO_4^- ion.

(e) If the frequency of the radiation absorbed by a complex ion in the visible region is $5{\cdot}30 \times 10^{14}$ s^{-1}, then what would be the colour of the complex ion?

(1+1)+(1+1)+3+3+2=12

(Turn Over)

UNIT—II

(Physical Chemistry)

(*Marks* : 24)

4. *(a)* Derive expressions for rate constants for a second-order reaction with different reactants.

(b) Explain why C_P is greater than C_V.

(c) State Lavoisier and Laplace law and Hess' law of thermochemistry.

(d) The rate constant of a second-order reaction is $5 \cdot 70 \times 10^{-5}$ dm^3 mol^{-1} s^{-1} at 25 °C and $1 \cdot 64 \times 10^{-4}$ dm^3 mol^{-1} s^{-1} at 40 °C. Calculate the activation energy and the Arrhenius pre-exponential factor. 3+2+3+4=12

5. *(a)* Explain why viscosity of gases and liquids behave differently with rise in temperature.

(b) Derive the expression

$$\Delta T = -\frac{(\partial H / \partial P)_T}{C_P} \cdot \Delta P$$

for an ideal gas.

(c) State Henry's law.

(d) 15 gm of glucose is added to 250 gm of water at 20 °C. If the vapour pressure of water at 20 °C is 17·535 mm, then calculate the relative lowering of vapour pressure of water at this temperature.

(e) What is reverse osmosis?

2+3½+2+3+1½=12

6. *(a)* Distinguish between *para-*, *dia-* and *ferro*-magnetism.

(b) How do you account for the fact that the dipole moment of ethyl chloride (2·05 D) is considerably larger than that of chlorobenzene (1·70 D)?

(c) Define parachor and explain the properties of parachor.

(d) Molar polarization of diethyl ether on dissolving it in cyclohexane at 20 °C at infinite dilution was found to be $58 \cdot 50$ cm^3 mol^{-1}. Its molar refraction was found to be $22 \cdot 40$ cm^3 mol^{-1}. Applying 5% correction to R_m, calculate dipole moment of diethyl ether.

(e) What is orientation polarisation?

3+2+3+3+1=12

★★★

TDP (Honours) 3rd Semester Exam., 2016

CHEMISTRY
(Honours)

THIRD (A) PAPER

Full Marks : 48

Time : 2 hours

The figures in the margin indicate full marks for the questions

Answer **four** questions, taking **two** from each Unit

UNIT—I

(Inorganic Chemistry)

(*Marks* : 24)

1. *(a)* Mention the difference between an ambidentate and a polydentate ligand with example.

(b) Write down the important postulates of Werner's coordination theory.

(c) Write the IUPAC nomenclature for the following :

(i) $[Co(ONO)(NH_3)_5]Cl_2$

(ii) $[Pt(NH_3)(Py)BrCl]$ (Py = Pyndine)

(iii) $[Fe(C_2O_4)_3]^{3-}$

(Turn Over)

(d) What types of ligand do qualify as π-acid ligands? Give one example of a π-acid ligand and discuss its role in stabilization of low oxidation states of metals.

3+3+3+3=12

2. (a) Draw all the possible geometrical isomers of $[Co(en)_2Cl_2]^+$ ion (where en = ethylene diamine).

(b) Explain from CFT why octahedral complexes of Ni(II) are paramagnetic, while square planar Ni(II) complexes are diamagnetic.

(c) What are the basic assumption of CFT? What modifications are made in adjusted CFT? What is nephelauxetic effect? Explain with an example.

(d) Explain why $[Sc(H_2O)_6]^{+3}$ is colourless, but $[Ti(H_2O)_6]^{+3}$ is pale purple in colour.

3+3+4+2=12

3. (a) On addition of conc. HCl, pink colour of $[Co(H_2O)_6]^{2+}$ changes to deep blue colour. Explain.

(b) Give one example each for *d-d*, MLCT and LMCT transitions.

(Continued)

(c) Calculate the crystal field stabilization energy for octahedral complexes of Fe^{+3} in a weak field and also in a strong field. Calculate the spin-only magnetic moment for the two complexes.

(d) What is paramagnetism? How does it originate?

2+3+4+3=12

UNIT—II

(Physical Chemistry)

(*Marks* : 24)

4. (a) Derive thermodynamically the relationship between C_P and C_V.

(b) What is meant by Joule-Thomson coefficient?

(c) Derive an expression for work done in isothermal reversible expansion of a gas.

(d) A dry gas at NTP is expanded adiabatically from 1 litre to 5 litres. Calculate the final temperature assuming ideal behavior. $(C_P / C_V = 1{\cdot}4)$

(e) What do you mean by molecularity of a reaction? Illustrate with example.

3+2+3+2+2=12

(Turn Over)

5. *(a)* Derive a relation between magnetic moment and number of unpaired electrons.

(b) By giving example explain additive and constitutive property.

(c) Establish the structure of quinone based upon parachor values.

[Parachor values for carbon, hydrogen, oxygen, double bond, six-membered ring are 4·8, 17·1, 20·0, 23·2, 6·1 respectively]

(d) The value of $[\alpha]_D^{20}$ for lactose is 55·4°. What is the concentration in grams per litre of a solution of lactose which gives a rotation of 7·24° in a 10 cm cell at 20° with sodium D-light? 3+3+3+3=12

6. *(a)* Derive $\Delta T_b = K_b \times m$.

(b) Discuss biological importance of osmosis.

(c) Derive an expression for rate constant of first-order reaction. Show that half-life for a first-order reaction is constant.

(d) A solution of 1·25 g of a certain non-electrolyte in 20 g of water freezes at 271·95 K. Calculate the molecular mass of the solute. 4+2+3+3=12

★★★

TDP (Honours) 3rd Semester Exam., 2015

CHEMISTRY

(Honours)

THIRD (A) PAPER

Full Marks : 48

Time : 2 hours

The figures in the margin indicate full marks for the questions

Answer **four** questions, taking **two** from each Unit

UNIT—I

1. *(a)* What is an ambidentate ligand? Give an example of this type of ligand.

(b) $[Ni(en)_3]^{2+}$ is 10^{10} times more stable than $[Ni(NH_3)_6]^{2+}$. Explain.
(en = ethylene diamine)

(c) Write the IUPAC nomenclature for the following :

(i) $[Pt(en)(NH_3)_2(NO_2)Cl]SO_4$

(ii) $K_3[MnF_6]$

(d) What are inner-metallic complexes? Write an important application of inner-metallic complexes in analytical chemistry.

(e) Giving appropriate examples, show the occurrence of (i) linkage and (ii) coordination isomerism in coordination compounds. Draw the possible geometrical isomers of the compound $[MX_2(A-B)_2]$. (X = monodentate ligand and $A-B$ = unsymmetrical bidentate ligand.) 2+2+2+2+4=12

2. (a) What is meant by crystal field splitting? Draw the diagram to show splitting of *d*-orbitals in octahedral crystal field.

(b) A solution of $[Ni(H_2O)_6]^{2+}$ is green but a solution of $[Ni(CN)_4]^{2-}$ is colourless. Explain.

(c) Considering valence bond theory, predict the geometries and magnetic behaviour of the following :

(i) $[Co(NH_3)_6]Cl_3$

(ii) $K_3[FeF_6]$

(d) $K_3[Fe(CN)_6]$ is inner-sphere complex but $K_3[FeF_6]$ is outer-sphere complex. Comment.

(e) Why does CO act as a stronger ligand than Cl^-? 3+2+3+2+2=12

3. (a) What is meant by magnetic susceptibility? How is it related to magnetic moment?

(b) Explain Curie and Neel temperatures with the help of qualitative diagram between magnetic susceptibility and temperature.

(c) $[Cu(CH_3COO)_2]_2 \cdot 2H_2O$, shows anomalous magnetic moment. Explain.

(d) What do you mean by the terms 'ferromagnetism' and 'antiferromagnetism'? Give examples.

(e) The magnetic moment of $[MnBr_4]^{2-}$ is 5·9 BM. What is the geometry of this complex ion? 2+2+2+3+3=12

UNIT—II

4. (a) State and explain the first law of thermodynamics. Give a mathematical expression for it.

(b) Justify the following statements :

(i) Every isolated system is closed.

(ii) Joule-Thomson effect is an isoenthalpic process.

(c) Heat of neutralization for the reaction between HCl and NaOH is the same as that between HNO_3 and KOH but is different for CH_3COOH and NaOH. Explain.

(d) 100 g of N_2 at 25 °C are held by a piston under 30 atm pressure. The pressure is suddenly released to 10 atm under adiabatic conditions. If the molar heat capacity of N_2 at constant volume be 4·95 cal/°, calculate the final temperature. (1+2)+(1+2)+3+3=12

5. (a) Derive an expression for rate constant of a second-order reaction with two reactants having different initial concentrations.

(b) How does rate of a reaction vary with temperature?

(c) Define the terms, 'molarity', 'molality' and 'normality'. When are molarity and normality same or different? What is the importance of molality?

(d) State and explain the original forms of Raoult's law and Henry's law. 3+2+5+2=12

6. (a) We write $T = 0$, not $T = 0$ K for the zero temperature on the thermodynamic temperature scale. However, we write 0 °C. Comment and justify.

(b) Define exothermic and endothermic reactions. Give one example of each.

(c) Explain Born-Haber cycle.

(d) What is flame temperature? 2+(2+2)+4+2=12

★★★