SECOND SEMESTER M.Sc. DEGREE (REGULAR/SUPPLEMENTARY) EXAMINATION, APRIL 2022

(CBCSS)

Chemistry

CHE 2C 08—ELECTRO CHEMISTRY, SOLID STATE CHEMISTRY AND STATISTICAL THERMODYNAMICS

(2019 Admission onwards)

Time : Three Hours   Maximum : 30 Weightage

General Instructions

1. In cases where choices are provided, students can attend **all** questions in each section.

2. The minimum number of questions to be attended from the Section/Part shall remain the same.

3. The instruction if any, to attend a minimum number of questions from each sub section/sub part/ sub division may be ignored.

4. There will be an overall ceiling for each Section/Part that is equivalent to the maximum weightage of the Section/Part.

Section A

Answer any **eight** *questions.*
Each question carries a weightage of 1.

1. Find the ionic strength of a 0.01 M solution of $LaCl_3$ in water.

2. Write elaborate reaction during charging of a lead acid battery.

3. Define zeta potential. Explain its significance.

4. Explain concentration polarisation.

5. Write Hermann Mauguin symbol of :

     (a) D_{2h}.   (b) C_{3v}.

6. A plane cuts x, y and z axis at $2a$, $3b$ and $6c$. Write Miller indices for the plane.

7. Define Fermi level. Explain its significance.

8. Rationalise third law of thermodynamics using statistical concepts.

9. Write equation for C_v of NH_3 using equipartition principle.

10. The fundamental vibrational frequency of a solid is 2990 cm^{-1}. Find the characteristic temperature.

                                            $(8 \times 1 = 8$ weightage)

Turn over

Section B

*Answer any **six** questions.*
Each question carries a weightage of 2.

11. Find mean ionic activity coefficient of 0.01 molal $CuSO_4$ at 25°C using Debye Hückel limiting law. $A = 0.509$.

12. Explain the working of polymer electrolyte fuel cell.

13. Write Butler–Volmer equation. Transform it into Tafel equation. Explain the significance of slope and intercept of a Tafel plot.

14. Show that 5-fold axis of symmetry does not occur in solids.

15. Draw stereographic projection for a monoclinic system. Discuss.

16. What is Meisner effect ? Discuss.

17. Calculate rotation partition function for H_2. The bond length is 0.74 Å , $T = 298$ K.

18. Calculate the capacity of diamond at 1000 K. Its characteristic temperature is 1860 K.

$(6 \times 2 = 12$ weightage$)$

Section C

*Answer any **two** questions.*
Each question carries a weightage of 5.

19. Define over voltage. What are the contributing factors of over voltage ? Discuss.

20. Apply Fermi Dirac statistics for electrons in metals. Discuss.

21. (a) Derive Maxwell Boltzman distribution law.

    (b) Calculate the ratio of population at 300 K. The ground state is non-degenerate and excited state is triply degenerate. Energy level spacing is 1000 cm^{-1}.

22. Write a brief account of magnetic properties of solids.

$(2 \times 5 = 10$ weightage$)$

SECOND SEMESTER M.Sc. DEGREE (REGULAR/SUPPLEMENTARY) EXAMINATION, APRIL 2022

(CBCSS)

Chemistry

CHE 2C 07—REACTION MECHANISM IN ORGANIC CHEMISTRY

(2019 Admission onwards)

Time : Three Hours   Maximum : 30 Weightage

General Instructions

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Section A

*Answer any **eight** questions.*
Each question carries a weightage of 1.

1. What is neighboring group participation in nucleophilic substitution ? How does it affect the stereochemical outcome of the reaction ?

2. Explain the effect of reaction medium on SE1 and SE2 reactions ?

3. The reaction of alkenes with singlet carbenes is stereospecific. Explain.

4. Indicate the mechanism and its evidence for $B_{Ac}2$ ester hydrolysis.

5. Predict the cyclic product obtained from 2Z, 4E-hexadiene on photochemical conditions. Specify the stereochemistry.

6. Illustrate photo-Fries rearrangement with a suitable example.

7. Show that Cope rearrangement is a [3, 3] sigmatropic shift.

8. What is Barton reaction ? Give one example.

Turn over

9. Write a short note on oxa di-*pi*-methane rearrangement.

10. Write a brief note on Emde degradation.

(8 × 1 = 8 weightage)

Section B

Answer any **six** *questions.*
Each question carries a weightage of 2.

11. Explain the addition-elimination mechanism of aromatic nucleophilic substitution with suitable examples.

12. Define the terms *ipso* substitution and *cine* substitution. Indicate the mechanisms involved with appropriate examples.

13. Substitution and elimination reactions are competing reactions. Explain. What are the major factors deciding the outcome ?

14. Which are the important factors contributing to the stability of carbocations ? Why cyclopropylmethyl cations are even more stable than benzyl type cations ?

15. In the following reaction, when racemic substrate is heated only one of the diastereomers of the product is formed.
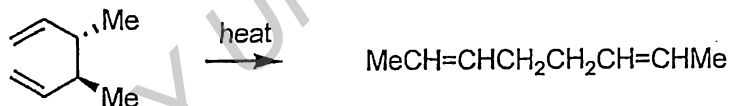
What class of pericyclic reaction is involved in the transformation ? Explain the terms suprafacial and antarafacial.

16. Explain any *two* photochemical reactions involving olefenic double bonds.

17. What information is deduced by Hofmann degradation of alkaloids ? Illustrate.

18. Outline the conversion of cholesterol into testosterone.

(6 × 2 = 12 weightage)

Section C

Answer any **two** *questions.*
Each question carries a weightage of 5.

19. With appropriate examples, discuss the mechanistic and stereochemical aspects of SN1, SN2 and SN2' reactions.

20. Write a detailed note on synthetically useful base catalysed condensation reactions of carbonyl compounds.

21. Using correlation diagram derive Woodward-Hoffmann rules for the electrocyclisation of a linear conjugated 4-electron *pi*-system under thermal conditions.

22. Outline the total synthesis of cephalosporin.

(2 × 5 = 10 weightage)

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SECOND SEMESTER M.Sc. DEGREE (REGULAR/SUPPLEMENTARY) EXAMINATION, APRIL 2022

(CBCSS)

Chemistry

CHE 2C 06—CO-ORDINATION CHEMISTRY

(2019 Admission onwards)

Time : Three Hours

Maximum : 30 Weightage

General Instructions

1. *In cases where choices are provided, students can attend* **all** *questions in each section.*

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Section A

Answer any **eight** *questions.*
Each question carries a weightage of 1.

1. Differentiate between thermodynamic stability and kinetic stability of metal complexes.

2. How do π-bonding ligands help in the stabilization of metal complexes with low oxidation states? Explain with suitable examples.

3. Calculate the CFSE for d^4 high-spin octahedral and d^5 low-spin octahedral metal complexes.

4. Which ligand gives higher splitting energy (Δ value) ; H_2O or OH^- ? Substantiate your answer.

5. How do Orgel diagrams differ from Tanabe-Sugano diagrams ?

6. Explain the terms ; Curie temperature and Niel's temperature.

7. What happens to the $v(C=N-)$ stretching frequency in N-salicylideneaniline on complexation with Cu^{2+} ? Explain.

8. How infrared spectroscopy can be used to identify monodentate and bidentate (chelating) NO_3^- groups ?

Turn over

9. What is anation reaction ? Explain with an example.

10. Explain photoisomerization reactions of metal complexes giving an example.

(8 × 1 = 8 weightage)

Section B

*Answer any **six** questions.*
Each question carries a weightage of 2.

11. Derive the relationship between step-wise stability constant and overall stability constant of a metal complex.

12. What is Jahn-Teller effect ? Discuss its consequences in the structure and spectra of transition metal complexes.

13. State and explain Curie-Weiss law.

14. Illustrate the use of ESR spectroscopy in the study of ambidentate co-ordination of ligand containing nitrogen and oxygen towards copper(II) ion.

15. Discuss the factors which influence the rates of substitution reactions in metal complexes.

16. Explain the Marcus theory of outer-sphere electron transfer reaction.

17. Explain the photoisomerization and photorecemization reactions of metal complexes with suitable examples.

18. Discuss the principle involved in Gouy method for magnetic moment measurement.

(6 × 2 = 12 weightage)

Section C

*Answer any **two** questions.*
Each question carries a weightage of 5.

19. Discuss the factors that favour the stability of metal complexes. Describe the spectrophotometric method for determining the stability of a metal complex.

20. Critically evaluate valence bond theory, crystal field theory and molecular orbital theory in the study of bonding in transition metal complexes.

21. Bring out the principle and experimental set up involved in Mossbauer spectroscopy. Explain how this technique is useful in the structural study of iron complexes.

22. Describe the D, A and I mechanisms of substitution reactions in octahedral metal complexes bringing out the factors which favour these mechanisms.

(2 × 5 = 10 weightage)

SECOND SEMESTER M.Sc. DEGREE (REGULAR/SUPPLEMENTARY) EXAMINATION, APRIL 2022

(CBCSS)

Chemistry

CHE 2C 05—GROUP THEORY AND CHEMICAL BONDING

(2019 Admission onwards)

Time : Three Hours   Maximum : 30 Weightage

General Instructions

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Section A

Answer any **eight** *questions.*
Each question carries a weightage of 1.

1. List the symmetry elements and operations associated with D_3d.

2. Explain with example (a) cyclic group ; (b) abelian group.

3. State and explain rearrangement theorem.

4. Show that $\sigma_{xy} \times \sigma_{xz} = c_2(x)$.

5. Generate matrices for (a) c_6 ; (b) σ_{xy} using positional coordinates x, y, z.

6. Explain 'transition moment integral'.

7. Distinguish between symmetric direct product and ordinary direct product.

8. O_2^+ is more stable than O_2^-. Why ?

Turn over

9. The energy of $\pi(p_1)$ molecular orbitals of benzene are $\alpha + 2\beta, \alpha + \beta, \alpha \times \beta, \alpha - \beta$ and $\alpha - 2\beta$. Find the delocalization energy.

10. Write spectroscopic term symbol of c_2.

(8 × 1 = 8 weightage)

Section B

Answer any six questions.
Each question carries a weightage of 2.

11. Show that the four symmetry operations $E, C_2(x), C_2(y)$ and $C_2(z)$ form a mathematical group under multiplication.

12. Ethylele belongs to $D_2h\left(E, C_2(x), C_2(y), C_2(z)\right) \ \sigma_{xy}, \sigma_{xz}, \sigma_{yz}, i$. Taking the positional coordinates of all atoms generate a reducible representation.

13. Rationalize mutual exclusion principle using group theory.

14. Find $\pi(p_1)$ molecular orbitals and their energies for allyl anion using HMO method.

15. Find allowed electronic transitions of Carbonyl group. Use C_2v character table :

C_2v	E	C_2z	σ_{vxz}	$\sigma_v'yz$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

16. Find IR and Raman active vibrations of NH_3. Use C_3v character table :

C_3v	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	-1	Rz	
E	2	-1	0	(x,y)	$(x^2 - y^2, xy)$
				(R_x, R_y)	(xz, yz)

17. The Pi molecular orbitals of *cis* butadiene are given below. Find the free valence around each c atom.

$$\Phi_1 = 0.372\, P_1 + 0.602\, P_2 + 0.602\, P_3 + 0.372\, P_4$$

$$\Phi_2 = 0.602\, P_1 + 0.372\, P_2 - 0.372\, P_3 - 0.602\, P_4$$

$$\Phi_3 = 0.602\, P_1 - 0.371\, P_2 - 0.372\, P_3 + 0.602\, P_4$$

$$\Phi_4 = 0.372\, P_1 - 0.602\, P_2 + 0.602\, P_3 - 0.372\, P_4$$

18. With the help of correlation diagram explain noncrossing rule.

(6 × 2 = 12 weightage)

Section C

Answer any two questions.
Each question carries a weightage of 5.

19. State Great Orthogonality Theorem. What are the consequences of the theorem ? Use the theorem to derive C_4v character table.

20. Find the molecular orbitals of H_2O. Use C_2v character table. Predict allowed electronic transitions.

21. Find the hybridized orbitals B in BF_3. Use D_3h character table :

D_3h	E	$2C_3$	$3C_2$	σ_h	$3S_3$	$3\sigma_d$		
A_1'	1	1	1	1	1	1		$x^2 + y^2 - z^2$
A_2'	1	1	−1	1	1	−1	Rz	
E'	2	−1	0	2	−1	0	(x,y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

22. Compare V.B. and M.O. theory of binding as applied to H_2. Which is found better ?

(2 × 5 = 10 weightage)

SECOND SEMESTER M.Sc. DEGREE (SUPPLEMENTARY) EXAMINATION APRIL 2021

(CUCSS)

Chemistry

CH 2C 06—CO-ORDINATION CHEMISTRY

(2015 Admissions)

Time : Three Hours   Maximum : 36 Weightage

Section A

Answer **all** *questions.*
Each question carries a weightage of 1.

1. In general, K_n values follow the sequence : $K_1 > K_2 > K_3$. Give an example of an exception for this and give the basis of exception.

2. What is template effect ? Explain.

3. Chloride ions give tetrahedral complexes with Ni (II) but form square planar complexes with Pt(II). Why ? Explain.

4. Jahn Teller effect is most pronounced in those cases where electrons are entering to the e_g level. Why ?

5. Arrange the following in the order increasing magnetic moment and justify your answer.

   Mn^{2+}, Cr^{2+}, Fe^{2+}, Co^{2+}.

6. Explain the reason for the dark purple colour of $KMnO_4$ solution.

7. What is meant by isomer shift ? Discuss its importance in Mössbauer spectroscopy.

8. How many peaks do you expect in the ESR spectrum of $\left[Mo(CN)_8 \right]^{3-}$? Explain.

9. 'The inert complexes are not necessarily thermodynamically stable'. Justify the statement with a suitable example.

10. Give Marcus equation and mention its applications.

Turn over

11. Discuss the role of bridging ligands in Inner sphere reaction mechanism.

12. State Adamson's rules.

<div align="right">(12 × 1 = 12 weightage)</div>

Section B

Answer any **eight** *questions.*
Each question carries a weightage of 2.

13. Write down the stepwise and overall formation constants for the reaction $Cu^{2+} + 4NH_3 \rightarrow \left[Cu\left(NH_3\right)_4\right]^{2+}$. Also Calculate β_4 value for the reaction if $\log k_1 = 4$, $\log k_2 = 3.2$, $\log k_3 = 2.7$ and $\log k_4 = 2$.

14. Give short notes for :

    (i) Ambidentate ligands ;

    (ii) Macrocyclic ligands ; and

    (iii) Chelate ligands.

15. Give a brief note on Racah parameters.

16. Sketch the splitting of d-orbitals in tetrahedral and square planar field.

17. Explain the determination of magnetic moment by Gouy method.

18. State and explain the selection rules for d-d transition.

19. Discuss the applications of ESR spectra to copper complexes.

20. Illustrate with suitable examples, the applications of ^{19}F and ^{31}PNMR in the study of inorganic metal complexes.

21. What is trans effect ? Propose efficient routes to synthesize 'cis' and trans $\left[PtCl_2\left(NH_3\right)\left(PPh_3\right)\right]$.

22. Arrange the following in the order of rate of substitution by H_2O and explain the reason for your answer. $\left[Co\left(NH_3\right)_6\right]^{3+}, \left[Rh\left(NH_3\right)_6\right]^{3+}, \left[Ir\left(NH_3\right)_6\right]^{3+}$

23. Distinguish between photoisomerisation and photorecimization.

24. Discuss the reducing and oxidizing character of $\left[\mathrm{Ru}\left(\mathrm{bipy}\right)_3\right]^{2+}$.

(8 × 2 = 16 weightage)

Section C

*Answer **two** questions.*
Each question carries a weightage of 4.

25. Discuss the merits of MOT over CFT and sketch the MO diagram for $\left[\mathrm{CoF_6}\right]^{3-}$ and predict its magnetic behavior.

26. Give a comparison between Orgel diagrams and Tanabe Sugano diagrams with special reference to their importance in the interpretation of electronic spectra.

27. Discuss the classification of substitution reaction mechanisms in octahedral complexes.

28. Give an account of the basic principles of Mössbauer spectroscopy and its applications in iron and tin complexes.

(2 × 4 = 8 weightage)