



0035014

K19P 1478

Reg. No. : .....

Name : .....

I Semester M.Sc. Degree (CBSS-Reg./Supple./Imp.)

Examination, October - 2019

(2014 Admission Onwards)

CHEMISTRY

CHE 1C 02 : INORGANIC CHEMISTRY-I

Time : 3 Hours

Max. Marks : 60

**SECTION-A**

Answer **All** questions in **one** word or **one** sentence. Each question carries **1** mark. (8×1=8)

1. Define standard deviation.
2. Differentiate between precision and accuracy.
3. Identify the conjugate acids of  $C_5H_5N$  and  $[Co(CO)_4]^-$
4. Arrange the following species in the increasing order of acid strength :  $BF_3$ ,  $BCl_3$ ,  $BBr_3$
5. Define nuclear reaction cross section.
6. What is the significance of 'Q-values' in nuclear reactions?
7. What is 'inorganic graphite'?
8. How is  $S_2N_2$  prepared?

**SECTION-B**

Answer any **Eight** questions. Answer may be in **Two** or **Three** sentences. Each question carries **2** marks. (8×2=16)

9. Explain the significance of Least Square Analysis in the analytical data.
10. Draw the titration curve for the titration of EDTA with  $Ca^{2+}$  and explain.
11. Calculate the standard deviation and relative standard deviation for the following set of analytical data for a sample Y  
7.12, 7.15, 7.11, 7.16, 7.18

26. Br...



12. Which is more acidic;  $\text{H}_2\text{CrO}_4$  or  $\text{HMnO}_4$ ? Justify your answer.
13. Prove that all Bronsted bases may not be Arrhenius bases.
14. What is Lux concept of acids and bases?
15. How breeder reactor differs from nuclear reactor?
16. How the average life of a radioactive element is related to its disintegration constant?
17. There is a steady level of  $^{14}\text{C}$  ( $t_{1/2} = 5740$  years) in the atmosphere corresponding to  $16.1$  disintegrations  $\text{min}^{-1}\text{g}^{-1}$ . Calculate the ratio of  $^{14}\text{C}/^{12}\text{C}$  in the atmosphere.
18. Classify the following compounds into *closo*, *nido* and *arachino* structures:  
 $\text{B}_5\text{H}_9$ ,  $\text{C}_2\text{B}_{10}\text{H}_{12}$ ,  $\text{B}_4\text{H}_{10}$ ,  $\text{C}_3\text{B}_3\text{H}_5\text{Fe}(\text{CO})_3$
19. What is the action of the following compounds on diborane?
  - a)  $\text{CO}$
  - b)  $(\text{CH}_3)_2\text{O}$  Give equation.
20. How is tetrasulphur tetranitride prepared? Comment on the thermochromism exhibited by this compound.

### SECTION-C

Short paragraph questions. Answer any **Four** questions. Each question carries **3** marks. (4×3=12)

21. In the extraction of cerium(IV) with 2-thenoyltrifluoroacetone in benzene the distribution ratio was 999. If the volume of the organic phase was 20ml and that of aqueous phase was 50ml, what was the percentage of extraction?
22. Explain selective masking and demasking technique in EDTA titrations, citing examples.
23. Arrange the conjugate acids of  $\text{SiO}_4^{4-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$  and  $\text{ClO}_4^-$  in the decreasing order of acidity. Give reasons for your answer.
24. Arrange the following oxides in the increasing order of their basicity:  $\text{B}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{BaO}$ ,  $\text{Cl}_2\text{O}_7$ ,  $\text{CO}_2$  and  $\text{SO}_3$ . Substantiate.
25. Describe the principle involved in the working of a GM counter.
26. Briefly discuss the shell model of nucleus.



27. Describe the synthesis, structure and properties of polythiazyl.
28. What are the different types of hydrogen atoms present in carboranes. Arrange them in the increasing order of acidity.

### SECTION-D

Essay type questions. Answer **four** questions. Each question carries 6 marks. (4×6=24)

29. a) Critically evaluate different types of solvent systems and their applications in solvent extraction technique.

(OR)

- b) Give an account of EDTA titrations, giving special emphasis to the theory different types of EDTA titrations, indicators used and the advantages.

30. a) Discuss the theoretical basis of classification of Lewis acids and bases into hard and soft acids and bases. How this classification is useful in the study of coordination compounds?

(OR)

- b) Give an account of the important reactions that take place in liquid ammonia. What are the advantages and disadvantages of using liquid ammonia as a non-aqueous solvent.

31. a) Describe the principle involved in the working of PWR and BWR.

(OR)

- b) Describe the principle and experimental set up involved in Fricke dosimeter. What is the procedure for determining absorbed dose using it?

32. a) Give any one method for the preparation of triphosphonitrilic chloride. Discuss the important reactions and structure of this compound.

(OR)

- b) Discuss the importance of icosahedral frame work of boron atoms in boron chemistry, giving examples.
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(2014 Admn. Onwards)

CHEMISTRY

CHE1C.01: THEORETICAL CHEMISTRY - I

Time : 3 Hours

Max. Marks : 60

**SECTION-A**

Answer **All** questions in one word or sentence. Each question carries 1 mark. (8x1=8)

1. Write down Hamiltonian operator for an N-particle system.
2. What are stationary states?
3. What are the conditions to be satisfied for the particle to be in a box?
4. Classify the following into even and odd functions:  $\tan x$ ;  $(3+x)(3-x)$
5.  $E_1$  and  $E_2$  correspond to the energies of proposed trial functions,  $\phi_1$  and  $\phi_2$  for a system with latter being the most realistic guess. If  $E_0$  is the real energy, write down these energies in ascending order.
6. What is Pauli's antisymmetry principle?
7. State Born-Oppenheimer approximation.
8. Calculate the number of basis functions for carbon atom using 6-31 1G basis set.

**SECTION - B**

Answer **Eight** questions. Answer may be **two** or **three** sentences. Each question carries 2 marks. (8 x 2= 16)

9. Normalize the function,  $\sin(2\pi x)$  with  $x$  varies between 0 and 1.
10. Express  $(x+iy)$  in terms of spherical polar coordinates.
11. Explain orthonormalized functions.

P.T.O.



12. Write down the del squared operator in spherical polar coordinates.
13. What is Rodrigues formula?
14. Give the potential energy diagrams of SHO and hydrogen molecule. Why do these differ?
15. Write down possible spin function and orbital functions for the electronic configuration,  $1s^1 2s^1$ .
16. State two limitations of perturbation methods.
17. Write down the Slater determinant for the ground state of Li atom and show that all three electrons cannot occupy the  $1s$  orbital.
18. What are split-valence basis sets? Give an example.
19. How will you calculate the  $\pi$ - charge density of conjugated molecule?
20. Write down the ground state term symbol of i)  $C_2$ ; ii) CO

### SECTION - C

Answer **Four** questions in short paragraph for each. Each question carries **3** marks. (4x3=12)

21. Explain Davisson-Germer experiment. What it demonstrates?
22. What is zero point energy? What are their values for a planar rigid rotor and SHO? Justify that these values are in agreement with Heisenberg's uncertainty principle.
23. Write down the Schrodinger equation of Hydrogen atom in spherical polar coordinates and separate the variables.
24. Write down the explicit form of complete wave function and energy of nonplanar rigid rotor explaining each term.
25. Explain self consistent field method.
26. State and prove variational theorem.
27. Differentiate between STO and GTO.
28. Give the MO and VB approximation for the ground state of  $H_2$  molecule and highlight the basic difference between the two.



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K19P 1477

**SECTION - D**

Answer either **a** or **b** of each question. Each question carries **6** marks.

**(4x6=24)**

29. a) Deduce time dependent Schrodinger equation from classical wave equation.

**(OR)**

- b) Explain the postulates of Quantum mechanics.

30. a) Arrive at the energy and wave function of planar rigid rotor.

**(OR)**

- b) Explain radial distribution functions. Plot these for 1s, 2s, 2p, 3p and 4d.

31. a) Derive first order perturbation correction to energy for a nondegenerate system.

**(OR)**

- b) Derive the various atomic term symbols for carbon atom and arrange them in the order of energy.

32. a) Explain Hartree-Fock theory for molecules.

**(OR)**

- b) Calculate the C-C  $\pi$ -bond order in benzene using Huckel molecular orbital treatment.
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(2014 Admission Onwards)

CHEMISTRY

CHE 1C.04 : PHYSICAL CHEMISTRY-I

Time : 3 Hours

Max. Marks : 60

**SECTION-A**

Answer **All** questions in one word or one sentence. Each question carries 1 mark. (8×1=8)

1. State third law of thermodynamics.
2. Distinguish between forces and fluxes with reference to irreversible thermodynamics.
3. Define ionic mobility.
4. Explain the term 'asymmetry effect'
5. What is electrode polarization?
6. Define half wave potential.
7. Write electrode reactions under acidic condition.
8. Explain the term 'impedance'.

**SECTION-B**

Answer **Eight** questions. Answer may be in one or two sentences. Each question carries 2 marks. (8×2=16)

9. Derive thermodynamic equation of state.
10. State and explain onsager reciprocal relation.
11. State criteria for equilibrium between phases.
12. Write Debye Huckel Onsager equation. How is it verified?
13. Predict the effect of the following on the thickness of the ion atmosphere.
  - a) Concentration of electrolyte.
  - b) Dielectric constant of the medium.

P.T.O.



14. The solubility product of a sparingly soluble salt at 25°C is  $8 \times 10^{-15}$ . Find the solubility of the salt.
15. What are the models of electrical double layer at electrode-electrolyte interface? Explain.
16. What are the advantages of dropping mercury electrode?
17. Explain concentration polarization.
18. Find the EMF of the cell

$Zn / Zn^{2+}_{a=0.1} // Cu^{2+}_{a=0.01} / Cu$  the standard electrode potentials of Zn and Cu are - 0.767 and +0.334v respectively.

19. Explain 'Passivation'
20. Explain terms
  - a) Corrosion current
  - b) Corrosion potential.

### SECTION-C

Answer **Four** questions. Each question carries **3** marks. (4×3=12)

21. Derive an equation for the rate of entropy production for one component system with heat and matter transport.
22. Define partial molal volume. How would you find partial molal volume of NaCl in water at room temperature. Discuss.
23. Define mean ionic activity coefficient. Find the activity of the following electrolytes in terms of molal concentration and mean ionic activity coefficient.
  - a)  $MX_3$
  - b)  $M_3X_2$
24. Write Debye Huckel limiting law. How would you test the validity of the law? Discuss.
25. Derive Loppmann equation.
26. Discuss one of the theories of hydrogen overvoltage.
27. Draw Pourbaix diagram for Fe. Discuss.
28. Discuss the applications of electrochemical Impedance Spectroscopy.

**SECTION-D**

Answer 'a' or 'b' of each question. Each question carries 6 marks. (4×6=24)

29. a) i) How would you determine third law entropy of a gas? Discuss.  
ii) Define phenomenological coefficients. Show that direct coefficients always dominate indirect coefficients.

(OR)

- b) Draw phase diagram for a ternary solution with common ion hydrate formation. Discuss.

30. a) Derive Debye Huckel Onsager equation.

(OR)

- b) Discuss briefly.

- i) Osmotic coefficient  
ii) Applications of conductance measurements.

31. a) What is meant by liquid junction potential. How is it measured? Discuss

(OR)

- b) Define overvoltage. What are the contribution factors for overvoltage? Discuss

32. a) Discuss kinetics of corrosion.

(OR)

- b) Discuss the applications of Electrochemical Impedance spectroscopy in corrosion science.
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(2014 Admission Onwards)

CHEMISTRY

CHE 1C.03 : ORGANIC CHEMISTRY-I

Time : 3 Hours

Max. Marks : 60

**SECTION-A**

Answer **All** questions in one word or one sentence. Each question carries **One** mark. (8×1=8)

1. Which has higher pKa-*O*-hydroxy benzoic acid or *p*-hydroxy benzoic acid?
2. Bromobenzene when treated with \_\_\_\_\_ generates benzyne.
3. \_\_\_\_\_ is an example of an enantiotopic molecule.
4. Methylene cyclopropane is synthesized from cyclopropane by the \_\_\_\_\_ reaction.
5. Reaction of R-2- butanol with \_\_\_\_\_ yields R-2-chlorobutane.
6. An anti-periplanar geometry favours \_\_\_\_\_ elimination.
7. What product is formed when *cis*- diazobenzene is exposed to light?
8. Cis-trans isomerization of \_\_\_\_\_ is responsible for vision chemistry.

**SECTION-B**

Answer any **Eight** questions. Answer may be two or three sentences. Each question carries **Two** marks. (8×2=16)

9. Depict the structure of DABCO and quinuclidine. Why are they strong bases?
10. Compare the pKa of maleic acid to fumaric acid.
11. Explain homoaromaticity with an example.
12. Depict the structure of an axially chiral allene and a biphenyl derivative.
13. Illustrate the major product formed when 4-tBu cyclohexanone is reduced?

P.T.O.



14. What product is formed when benzyl phenyl ketone is treated with
- $\text{NH}_2\text{OH}$
  - $\text{PCl}_5$
  - Dilute acid.
15.  $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$  can be hydrolyzed much faster than pentyl chloride. Why?
16. Illustrate the Cope elimination reaction.
17. Give examples of two polar aprotic solvents depicting their structure.
18. Illustrate the Paterno Buchi reaction.
19. Mention any one photo reaction of Vitamin D.
20. Explain Di-pi-methane rearrangement.

### SECTION-C

Short paragraph questions. Answer any **Four** questions. Each question carries **Three** marks. (4×3=12)

21. Exemplify the following by providing a structure
- metallocene
  - Mesoionic compound
  - Singlet carbene.
22. How is anisole converted to 1,3-dimethoxy benzene?
23. What is atropisomerism? Provide examples and designate.
24. Illustrate Curtius and Schmidt rearrangement reactions.
25. Cyclohexanol on treatment with mesyl chloride yields A. The latter on treatment with a base and diethyl malonate yields B. Identify A and B.
26. Depict the Hoffmann and Saytzeff elimination reactions.
27. Give an example of a remote functionalization reaction.
28. How is singlet oxygen generated? Give an application.

### SECTION-D

Essay type questions. Answer **Four** questions. Each question carries **Six** marks. (4×6=24)

29. a) Compare and explain the aromaticity of thiophene, furan, pyrrole, pyridine, imidazole and pyrazole.



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K19P 1479

(OR)

- b) N, N-dimethyl aminopyridine is more basic than pyridine. Explain.
30. a) Designate the prochiral faces of benzaldehyde. What products are formed when benzaldehyde is treated with methyl magnesium bromide?

(OR)

- b) Illustrate the product formation when meso-2, 3-dibromobutane is treated with zinc.
31. a) What is the major product formed when 2-acetyloxy cyclohexane carboxylic acid ethyl ester is heated?

(OR)

- b) Illustrate
- i) Demjanov ring expansion and
  - ii) Beckmann rearrangement.
32. a) Explain the chemistry behind the vision process.

(OR)

- b) Illustrate photo Fries rearrangement and Norrish type II cleavage.
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