

Ph.D. Competitive examination ( Analytical Chemistry

NOTE : (10marks) for each question

دکتوراہ / تھمیلہ

Q1:A- In voltametric titration is the plot of (tick the correct variable)

diffusion current versus : time ( ), volume ( ), potential (E) ( ), Concentration ( ), weight ( ), Flow rate ( ) .

B- The condition for the occurrence of Rayleigh scattering is .....

While Mie scattering occurring when .....

C- CHNS Analyser is used ..... as a detector (tick the correct answer):

a- FID b- TCD c- ECD d- PMT e- photodiode f- IR- Detector g- Thermo Couple

Q2 : 1- The frequency of stretching vibrations is more than bending vibrations at IR

Spectroscopic due to : A-..... B-.....

2- Explain in a short brief ionization in MS by FAD & DART

3- The conductivity for 0.01M KCL solution if the resistance for KCL solution is 2171 ohm and for distilled water is 426 K ohm is ..... ((tick the correct answer):

a-  $3.58 \times 10^{-4}$  b-  $1.58 \times 10^{-4}$  c-  $4.58 \times 10^{-4}$  d-  $5.58 \times 10^{-4}$  e-  $1.58 \times 10^{-5}$  f-  $2.58 \times 10^{-6}$

Q3- A- Quantitative elemental analysis shows that the empirical formula of a

compound is  $C_2H_4ON_2$  . The molecular weight is found to be 360 . What is the molecular formula .....

B- In Jablonski diagram , the internal conversion occurs between .....

While the vibration relaxation occurs .....

And external conversion occurs .....

C- In CHN elemental analyser is used ..... to remove  $CO_2$  (tick the correct answer):

a-  $O_2$  gas b- He gas c- Ascarite Na  $ClO_4$  d-  $H_2$  gas e-  $N_2$  gas f- Ascarite NaOH  
H- Ascarite Mg  $ClO_4$

Q4 A- Give reasons for Preference of using :

- combustion in oxygen flask for analysis of element (Give one example)

- In IR Spectroscopy using Nujol oil or KBr through analysis of solid sample

B- Compare between : Accuracy & Precision

C- Auger Emission spectroscopy occurs .....

While continuous ( bremsstrahlung ) x-ray occurs.....

5- A- (tick the correct answer):

1- component A eluted at first while component B eluted at last , depending on :

\* D \*  $R_s$  \* H \* N \* Flow rate \*  $D_{gas}$  \*  $\alpha$  \*  $\mu$

2- The normal Chromatographic is depend on :

\* mobile phase more polarity from stationary phase

\* mobile phase less polarity from stationary phase

\* mobile phase non polarity

\* mobile phase the same polarity from stationary phase.

\* mobile phase not depending on polarity of stationary phase .

B- Explain Ultrasonic Nebulizer in AAS

Q6:A- Amplification of Hypo chloride ion by iodide is .....( Choose the correct answer )

a- 6 times b- 12 times c- 24 times d- 36 times e- 38 times f- 48 times

B- 3.5 g/l concentration of  $NH_4OH$  . The PH of this solution when  $k_b = 10^{-5}$  for  $NH_4OH$  is ...

a- 8 b- 9 c- 10 d- 11 e- 11.23 f- 12.34 g- 11.12 h- 9.24



**Q7-A- Amplification of  $As^{+5}$  by ..... is 12 times .( Choose the correct answer )**

- a- iodide ion   b- iodate ion   c- periodate ion   d- hydrogen peroxide  
e- Hydrazine   f- Bromide   g- iodine .

**B- Amplification of hydrazine by periodate ion is .....( Choose the correct answer )**

- a- 6 times   b- 12 times   c- 24 times   d- 36 times   e- 48 times   f- 38 times  
f- 58 times   h- 68 times

**C- How these pair of ions can be analysis and amplified : Bromide & Chloride**

**Q8 :A- Choose the correct answer :**

**1- Methone is used for determination of .....**

- a- carboxylic acid   b- Ketones   c- Hydroxyl compounds   d- Aldehydes  
e- Amino acid   f- acetic anhydride   g- Epoxide compounds  
g- amino compounds.

**2- The percentage of chloride ion in a sample weight 0.45 g which titrated by volhard method .18.5 ml of 0.1N  $AgNO_3$  were added when 2 ml of 0.15 N KSCN was needed for end point to be reach is .....**

- a - 8.23 %   b- 10 .23 %   c- 12 .23 %   d- 14.23%   e- 16.23 %   f-18.235   g- 25.23%

**3 -  $CS_2$  / 2-Ethyl hexaldehyde is used for determination of .....**

- a- secondary amine in the presence of primary amine  
b- carboxylic acid   c- secondary alcohol in the presence of primary alcohol  
d- primary amine in the presence of secondary amine  
e- primary amine in the presence of primary alcohol

**B - Suggest a useful analytical reactions for analysis of these pair :**

**ethylene glycol & glycerol**

**C- Suggest a useful analytical method for analysis of compound:**

**p-methoxy phenol ( P-  $HOC_6H_4OCH_3$  )**

**Q9 : A- Molecular Emission cavity analysis method in the presence of sodium bisulphite is used for analysis of .....( Give one example )**

**B- ( Choose the correct answer )**

**1- Dye LASER ( modulation LASER ) as a type of .....**

- a-Liquid state laser   b- gas state laser   c- fluid state laser   d- solid - gas state laser   e -Ionic state laser  
f- solid - liquid state laser   g- atomic state laser   h- gas - liquid state laser

**2- The wavelength of an excimer is usually in the .....**

- a- IR region   b- Micro wave region   c- NMR region   d- UV region   e-UV- VIS region  
F- NIR region   g- X- ray region

**3- In Thermal analysis , DTA, recorded .....**

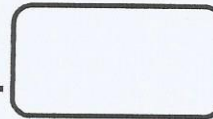
- a- Any change in weight between sample and reference  
b- Any difference in temperature between sample and reference  
c- Any same in temperature between sample and reference  
d- Any loss or added in energy until sample and reference are different in temperature  
e- Any same loss or added in energy until sample and reference are different in temperature

**Q10:A- Magnetron in microwave consist essentially of three components;**

**numerate them.**

- 1-  
2-  
3-





Put X or  $\sphericalangle$  For the following sentences and correct the wrong ones

- 1-  $PV/RT$  is called compression number which equal to values  $\leq 1$  for ideal gas and  $\geq 1$  for real gas. ( )
- 2- Photochemistry related to the chemical reaction enhanced by IR ray. ( )
- 3- First order rate equation is  $(\ln C_0/C = kt)$ , where  $k$  is the equilibrium constant. ( )
- 4- Electro oxidation reaction occur on anode in all electrical cell. ( )
- 5- Isothermal process include work in constant temperature & pressure. ( )
- 6- The units of rate constant is  $[time^{-1}][con^{n-1}]$  where  $n = \text{half life time}$ . ( )
- 7- Relation between rate constant & reciprocal temperature called Nernst eq. ( )  
Which written as.....
- 8- Catalysis rise the rate of reaction by increasing its activation energy barrier. ( )
- 9- Phosphoresces is similar with fluorescence. ( )
- 10- Michaelis constant have not any relation with equilibrium constant ( )





**Q1 Answer True or False**

- 1) In electrophilic substitution reaction pyridine is more reactive than benzene
- 2) The  $S_N1$  mechanism occurs in one step with inversion.
- 3) Reaction of ketone with Grignard reagent gives tertiary alcohol.
- 4) Halohydrins form when halogen is added to an alkene in the presence of peroxide.
- 5) Hofmann synthesis is between an amide and hypobromite.
- 6) In alkenes the Z isomer has the higher priority groups on the same side.
- 7) In  $^1\text{H-NMR}$  spectroscopy the phenolic hydrogen appears in the low field region.
- 8) A racemic mixture consists of equal parts of enantiomers.
- 9) Quinone reacts as a dienophile in a Diels-Alder reaction.
- 10) Pyrrole is more basic than pyrrolidine.

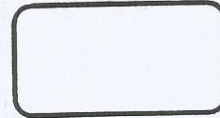
**Q2) Choose the right answer:**

- 1) Cannizzaro reaction gives:
  - a) Two alcohols
  - b) Aromatic acid and alcohol
  - c) Two aromatic acids
- 2) Anthracene is prepared from:
  - a) Benzene and phthalic anhydride
  - b) Benzene and succinic anhydride
  - c) Benzene and succinic acid
- 3) The more reactive carboxylic acid derivatives are:
  - a) Ester
  - b) Acid chloride
  - c) Acid anhydride

- 4) The Bischler – Napieralski synthesis is a method for synthesis:
- a) Quinoline                      b) Isoquinoline                      c) Benzoquinoline
- 5) Benzyne is:
- a) An unstable compound having a triple bond in benzene ring
- b) An unstable compound having a free radical in benzene ring
- c) An unstable compound having conjugated double bond with benzene ring
- 6) Cyclohexane has
- a) Planer conformation                      b) Chair and boat conformation
- c) Chair, boat and twist conformation
- 7) Deshielding is:
- a) An effect in NMR that cause a nucleus to absorb down field on the left
- b) An effect in NMR that cause a nucleus to absorb down field on the right
- c) An effect in NMR that cause a nucleus to absorb high field on the left
- 8) Wolf – Kishner reagent is:
- a) Zinc amalgam and acid    b) Zinc and acid    c) Hydrazine and base
- 9) Malonic ester ion is:
- a) Stable anion                      b) Unstable anion                      c) Stable cation
- 10)  $\alpha$  -  $\beta$  – Unsaturated carbonyl compounds undergo:
- a) Only electrophilic addition reaction
- b) Only nucleophilic addition reaction
- c) Electrophilic and nucleophilic addition reaction

**Good luck**





- 5- At the end of glycolysis, each molecule of glucose has yielded 2 molecules of \_\_\_\_\_, 2 molecules of \_\_\_\_\_, and a net of 2 molecules of \_\_\_\_\_.
- FAD; NAD<sup>+</sup>; ADP.
  - CO<sub>2</sub>; NAD<sup>+</sup>; ADP.
  - Lactic acid; ethanol; CO<sub>2</sub>.
  - Pyruvate; NADH; ATP.
- 6- Deamination is \_\_\_\_\_ of amino group.
- Removal.
  - Addition.
  - Supplementation.
  - None of these.
- 7- A polysaccharide which is often called animal starch is
- Starch.
  - Inulin.
  - Glycogen.
  - Dextrin.
- 8- Which of the following statements best describes an allosteric binding site?
- It is a binding site containing amino acids with aliphatic side chains.
  - It is a binding site that can accept a wide variety of differently shaped molecules.
  - It is a binding site, which is separate from the active site, and affects the activity of an enzyme when it is occupied by a ligand.
  - It is a description of an active site which has undergone an induced fit.
- 9- Absorbance at 280nm exhibited by protein is due to
- Aliphatic amino acids
  - All amino acids
  - Non-polar amino acids
  - Aromatic amino acids
- 10- What role does small nuclear RNA play in the synthesis of proteins?
- It catalyses the process.
  - It modifies messenger RNA molecules prior to protein synthesis.
  - It provides the genetic blueprint for the protein.
  - It translates the genetic code to a specific amino acid.





Choose the correct answer: (20 degree)

- 1- Polysaccharides are:
  - a) Polymers.
  - b) Acids.
  - c) Proteins.
  - d) Oils.
  
- 2- Which of the following statements is not true about receptors?
  - a) Most receptors are proteins situated in the cell membrane.
  - b) Receptors contain a hollow or cleft on their surface which is known as a binding site.
  - c) Receptors bind chemical messengers such as neurotransmitters or hormones.
  - d) Receptors catalyze reactions on chemical messengers.
  
- 3- Which of the following statements about the oxidative decarboxylation of pyruvate is correct?
  - a) The oxidative decarboxylation of pyruvate formed in aerobic glycolysis occurs in the cytosol.
  - b) The oxidative decarboxylation of pyruvate is catalyzed by the enzyme pyruvate decarboxylase.
  - c) The oxidative decarboxylation of pyruvate is reversible since there is a large decrease of free energy in the reaction.
  - d) The oxidative decarboxylation of pyruvate forms acetyl-CoA which is fed into the citric acid cycle.
  
- 4- Identify the strongest form of intermolecular bonding that could be formed involving the residue of the amino acid serine.
  - a) ionic bond
  - b) hydrogen bond
  - c) van der Waals interactions
  - d) none of the above





*Competition Examination for Ph.D Candidates in Inorganic Chemistry*

Q1. In the molecules  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  and  $\text{CH}_4$ .

- (a) The bond angles are same.
- (b) The bond distances are same.
- (c) The hybridizations are same.
- (d) The shapes are same.

Ans.

Q2. The pair of compounds having metals in their highest oxidation state is

- a-  $\text{MnO}_2$ ,  $\text{FeCl}_2$
- b-  $[\text{NiCl}_4]^{2-}$ ,  $[\text{CoCl}_4]^-$
- c-  $[\text{Fe}(\text{CN})_6]^{2-}$ ,  $[\text{Co}(\text{CN})_2]$
- d-  $[\text{MnO}_4]^-$ ,  $\text{CrO}_2\text{Cl}_2$ .

Ans.

Q3. The value of the 'spin only' magnetic moment for one of the following configurations is 2.84 BM. The correct one is :

- a-  $d^4$  (in strong ligand field)
- b-  $d^4$  (in weak ligand field)
- c-  $d^5$  (in strong ligand field)
- d-  $d^3$  (in weak as well as in strong fields)

Ans.



Q4. Which has maximum paramagnetic character ?

- a-  $[\text{Fe}(\text{CN})_6]^{4-}$       b-  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$       c-  $[\text{Cu}(\text{NH}_3)_4]^{2+}$       d-  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$

Ans.

Q5. A solution of potassium ferrocyanate would contain ions :

- a- 2      b- 3      c- 4      d- 5

Ans.

Q6. The crystal field Splitting energy for octahedral ( $\Delta_{o,h}$ ) and tetrahedral ( $\Delta_t$ ) complexes is related to :

- a-  $(\Delta_t) = (1/2) (\Delta_{o,h})$       b-  $(\Delta_t) = (4/9) (\Delta_{o,h})$       c-  $(\Delta_{o,h}) = 2\Delta_t$   
d-  $(\Delta_{o,h}) = (4/9) \Delta_t$

Ans.

Q7. Which one of the following statement is incorrect?

- (a) Greater the formation of ( $K_f$ ) of a complex ion, greater is its stability.  
(b) Greater the positive charge on the central metal ion, greater is the stability of the complex.  
(c) Greater is the basic character of the ligand, lesser is the stability of the complex.  
(d) Chelate complexes have high stability constants.

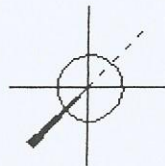
Ans.



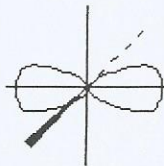


Q8. The probability area that best represents the shape of an atomic 3p orbital is...

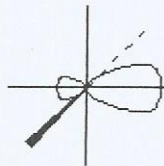
(a)



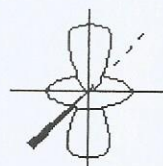
(b)



(c)



(d)



Ans.

