Con No. 309-11. **MM-2226**

(3 Hours) **[Total Marks:100]**

N.B. 1) **All** questions are **compulsory.**

2) Figures to the **right** indicate **full** marks.

3) Use of logarithmatic table/non programmable calculator is **allowed.**

Q.1 Select the most appropriate choice for the following: **40**

A) A chemical reaction becomes faster in the presence of a catalyst, because
a) it supplies additional energy to the reactants
b) it increases the number of collisions between the reactants
c) it stabilizes the product
d) it lowers the activation energy for the reactants.

B) The eigen functions are normalized when
a) $\int \psi_n {}^* \psi_m \, d\tau = 1$
b) $\int \psi_n {}^* \psi_m \, d\tau = 0$
c) $\int \psi_n {}^* \psi_m \, d\tau = 2$
d) $\int \psi_n {}^* \psi_m \, d\tau = 3$

C) The units of the molecular functions are
a) cm^{-1} b) s^{-1} c) $JK^{-1}mol^{-1}$ d) dimensionless

D) The triple point is the point where
a) three components are in equilibrium
b) the number of degree of freedom is three
c) the number of degree of freedom is zero
d) the number of degree of freedom is two.

E) The Wein effect is
a) conductance under high A.C. frequencies
b) conductance under high resistance
c) conductance under high D.C. frequencies
d) conductance under high potential gradient.

F) The molecules NF_3, CH_2Cl_2, H_2O, BF_3 can be best described by the following point groups respectively,
a) C_{3v}, C_{2v}, C_{2v}, D_{3h}
b) C_{3v}, D_{3h}, C_{2v}, C_{3v},
c) C_{3v}, C_{4v}, C_{3v}, D_{3h},
d) D_{3h}, C_{2v}, C_{2v}, C_{3v},

G) Although the Ag^+ / Ag couple has an E0 = 0.80 V, silver iodide, AgI is not reduced to metallic silver from its solution in KI. This is because
a) The bond between Ag- I is very strong.
b) Potassium iodide is a strong electrolyte
c) Ag(I) iodide is a strong electrolyte
d) Oxidation potential for formation of iodine is very high

H) The simplest of all the redox reactions are those that involve
a) Formation of ionic bonds
b) Formation of coordinate bonds
c) Transfer of electron
d) Transfer of proton

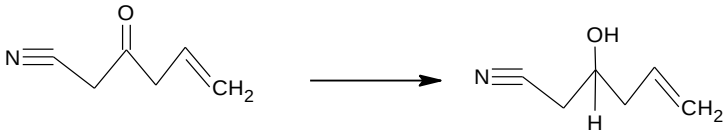
I) Stability of organometallic compounds is
a. The variable oxidation state of metal ion
b. High field strength of ligands
c. High electron density of ligands
d. Synergistic effects.

J) During the reduction of potassium dichromate to Cr (III), the potassium ion acts as
a. Reducing agent
b. Acceptor of electrons
c. Oxidising agent
d. Spectator ion

K) Which of the following alkenes would have the largest λ_{max}?

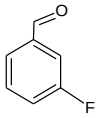
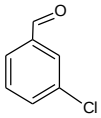
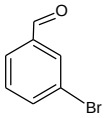
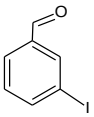
a)  b)  c)  d) 

L) Which of these reagents could accomplish the following reduction?

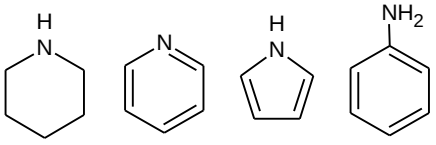


a) $NaBH_4$ b) $LiAlH_4$
c) H_2, poisoned catalyst, low pressure d) H_3O^+

M) Which of the following compounds will show the carbonyl stretching frequency a higher wave number

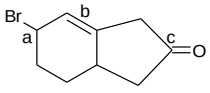
a)  b)  c)  d) 

N) Which of the following compounds is the best Bronsted Base?



(a) (b) (c) (d)

O) Which of the functional groups on the following molecule are susceptible to nucleophilic attack



a) a & b b) a & c c) b & c d) a , b & c

P) The unit of chemical shift in NMR is
a) nanometer b) centimetre c) angstrom d) tau

Q) NMR spectroscopy is studies in____ region of EMR.
a) UV b) IR c) Microwave d) Radiofrequency

R) The half wave potential for the reduction of metal complex is
a) zero
b) same as that for the reduction of metal ion
c) more negative than that for the reduction of metal ion
d) more positive than that for the reduction of metal ion

S) The figure of merit of precision is
a) absolute error b) coefficient of variation
c) analytical sensitivity d) relative error

T) 100 cm^3 of an aqueous solution was extracted with 10 cm^3 of an organic solvent and 80% of the solute was extracted in organic phase. The value of distribution ratio(D) must be
a) 40 b) 4 c) 400 d) 0.4

Q.2 Attempt any three of the following sub questions:

A) a) Write thermodynamic w=equation for the following terms **5**
i) First law of thermodynamics ii) Ideal gas equation
iii) Maximum work for isothermal reversible expansion of an ideal gas
iv) Enthalpy v) Free energy.

b) Describe the Lindenmann theory of unimolecular reactions. **5**

B) **a)** Explain why:
I. The electron transfer between $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ is much faster than between $[Co(NH_3)_6]^{3+}$ and $[Co(NH3)_6]^{2+}$. **2**

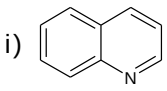
II. The bond angle H-N-H in ammonia is $106^0 45'$ while in PH_3 it is 94^0. **2**

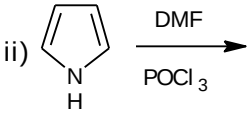
b) 25cm^3 of a 0.0500 molar solution of sodium oxalate reacted with 24.7 cm^3 of a solution of potassium permanganate 'C' in presence of excess sulphuric acid. 25.0 cm^3 of a 0.0250 molar solution of hydrazine (N2H4) when treated with excess of alkaline hexacyanoferrate (III) $[Fe(CN)_6]^{-3}$ solution gave hexacyanoferrate (II) $[Fe(CN)_6]^{-4}$and a product 'D'. The hexacyanoferrate (II) formed was oxidised to hexacyanoferrate (III) by 24.80 cm^3 of solution C. D did not interfere with the titration. What can you deduce concerning the identity of 'D'?' **4**

c) Titanium crystallises out in an hcp model. Calculate its density (Given a= b=295.3 pm; c=473 pm) **2**

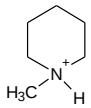
C) **a)** Deduce the structure of a compound C_7H_5O having following spectral data. Justify your answer.
IR: 3350 (broad), 1600, 1100, 760 cm^{-1}
PMR : δ 3.8 (1H), 4.3 (2H), 7.2 (5H)

b) Predict the products of the following reactions:

i) 

ii) 

c) Devise SN^2 reactions for the synthesis of following



D) a) Discuss cyclic voltammetry with respect to potential-time curve and current-voltage curve. **4**

b) What is meant by 'absorption edge' with reference to X-ray absorption spectra? Why is the wavelength of X- ray fluorescence greater than absorption edge? **3**

c) Describe the sample preparation methods used in IR spectroscopy. **3**

E) a) The ionic strength of 0.001 Molal sodium sulphate is 0.003. Calculate its mean activity coefficient. (Given: A= 0.509) **2**

b) Hydrolysis constant of Cu(II) is 5×10^{-6}. If one mole of copper sulphate is dissolved in one litre of water, what will be the pH of the solution? **3**

c) Compound shows the following mass spectral fragmentation pattern. Deduce the structure, explaining the formation of ions **2**
MS (m/z) : 121 (M+1, 9.9% of M), 120, 105, 77, 51.

d) When a constant current of 2.0 amperes was passed through an electrolytic cell for 20 minutes at NTP, nickel was deposited at cathode and oxygen was liberated at anode. Calculate the amount of nickel deposited and oxygen liberated at the electrodes. **3**
(Given: At.Wt. of nickel= 58.71, oxygen= 16, 1 Faraday= 96,500 coulombs)

Q.3 Attempt any two of the following sub-questions:

A) a) Discuss the Lippmann equation. How is it applied to get electrocapillary curves? **8**

b) Describe the stopped flow method for studying the kinetics of fast reactions. **7**

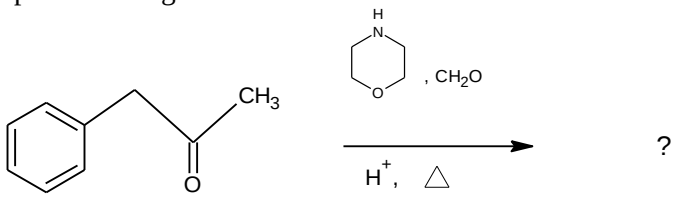
B) a) Write notes on
i) Fermi energy level ii) Calcium ion pump **8**

b) Discuss the rules for writing resonating structures. **4**

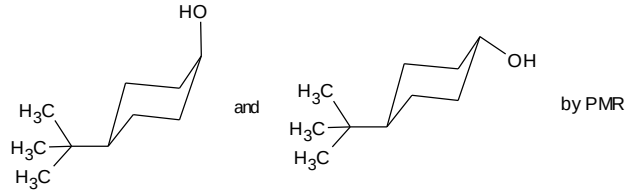
c) Comment on the Hume-Rothery rules.

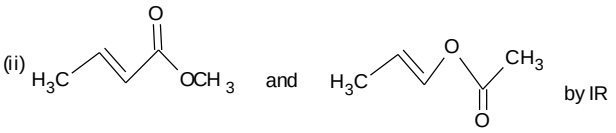
C) a) Assign the structure to compound which exhibits the given data: **6**
Mol. Formula: C_8H_7OCl
IR: 3000, 1690, 1600, 1500, 830 cm^{-1}
MS: M^- at 154/156 (3:1); 139/141 (3:1); 111/113(3:1)
PMR: 2.5 (3H, s); 7.35 (2H, d, J=8Hz); 7.9 (2H, d, J= 8Hz).

b) Predict the product and give the mechanism involved in the following reaction **4**



c) How will you distinguish between the following pairs by the indicated spectral method? **5**

(i) 

(ii) 

D) a) Draw a neat labelled diagram of hollow cathode lamp used in atomic absorption spectroscopy. Describe the dual wavelength spectrophotometer with a block diagram. **7**

b) What are WCOT and FSOT columns? Why the WCOT columns are replaced by FSOT columns. **4**

c) With the help of labelled diagram, describe the construction and working of differential refractive index detector. **4**

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