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Session: 2017 - 18

Delhi Technological University
B.Tech. 1st year Assignment

Assignment - 1

Q-1 The titration between EDTA and Ca^{2+} metal ion has a 1:1 mole ratio.

$$\text{millimoles of EDTA} = \text{millimoles of } \text{Ca}^{2+}$$

$$M_{\text{EDTA}} \times V_{\text{EDTA}} = \text{millimoles of } \text{Ca}^{2+} \text{ in 10 ml aliquot}$$

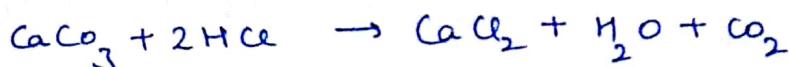
$$M_{\text{EDTA}} = 0.04988 \text{ M} \quad V_{\text{EDTA}} = 44.11 \text{ ml (given)}$$

$$(0.04988) (44.11) = 2.2046178$$

$$\text{millimoles ion of } \text{Ca}^{2+} \text{ in 10 ml aliquot} = 2.2046178$$

$$\text{millimoles of } \text{Ca}^{2+} \text{ in 250 ml aliquot} = \frac{2.2046178}{10} \times 250$$

$$= 55.115445$$



$$\text{millimoles of HCl present} = 25 \text{ ml} \times 6 \text{ M} = 150$$

even if the sample is 100% pure, maximum number of millimoles of CaCO_3 in egg shell can be $5.6313 \times 10^3 = 56.313 (< 75)$

$$(\text{ml. wt. CaCO}_3)^{100}$$

\Rightarrow HCl is limiting reagent

\Rightarrow All CaCO_3 becomes $\text{Ca}^{2+}\text{Cl}_2$ (for Ca^{2+} to be titrated).

$$\cancel{\text{wt. of CaCO}_3} \text{ millimoles of } \text{CaCO}_3 \text{ in sample} = \text{millimoles of } \text{Ca}^{2+}$$

$$= 55.115445$$

$$\text{wt. of } \text{CaCO}_3 \text{ in sample} = 55.11544 \times 10^{-3} \times 100 (\text{M}_{\text{CaCO}_3}) = 5.51155$$

$$\text{w/w \% of } \text{CaCO}_3 = \frac{\text{wt. of } \text{CaCO}_3 \text{ in sample}}{\text{wt. of sample}} \times 100 = \frac{5.5115544}{5.613} \times 100 = 98.19\%$$

\therefore Eggshell ~~sample~~ has 98.19% CaCO_3 w/w.

-(1)-

Q.2 At the equivalence point of the titration



$$\Rightarrow n_{\text{Na}_2\text{C}_2\text{O}_4} \times V_{\text{Na}_2\text{C}_2\text{O}_4} = n_{\text{KMnO}_4} \times V_{\text{KMnO}_4} \quad (\text{all volumes are in ml})$$

$$\Rightarrow n_{\text{Na}_2\text{C}_2\text{O}_4} \times M_{\text{Na}_2\text{C}_2\text{O}_4} \times V_{\text{Na}_2\text{C}_2\text{O}_4} = n_{\text{KMnO}_4} \times M_{\text{Na}_2\text{C}_2\text{O}_4 \text{ KMnO}_4} \times V_{\text{KMnO}_4}$$

$n_{\text{Na}_2\text{C}_2\text{O}_4} = 2$ (C changes from +2 to +3, and an Oxalate ion has 2 C's)

$n_{\text{KMnO}_4} = 5$ (MnO_4^- changes to Mn^{2+} +7 to +2)

$V_{\text{KMnO}_4} = 35.62 \text{ ml}$ (given)

$M_{\text{KMnO}_4} = .04 \text{ M}$ (given)

$$(M_{\text{Na}_2\text{C}_2\text{O}_4} \times V_{\text{Na}_2\text{C}_2\text{O}_4}) = \text{millimoles of } \text{Na}_2\text{C}_2\text{O}_4 = \frac{\text{wt. of } \text{Na}_2\text{C}_2\text{O}_4 \text{ in sample} \times 10^3}{\text{molecular wt. of } \text{Na}_2\text{C}_2\text{O}_4}$$

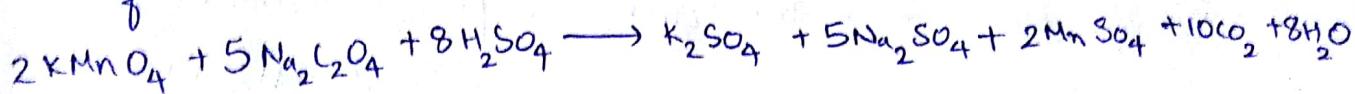
molecular wt. $\text{Na}_2\text{C}_2\text{O}_4 = 134 \text{ g mol}^{-1}$

$$2 \times \frac{\text{wt. of } \text{Na}_2\text{C}_2\text{O}_4 \times 10^3}{134} = 5 \times .04 \times 35.62$$

$$\text{wt. of } \text{Na}_2\text{C}_2\text{O}_4 = \frac{5 \times .04 \times 35.62 \times 134 \times 10^{-3}}{2} = .477308 \text{ g}$$

$$\% \text{ w/w of } \text{Na}_2\text{C}_2\text{O}_4 = \frac{\text{wt. of } \text{Na}_2\text{C}_2\text{O}_4}{\text{wt. of sample} (= .5116 \text{ g})} \times 100 = \frac{.477308}{.5116} \times 100 = 93.2971\%$$

Equation of titration:



This titration

PS: it is assumed that this titration has been carried out in acidic medium in which MnO_4^- can act as a self indicator.

- (2) +

Q3

Type Shape of the curve

Interpretation

1.

This type of curve exhibits no weight change throughout the complete temperature range used for analysis. The possible reason may be due to the fact that the thermal stability of sample is higher than temperature range.

2.



This type of curve exhibits mass loss region which is then followed by a constant line. TGA curves are of this type results during certain processes such as drying.

3.



single stage decomposition

4.



multi stage decomposition in which reaction can be resolved.

5.



multi stage decomposition in which reaction cannot be resolved.

6.



this curve shows increase in mass which may happen due to surface oxidation in the presence of an interacting atmosphere.

7.



surface oxidation followed by decomposition of products.

- (3) -

All curves contain majority only 2 regions

- (1) flatness : indicates region in which there is no weight loss a long plateau implies good thermal stability of material.
- (2) curved portion : indicate mass loss in type 2,3,4,5 and indicate mass increase in type 6 and initial increase then decrease in type 7.

Q-4

1. $\sigma \rightarrow \sigma^*$

σ^- are strongly bonded in the molecule and transition from σ bonding to σ^* (anti-bonding) this transition requires large energy corresponding to absorptions like in the region 120-200nm and in the molecule can be a saturated compound.

2. $\pi \rightarrow \pi^*$

it takes place in compound containing double or triple bond, the excitation of π^- 's requires less energy and hence transition occurs in longer wavelength region, 170-240nm and the compound must be alkene/ alkyne or conjugated system.

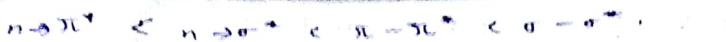
3. $n \rightarrow \pi^*$

In this transition an e^- of unshared e^- pair on a heteroatom is excited to π^* antibonding orbital, this transition occurs in double & bond involving heteroatom having unshared pair of e^- , like $C=O$, $C=S$, $GN=O$, eg:- aldehyde and ketone.

4. $n \rightarrow \sigma^*$.

The excitation of an e^- of an unshared pair of e^- (nonbonding) to σ^* orbital is called ($n-\sigma^*$) such transitions require less energy compared to $\sigma-\sigma^*$ transition, the compound undergoing this type of transition are saturated halides, ethers, etc.

-(4)-



(a). $\text{n} \rightarrow \sigma^*$. (~~$\pi \rightarrow \pi^*$~~).

(b). $\pi \rightarrow \pi^*$ and $\text{n} \rightarrow \pi^*$.

Q-5. The carboxylic group combines the features of alcohols and ketones because it has both O-H and C=O bond, covering a wide range between $2800 - 3500 \text{ cm}^{-1}$ for O-H stretch at the same time they also show stake-shaped band in the middle around 1710 cm^{-1} (C=O stretch).

- Aldehydes show strong, prominent, stake-shaped band around $1710 - 1720 \text{ cm}^{-1}$ and because they contain C-H where the carbon is sp^2 hybridised they a pair of medium strength bands about $2700 - 2800 \text{ cm}^{-1}$.
- Amides show medium stake shaped band in the middle of the spectrum 1710 cm^{-1} (C=O) and a very broad band in the range $3100 - 3500 \text{ cm}^{-1}$ (N-H) stretch.

Q-6 Hooke's Law

The vibrational motion of a diatomic molecule is akin to vibration of simple harmonic oscillator, whose restoring force (F) is proportional to the displacement x , i.e.

$$F = -kx$$

Hydrogen Bonding

The stronger the hydrogen bond, the longer the O-H bond, the lower the ~~vibration~~ vibration frequency and broader and more intense will be absorption band.

The N-H stretching frequencies of amines is also affected by H bonding as that of hydroxyl group but frequency shifts for amines are lesser than that of hydroxyl compounds.

Intermolecular H bonds give rise to broad bands, while ~~inter~~ intramolecular H bonding gives sharp and well defined ~~to~~ bonds.

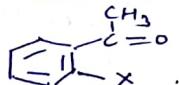
Electronic Effects → Inductive effect
The introduction of alkyl group (orange giving group) causes +I effect which results in weakening of the bond the force constant is lowered and wave number of absorption decreases.

Introduction of electronegative atom or group causes -I effect which increases the force constant and wave number rises.

Mesomeric Effect
It causes lengthening or weakening of a bond leading in lowering of absorption frequency.

Field effect

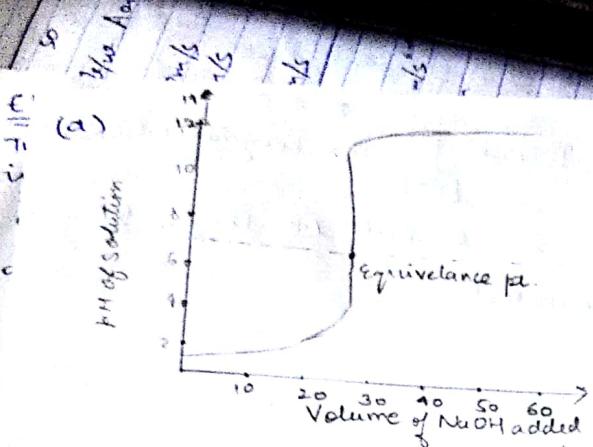
In ortho substituted compounds, the lone pair of electrons on 2 atoms influence each other through space interactions and change the vibrational frequency of both the groups.



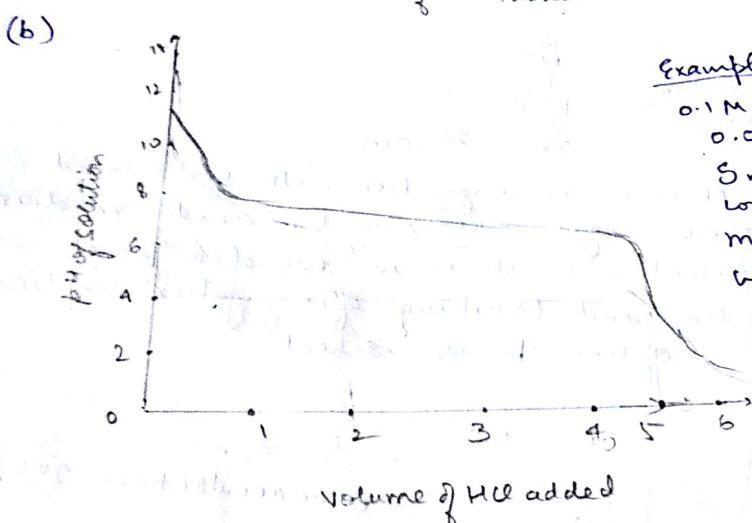
Q-7 The term 'titrimetric analysis' refers to quantitative chemical analysis carried out by determining the solution of accurately known concentration which is required to react quantitatively with a measured volume of a solution of the substance to be determined. The solution of accurately known strength is called standard solution.

Mandatory conditions

1. There must be a simple reaction which can be exactly expressed by a chemical equation; the substance to be determined should react completely with the reagent in stoichiometric proportions.
2. The reaction should be relatively fast. (All most ionic reactions are). Catalyst may be needed.
3. There must be some alteration in some physical or chemical property of solution at equivalence point.



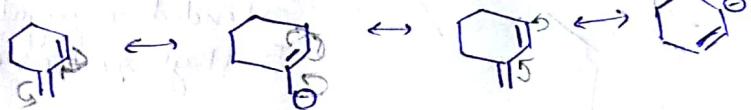
Example
In the given diagram 0.20 M NaOH is slowly added to some 0.1 M HCl equivalence pt. is obtained at 25 mL and end point can be detected by Phenolphthalein.



Example
0.1 M HCl is titrated with 0.05 M NH_3 of some ammonia. Some of HCl have been consumed to reach the mid point. which will be indicated by Methylorange.

Q-8

(1)



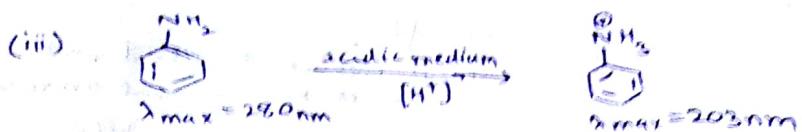
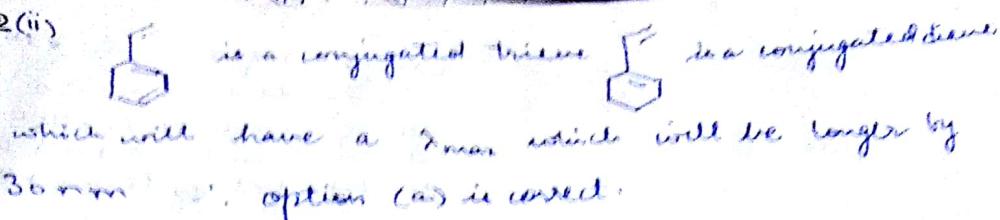
clearly option (a) displays resonance

but in option (b) resonance cannot be observed.

∴ option (a) will show Bathochromic shift.

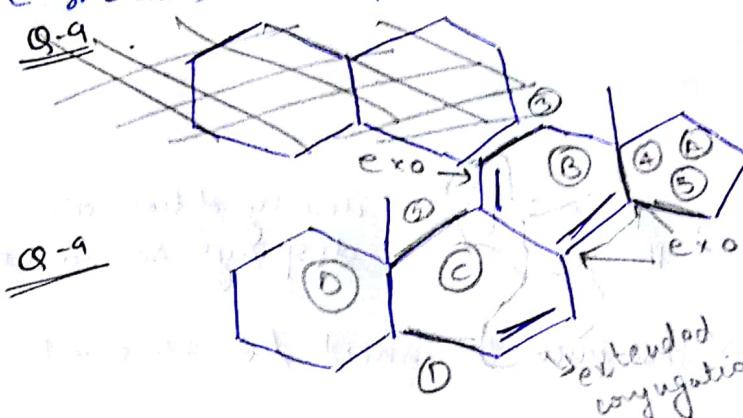
— (7) —

Q-8 (ii)



The lone pair of N was in conjugation with the π bond system of the benzene ring, however in the acidic medium, anilinium ion is formed in which it can clearly not contribute to conjugation and breaking of conjugation implies bathochromic shift. \therefore option (b) is correct.

Chrysanthemum Blue Shift

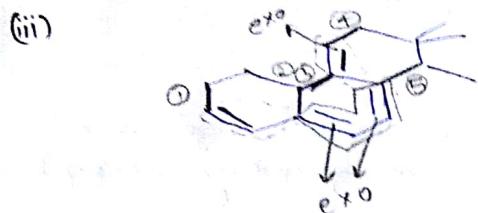


$$\begin{aligned}
 & \text{Homoannular diene: } 253\text{ nm} \\
 & \text{exo } \times 5 = 5 \times 3 = 15\text{ nm} \\
 & \text{extended conjugation} = 30\text{ nm} \\
 & \text{Sulfoxide residue} = 5 \times 5 = 25\text{ nm} \\
 & \quad + \\
 & \text{calculated } \lambda_{max} = 323\text{ nm}
 \end{aligned}$$

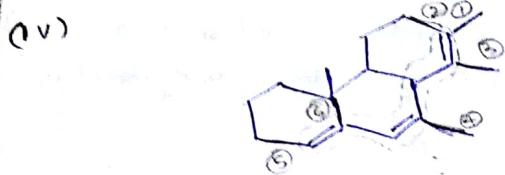
— (8) —



acyclic diene = 214 nm
 2 alkyl residues = $2 \times 5\text{ nm}$
 calculated $\lambda_{max} = 224\text{ nm}$



Homoannular diene : 253 nm
 2 carbon extended conjugation : $2 \times 30 = 60\text{ nm}$
 5 alkyl residues : $5 \times 5 = 25\text{ nm}$
 3 exocyclic C=C's : $3 \times 5 = 15\text{ nm}$
 Calculated $\lambda_{max} = 353\text{ nm}$



Heteroannular diene : $214 = 214\text{ nm}$
 1 carbon extended conjugation : $1 \times 30 = 30\text{ nm}$
 6 alkyl residues : $6 \times 5 = 30\text{ nm}$
 1 exocyclic C=C : $5 \times 1 = 5\text{ nm}$
 calculated $\lambda_{max} = 279\text{ nm}$

Q-10 (i) In symmetric stretching of C=C in ethylene the C₂H₄ molecule cannot absorb IR radiation because it has a totally symmetric vibration i.e. extending/contracting along its axis does not produce any dipole moment.

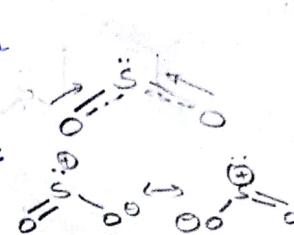
(ii) It ~~gives peaks~~ is IR active in both symmetric and asymmetric stretching along H-C-H bond. It is due to wagging out of plane wagging of H-C-H and scissoring.

(iii) N≡N is non polar and hence IR inactive.

-(9)-

Q-8(ii)

- (iv) symmetrical stretching does not alter the dipole moment of SO_2 and it is IR inactive according to empirical data so symmetrical stretching ~~not~~ barely alters dipole moment of SO_2 .



- (v) the symmetric stretching mode involves no dipole change, so is inactive in the IR region so no corresponding absorption of energy.

- * (vi) The carbon-carbon bond of ethane will not observe an IR stretch and is inactive as the C-C bond is symmetric.

Ans: (i) CH_3OH (ii) C_2H_4 (iii) $\text{CH}_3\text{CH}_2\text{Cl}$

- (10) -