Applied Chemistry
Assignment 1

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B2
317

Ques1 Explain back titration by taking the example of Volhard's method for the determination of chloride ions.

Solution In chemistry, back titration is a technique used to determine the strength of an analyte through the addition of a known molar concentration of excess reagent. A titration is then performed on the remaining amount of the known solution to determine how much is in excess and to measure the quantity consumed by the analyte.

Volhard's method for the determination of chloride ions uses a back titration with KSCN to determine the concentration of chloride ions in a solution. Before the titration an excess volume of $AgNO_3$ solution is added to the solution containing Cl^- ions, forming a precipitate of AgCl.

$$Ag^+ + Cl^- \longrightarrow AgCl(s)$$

The indicator Fe^{3+} (ferric ion) is then added and the solution is titrated with KSCN solution. The titrate remains pale yellow as the excess (unreacted) silver ions react with thiocyanate ions to form silver thiocyanate ppt.

$$Ag^+(aq) + SCN^-(aq) \longrightarrow AgSCN(s)$$

Once all the silver ions have reacted, the slightest excess of SCN^- ions react with Fe^{3+} to form a dark red complex.

$$Fe^{3+} + SCN^- \longrightarrow [FeSCN]^{2+}$$

The concentration of chloride ions is determined by subtracting the titration findings of the moles of silver ions that reacted with the thiocyanate from the total moles of $AgNO_3$ added.

Quess The percentage transmittance of an aqueous solution of an unknown compound is 20% at 25°C and 300nm for a 4×10^{-5} M solution in a 2cm long cell. Using this data, calculate

(i) The absorbance of the solution
(ii) The molar extinction coefficient of the compound

Solution Absorbance of the soln = $2 - \log(\%T)$

$= 2 - \log(20)$

$= 0.698$

Using Beer's Law

$0.698 = \epsilon LC$

$= \epsilon \times 2 \times 4 \times 10^{-5}$

$\Rightarrow \epsilon = \frac{0.698 \times 10^5}{8}$

$= 0.087 \times 10^5$ L/mol/cm.

Quess 3 The formaldehyde content of a pesticide preparation was determined by weighing 0.3124 g of the liquid sample into a flask containing 50mL of 0.0996 M NaOH and 50mL of 3% H_2O_2. On heating the following rxn. took place.

$$OH^- + HCHO + H_2O_2 \longrightarrow HCOO^- + 2H_2O$$

After cooling, the excess base was titrated with 23.3mL of 0.05250M H_2SO_4. Calculate the percentage of HCHO in the sample

Solution Moles of NaOH = $\frac{0.0996 \times 50}{1000}$

or 4.98 mmoles

Weight of H_2O_2 added = $\frac{3 \times 50}{100}$

$= 1.5$g.

Moles of H_2O_2 = $\frac{1.5}{34}$ = 44.1 mmoles

Moles of H_2SO_4 = 23.3 × 0.05250 mmoles
= 12.23 mmoles

Equivalents of H_2SO_4 (H+) = 1.223 meq × 2
= 2.446 meq.

Co reacted base = (4.98 − 2.446) meq.
= 2.534 meq.

Hence ~~eq.~~ moles of HCHO = 2.534 mmoles
= 76.02 mg.
= 0.076 g.

% strength of HCHO = $\frac{0.076}{0.3124} \times 100$
= 24.33%

Ques 4 Describe the principle of Differential Thermal Analysis (DTA) and its comparison with DSC.

Solution Differential Thermal Analysis is a thermoanalytic technique. In DTA, the material under study and an inert reference are made to undergo identical thermal cycles, while recording any temperature diff between sample and reference. This differential temperature is then plotted against time. Changes in the sample, either exothermic or endothermic, can be detected relative to the inert reference. Thus a DTA curve provides data on the transformations that have occurred, such as glass transitions, crystallisation, melting and sublimation. The area under a DTA peak is the enthalpy change and is not affected by the heat capacity of the sample.

DTA

1. The temperature of the sample is compared with that of a reference material as both are heated at a uniform rate

2. A DTA output plots $\Delta T = T_r - T_s$ vs temperature of the furnace (T_o)

3. It provides calorimetric accuracy at the temperature range of −190°C to 1,600°C.

4. The area under a peak in ordinary DTA is a complex function of sample geometry, heat capacity and heat losses.

5. No secondary power source is required

DSC

1. The heat energy is supplied at a varying rate to the sample or reference, so as to keep their temperature equal

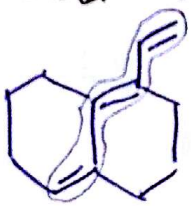
2. A DSC output plots heat energy supplied to the sample vs. identic temperature of two

3. It provides calorimetric accuracy in the temp. range of −170°C to 750°C

4. The area under a peak can be directly related to enthalpy change occuring

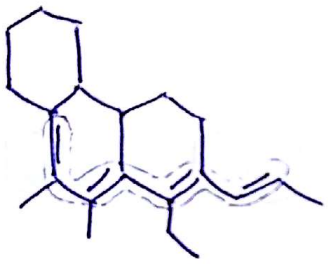
5. To keep the equal temperature of reference and sample, secondary power sources are required for supplying heat to either the sample or reference.

Ques Predict the λmax for the following compounds using the Woodward Fieser rule



Solution

Base value (Heteroanular system) = 215
Extended Conjugation = 30
Ring Residue (4) = 20
Exo to Ring (2) = 10
275nm



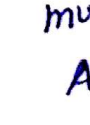
Solution

Base Value (Homo-anular system) = 253
Extended Conjugation (2) = 60
Allylic Substitution (4) = 20
Exo (2) = 10
Ring Residue (4) = 20
363nm

Ques 6: (a) Arrange the expected electronic transition for 2-pentanone in order of their increasing energy.

Solution

2-pentanone is a saturated Ketone so $\sigma \rightarrow \sigma^*$ transition must be present (<160nm)

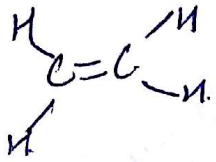
Also  group is present, so $\pi \rightarrow \pi^*$ (189 nm)
$n \rightarrow \pi^*$ (279nm)

Order of Increasing energy. $n \rightarrow \pi^* < \pi \rightarrow \pi^* < \sigma \rightarrow \sigma^*$

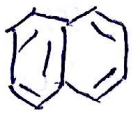
Ques 6. (b) Arrange the following compounds in order of their increasing wavelen of UV absorption maxima.

(a) Ethylene (b) Naphthalene (c) Anthracene (d) 1,3 Butadiene

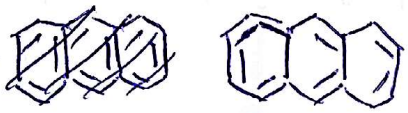
Ethylene :



Naphthalene :



Anthracene :



1,3 Butadiene

Order

As with increasing conjugation λ_{max} increases.

Ques] Indicate which of the following vibrations will be IR active or inactive.

Molecule	Vibration
(a) $CH_2=CH_2$	C=C stretching

IR inactive as $\mu = 0$ and $\frac{d\mu}{dx} = 0$

(b) $CH_2=CH_2$.	C–H stretching.

IR active as $\mu \neq 0$

(c) N_2.	N triple bond N stretching

IR inactive as $\mu = 0$

(v) CO_2. Symmetric Stretching.

The symmetric stretching mode involves no dipole change, so is inactive in the IR region

(vi) CH_3CH_3 C–C Stretching

IR inactive as no dipole change [Both C are identical]

Quest: A solution of sodium hydroxide contained 0.250 mol/dm^3. Using phenolphthalein indicator titration of 25cm^3 of this solution required 22.5cm^3 of a hydrochloric acid solution for complete neutralisation

(a) Write the equation for the titration reaction

$NaOH + HCl \longrightarrow NaCl + H_2O$

(b) What apparatus would you use to measure out:

(i) The sodium hydroxide solution.

Volumetric pipette

(ii) the hydrochloric acid solution

Burret

(c) What would you rinse your apparatus out with before doing the titration.

Ans Water

(d) What is the indicator color change at the end point.

The indicator changes from pink to colorless.

(e) Calculate the moles of hydrochloric acid neutralised.

No. of moles of HCl = No. of moles of NaOH.

No. of moles of HCl = $0.250 \times 25.0 \times 10^{-3}$

= 6.25mmoles

(f) Calculate the moles of sodium hydroxide neutralised.

No. of moles of NaOH = 0.250×25.0 mmoles

= 6.25mmoles

(g) Calculate the concentration of HCl in mol/dm³.

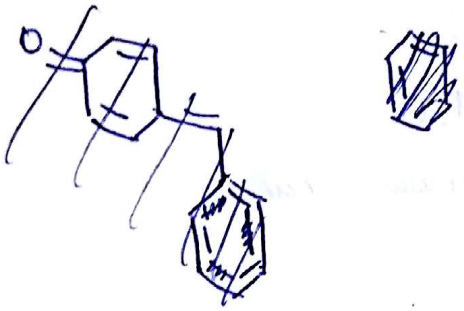
Concentration of HCl = $\frac{\text{No. of moles of HCl}}{\text{Volume of HCl.}}$

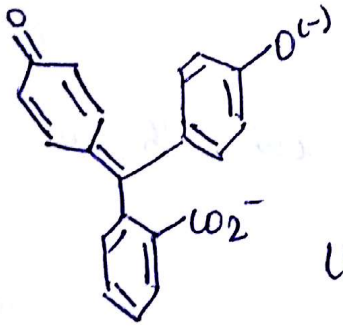
$= \frac{6.25 \times 10^{-3}}{22.5}$

$= 0.277 \text{ mol/dm}^3$

Ques 9 At pH > 12, Phenolphthalein becomes colorless. Explain with the help of molecular structure.

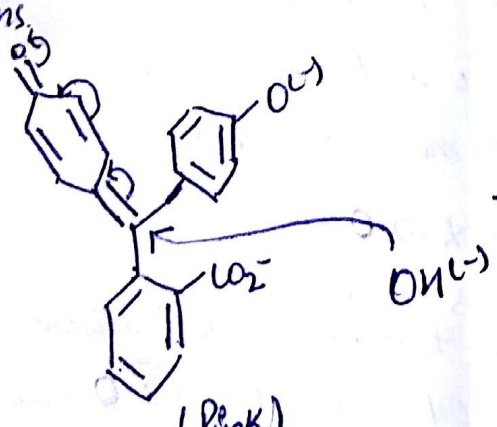
Solution In mild basic conditions the structure of phenolphthalein is.





(Pink)

But when excess of OH^- ions are present i.e. extreme basic conditions.



(Pink)

(Colorless)

Q.10 In Iodometric titration what should be the nature (oxidative / reductive) of the analyte? Explain with chemical reactions.

Solution In Iodometric titration, the nature of the analyte must be oxidative.

To a known volume of sample, an excess but known amount of iodide is added, which the oxidizing agent oxidises iodide to iodine. So

$$10I^{(-)} + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$$

The Iodine dissolves in the iodide-containing solution to give triiodide ions, which have a dark brown color

$$I^- + I_2 \longrightarrow I_3^{(-)}$$

The triiodide ion solution is then titrated against standard thiosulfate solution to give iodide again using starch indicator.

$$I_3^- + 2e^- \rightleftharpoons 3I^-$$

$$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$$

The Overall reaction is thus

$$I_3^- + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 3I^-$$

The disappearance of deep blue color due to the decomposition of the iodine-starch clathrate marks the end point.