Applied Chemistry (AC102)

Assignment -1.

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Que 1 Explain back titration by taking the example of volhard's method for determination of chloride ions.

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

Volhard's method for 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 chlorine of $AgNO_3$ soln is added to 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 silver ions react with thiocynate ions to form silver thiocynate ppt.

$$Ag^+ + SCN^- \longrightarrow AgSCN.$$

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

Moly

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

i) The absorbance of soln.

ii) The molar extinction coefficient of compound.

Ans Absorbance of soln = 2 − log (%T)

= 2 − log(20)

= 0.698.

Using Beer's Law.

0.698 = eLC

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

$\Rightarrow e = \frac{0.698 \times 10^5}{8} = 0.087 \times 10^5$ L/mol/cm.

Q.3 The formaldehyde content of a pesticide preparation was determined by weighing 0.3124 g of liquid sample into a flask containing 50 ml of 0.0996 M NaOH & 50 ml of 3% H_2O_2. On heating, the following took place:-

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

After cooling the excess base was titrated with 23.3 ml of 0.05250 M H_2SO_4. Calculate the % of HCHO in sample

Ans Moles of NaOH = $\frac{0.0996 \times 50}{1000}$ or 4.98 m moles.

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.

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Moles of H_2SO_4 $= 23.3 \times 0.05250$ mmoles

$= 12.23$ mmoles.

Equivalents of H_2SO_4 (H^+) $= 1.223$ meq $\times 2$

$= 2.446$ meq.

reacted base $= (4.98 - 2.446)$ meq.

$= 2.534$ meq.

Hence moles of HCHO $= 2.534$ mmoles.

$= 76.02$ mg $= 0.076$ g.

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

$= 24.33\%$.

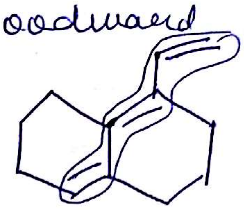
Q.4 Describe the principle of differential thermal analysis (DTA) & its comparisson with DSC.

Ans Differential Thermal Analysis is a theromonalytic technique. In DTA, the material under study & an inert reference are made to undergo identical thermal cycles, while recording any temp. difference b/w sample & reference. This differential temp. 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 occured, 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.

Q...

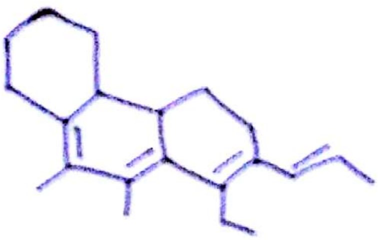
DTA	DSC
1) The temp. of sample is compared with that of a reference material as both are heated at uniform rate.	1) The heat energy is supplied at a varying rate to sample on reference, so as to keep their temperature equal.
2) A DTA output plots $\Delta T = T_r - T_s$ vs temp. of furnace (T_0)	2) A DSC output plots heat energy supplied to sample vs identic. temp. of two.
3) It provides colorimetric accuracy of temp range of $-190°C - 1600°C$.	3) It provides colorimetric accuracy in temp. range of $-170° - 750°C$.
4) The area under peak in ordinary DTA is complex f^n of sample geometry, heat capacity & heat losses	4) The area under a peak can be directly related to enthalpy change occuring.

Q-5 Predict the λmax for following compounds using the woodward Fiser rule.



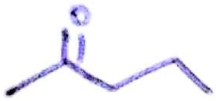
Ans Base value = 215
Extended configation = 30.
Ring Residue (4) = 20
Exo to Ring (2) = 10

275 nm



Ans Base value = 253
Extended conjugation (2) = 60
Allylic substitution (4) = 20
Exo (2) = 10
Ring Residue (4) = 20
363 nm

Q.6 a) Arrange the expected electronic transition for 2-pentanone in order of incr. energy

Ans 

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

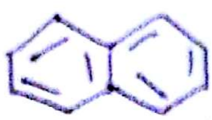
Also  gp. is present, so $\pi \rightarrow \pi^*$ (189 nm)
$n \rightarrow \pi^*$ (279 nm)

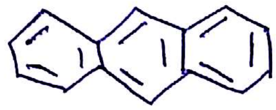
Order of inc energy $n \rightarrow \pi^* < \pi \rightarrow \pi^* < \sigma \rightarrow \sigma^*$

b) Arrange the following compds in order of their inc wavelength of UV absorption

a) Ethylene b) Napthlene c) Anthracene d) 1-3 Butadiene

Ans Ethylene :- 

Napthlene :- 

Anthrascene : 

1, 3 Butadiene : 

Order :- Ethylene < 1, 3 Butadiene < Napthlene < Anthrascene.

Q. 7 Indicate which of following vibrations will be IR active or inactive.

Molecule | Vibration.

a) $CH_2=CH_2$ — $C=C$ stretching

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

b) $CH_2=CH_2$ — $C-H$ stretching

IR active as $\mu \neq 0$

c) N_2 — N triple N stretching.

IR inactive as $\mu = 0$

d) CO_2 — Symmetric stretching

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

Q. 8 A solution of sodium hydroxide contained 0.250 mol/cm³. Using phenolpthelein indicator titration of 25 cm3 of this, solution required 22.5 cm³ of a hydrochloric acid solⁿ for complete neutralisation

a) Write the eqⁿ for titration.

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

b) what apparatus would you use to measure out.

i) The sodium hydroxide solⁿ.

Ans. volumetric pipette.

ii) HCl solⁿ.

Ans burret.

c) what would you rinse your apparatus but with before doing the titration.

Ans water

d) Calculate the moles of NaOH neutralised.

No. of moles of NaOH $= 0.250 \times 25.0$

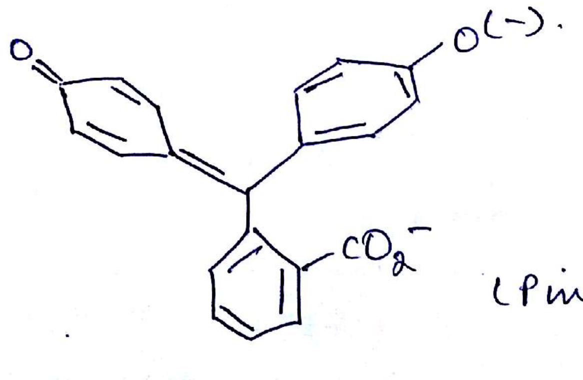
$= 6.25$ mmoles.

e) Calculate the conc. of HCl in mol/dm³.

$$\text{conc. of HCl} = \frac{6.25 \times 10^{-3}}{22.5} = 0.277 \text{ mol/dm}^3$$

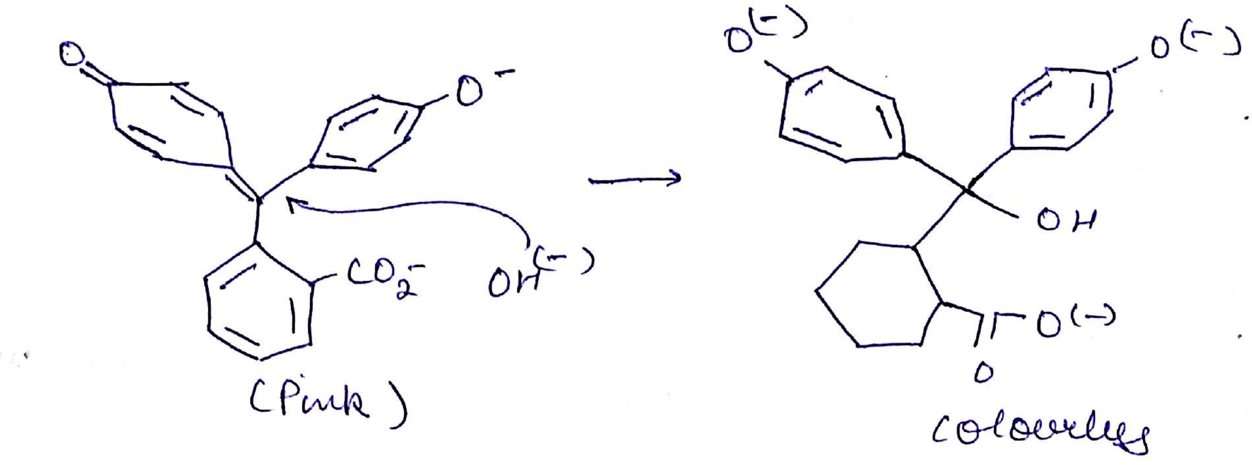
Q.9 At pH > 12, phenolpthalein becomes colorless. explain with the help of molecular structure.

Ans. In mild basic conditions, the structure of phenolpthalein is.



(Pink)

But when excess of OH^- ions are present.



Q. 10 In iodometric titration, what should be nature of analyte? Explain with chemical rxns.

Ans In iodometric titration, the nature of analyte must be oxidative.

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

eg. $I^- + 2MnO_4^- + 10H^+ \longrightarrow 2Mn^{2+} + I_2 + 8H_2O$.

The iodine dissolves in the iodide-containing soln to give triiodide ions, which have a dark brown colour

$I^- + I_2 \rightarrow I_3^-$

The triiodide ion soln is then titrated agnst. std. thiosulphate to give iodide again.

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

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

The overall rxn is thus.

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