30

Principles Related to Practical Chemistry

TOPIC 1

Detection of Extra Elements and Functional Groups

01 Which one of the following tests used for the identification of functional groups in organic compounds does not use copper reagent ?

[2021, 27 Aug Shift-II]

(a) Barfoed's test
(b) Seliwanoff's test
(c) Benedict's test
(d) Biuret test for peptide bond

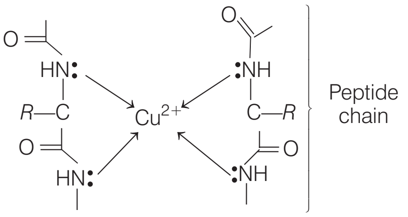
Ans. ***(b)***

Barfoed's test is used to detect monosaccharides.
In this test, the aldehyde group of monosaccharides reduces Cu(II) acetate to Cu(I) oxide which result in the formation of brick red ppt.

$$RCHO + 2\,Cu^{2+} + H_2O \longrightarrow RCOOH + \underset{\text{(ppt.)}}{Cu_2O}\downarrow + 4H^{+}$$

Benedict's test is used to test the presence of reducing sugar. Copper (II) sulphate is used in Barfoed's test.

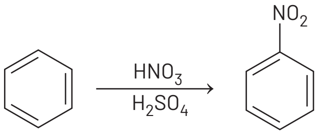
Biuret test is used to test the presence of peptide bond. The biuret reagent contains hydrated copper sulphate, sodium hydroxide and Rochelle salt (sodium-potassium tartarate). When the aqueous, solution of protein is treated with this reagent, the solution turns purple confirming the presence of amide bond.



Chelated complex of Cu^{2+} ions formed gives purple colour to the solution.

So, correct answer is option (b) Seliwanoff's test which is used to distinguish between ketoses and aldoses. The Seliwanoff's reagent contains resorcinol and HCl.

02



In the above reaction 3.9 g of benzene on nitration gives 4.92 g of nitrobenzene. The percentage yield of nitrobenzene in the above reaction is .... % (Round off to the nearest integer).
(Given, atomic mass C : 12.0 u, H : 1.0 u, O : 16.0 u, N : 14.0 u)

[2021, 17 March Shift-I]

Ans. ***(80)***

$$C_6H_6 \xrightarrow[H_2SO_4]{HNO_3} C_6H_5NO_2 \qquad \text{(Molar mass} = 123)$$

$$\text{Moles of } C_6H_6 = \left(\frac{3.9}{78}\right) = 0.05$$

So, moles of $C_6H_5NO_2$ formed should be $\frac{3.9}{78}$.

$$\text{Mass of } C_6H_5NO_2 = \text{Moles} \times \text{Molar mass}$$

$$= \frac{3.9}{78} \times 123 = 6.15\text{ g}$$

By conserving moles of carbon, mole or $C_6H_5NO_2$.

$$\%\text{ yield} = \frac{\text{Weight actually formed}}{\text{Weight theoretical}} \times 100$$

$$= \frac{4.92}{6.15} \times 100 = 80\%$$

03 In Duma's method of estimation of nitrogen, 0.1840 g of an organic compound gave 30 mL of nitrogen collected at 287 K and 758 mm of Hg pressure. The percentage composition of nitrogen in the compound is .... (Round off to the nearest integer).
[Given: Aqueous tension at 287 K = 14 mm of Hg]

[2021, 16 March Shift-II]

Ans. ***(19)***

Given, mass of organic compound 0.1840 g
Total pressure = 758 mm of Hg
Aqueous tension = 14 mm of Hg

Partial pressure of dry $N_2 = 758 - 14 = 744$ mm of Hg

For N_2,

$$V = 30\text{ mL} = 0.03\text{ L}$$
$$T = 287\text{ K}$$
$$p = 744\text{ mm of Hg} = \frac{744}{760}\text{ atm}$$

So, moles of N_2 $(n) = \frac{pV}{RT} = \frac{744}{760} \times \frac{0.03}{0.0821 \times 287}$

$$n = 1.25 \times 10^{-3}\text{ moles of } N_2$$

Weight of N_2 = Moles × Molar mass

$$= 1.25 \times 10^{-3} \times 28 = 35 \times 10^{-3}\text{ g}$$

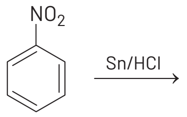
% composition of N_2

$$= \frac{\text{Mass of } N_2}{\text{Mass of organic compound}} \times 100 = \frac{35 \times 10^{-3}}{0.1840} \times 100 = 19\%$$

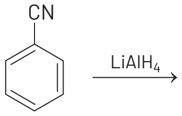
04 The Kjeldahl method of nitrogen estimation fails for which of the following reaction products?

[2020, 3 Sep Shift-I]

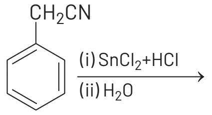
I.



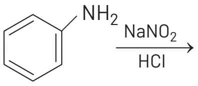
II.



III.



IV.



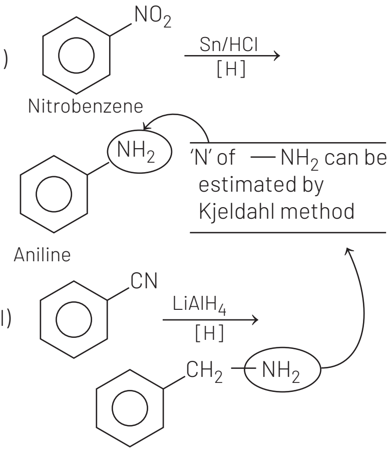
(a) III and IV (b) I and IV (c) I, III and IV (d) II and III

Ans. ***(a)***

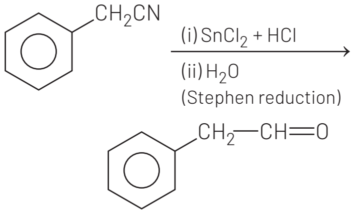
Complete reactions I, II, III, IV are as follows :

(I)

(II)



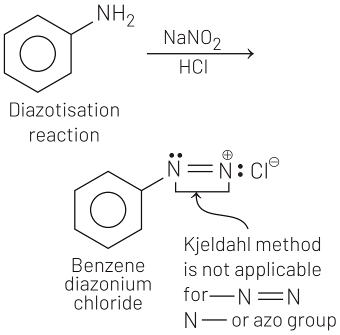
(III)



(2-phenyl ethanal)

This compound does not contain 'N'. So, Kjeldahl method is not applicable.

(IV)



So, products of reactions (c) and (d) (option-a) fail to give Kjeldahl's method. So, option (a) is correct.

05 The correct match between Item I and Item II is

	Item I		**Item II**
A.	Ester test	P.	Tyr
B.	Carbylamine test	Q.	Asp
C.	Phthalein dye test	R.	Ser
		S.	Lys

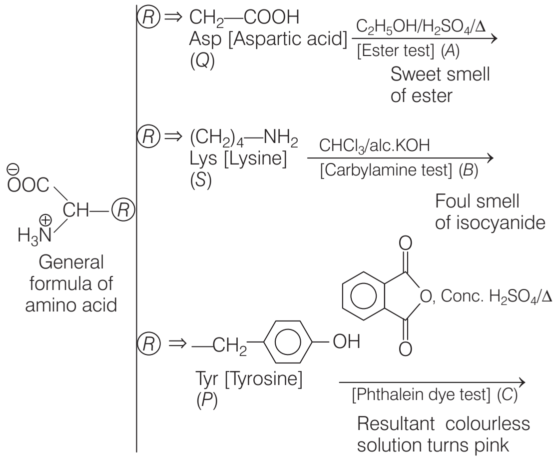
[2019, 11 Jan Shift-II]

(a) A → Q; B → S; C → R
(b) A → R, B → Q; C → P
(c) A → R; B → S; C → Q
(d) A → Q; B → S; C → P

Ans. ***(d)***

The correct match is :

A → (Q); (B) → (S) (C) → (P)



(A) Ester test confirms the presence of —COOH group.

(B) Carbylamine test confirms the presence of —NH_2 group (1°).

(C) Phthalein dye test confirms the presence of phenolic —OH group.

TOPIC 2

Chemistry Involved in Organic and Inorganic Compounds

06 An inorganic compound 'X' on treatment with concentrated H_2SO_4 produces brown fumes and gives dark brown ring with $FeSO_4$ in presence of concentrated H_2SO_4. Also compound 'X' gives precipitate 'Y', when its solution in dilute HCl is treated with H_2S gas. The precipitate 'Y' on treatment with concentrated HNO_3 followed by excess of NH_4OH further gives deep blue coloured solution, compound 'X' is **[2021, 20 July Shift-I]**

(a) $Co(NO_3)_2$ (b) $P(NO_2)_2$
(c) $Cu(NO_3)_2$ (d) $Pb(NO_3)_2$

Ans. ***(c)***

Compound 'X' is copper nitrate, i.e. $Cu(NO_3)_2$ is an inorganic compound. On treatment with concentrated H_2SO_4 produces brown fumes and gives dark brown ring with $FeSO_4$ in presence of concentrated H_2SO_4. Chemical reaction is as follows

$$\underset{\substack{X \\ \text{(Anion)}}}{NO_3^-} + \underset{\text{(Conc.)}}{H_2SO_4} \longrightarrow \underset{\text{(Brown fumes)}}{NO_2\uparrow} + H_2O$$

$$\underset{\text{(Sol)}}{FeSO_4} + \underset{\text{(Conc.)}}{H_2SO_4} + \underset{X}{NO_3^-} \longrightarrow \underset{\text{(Dark brown)}}{[Fe(H_2O)_5(NO)]}$$

Cu^{2+} is a group II cation with group II reagents (HCl/H_2S), it gives black coloured precipitates. These precipitates gives blue colour solution on treatment with HNO_3 followed by excess of NH_4OH.

$$\underset{\substack{X \\ \text{(Cation)}}}{Cu^{2+}} + \underset{\text{(Group-II, reagent)}}{(\text{Dil } HCl + H_2S)} \longrightarrow \underset{\substack{\text{(Black ppt.)} \\ Y}}{CuS\downarrow}$$

$$\underset{Y}{CuS} \xrightarrow{\text{Conc. } HNO_3} \underset{\substack{X \\ \text{(Soluble)}}}{Cu(NO_3)_2} + NO_2 + H_2SO_4 + H_2O$$

$$\xrightarrow{\text{Excess } NH_4OH \text{ sol.}} \underset{\text{(Deep blue colour)}}{[Cu(NH_3)_2]^{2+}}$$

$$\therefore \quad X \longrightarrow \underset{\text{Copper nitrate}}{Cu(NO_3)_2}$$

07 Match List-I with List-II.

	List-I (Test / Reagents / Observation(s))		**List-II** (Species detected)
A.	Lassaigne's test	(i)	Carbon
B.	Cu(II) oxide	(ii)	Sulphur
C.	Silver nitrate	(iii)	N, S, P, and halogen
D.	The sodium fusion extract gives black precipitate with acetic acid and lead acetate	(iv)	Halogen specifically

The correct match is **[2021, 16 March Shift-II]**

(a) A-(iii), B-(i), C-(ii), D-(iv)
(b) A-(i), B-(iv), C-(iii), D-(ii)
(c) A-(iii), B-(i), C-(iv), D-(ii)
(d) A-(i), B-(ii), C-(iv), D-(iii)

Ans. ***(c)***

(A) Lassaigne test is used to detect N, S, P, *X* elements.

The elements present in the compound are converted from covalent form into the ionic form by fusing the compound with sodium metal. Following reactions take place.

$$Na + C + N \xrightarrow{\Delta} NaCN$$

$$2Na + S \xrightarrow{\Delta} Na_2S$$

$$Na + X \xrightarrow{\Delta} NaX \quad (X = Cl, \text{ Br or I})$$

(B) Carbon and hydrogen are detected by heating the compound with copper (II) oxide.

$$C + 2CuO \longrightarrow 2Cu + CO_2$$

$$2H + CuO \longrightarrow Cu + H_2O$$

(C) Halides are detected by silver nitrate.

They form precipitate of Ag*X*except fluorine.

$$Ag^+(aq) + X^-(aq) \longrightarrow AgX(s)$$

(D) Sodium fusion extract gives black precipitate of PbS with acetic acid and lead acetate to confirm the presence of sulphur.

$$Na_2S + (CH_3COO)_2Pb \longrightarrow \underset{\text{Black ppt.}}{PbS} + 2CH_3COONa$$

08 Seliwanoff test and xanthoproteic test are used for the identification of .... and .... respectively. **[2021, 26 Feb Shift-II]**

(a) aldoses, ketoses (b) proteins, ketoses
(c) ketoses, proteins (d) ketoses, aldoses

Ans. ***(c)***

Seliwanoff and xanthoproteic tests are used for the identification of ketoses and proteins respectively.

Seliwanoff test It is a chemical test which distingusihes between aldose sugars (e.g. glucose and maltose) and ketose sugars (e.g., fructose and sucrose). The test is based on the principle that, when heated with acid, ketoses are more readily dehydrated than aldoses. The reagents used in the test consist of conc. HCl and resorcinol.

For ketoses, a deep cherry red colour is formed rapidly indicating a positive test.

Xanthoproteic test It is qualitative test to detect the presence of protein soluble in a solution using HNO_3.

In this test, solution of protein is first heated with conc. HNO_3 and then the mixture is neutralised by 40% NaOH solution. If the colour changes from yellow to orange, this confirms presence of a protein.

$$\text{Protein solution} \xrightarrow[\text{(ii) 40\% NaOH}]{\text{(i) Conc. } HNO_3/\Delta} \text{Yellow colouration which}$$

finally changes into orange colour.

09 Which of the following is a false statement?

(a) Carius tube is used in the estimation of sulphur in an organic compound **[2021, 26 Feb Shift-I]**

(b) Carius method is used for the estimation of nitrogen in an organic compound

(c) Phosphoric acid produced on oxidation of phosphorus present in an organic compound is precipitated as $Mg_2P_2O_7$ by adding magnesia mixture

(d) Kjeldahl's method is used for the estimation of nitrogen in an organic compound

Ans. ***(b)***

Statement (b) is false whereas all other statements are true.

There are two methods for estimation of nitrogen in an organic compound which are Duma's method and Kjeldahl's method.

So, the statement in option (b) is false.

10 Which of the following compound is added to the sodium extract before addition of silver nitrate for testing of halogens? **[2021, 25 Feb Shift-II]**

(a) Hydrochloric acid	(b) Sodium hydroxide
(c) Nitric acid	(d) Ammonia

Ans. ***(c)***

Nitric acid is added to sodium extract before addition of silver nitrate for testing halogens. Because it decomposes NaCN and Na_2S or else they interfere in the test.

The reaction are as follows :

$$NaCN + HNO_3 \longrightarrow NaNO_3 + HCN\uparrow$$

$$\underset{\text{Sodium extract}}{Na_2S} + \underset{\text{Nitric acid}}{HNO_3} \longrightarrow NaNO_3 + H_2S\uparrow$$

11 On heating compound (*A*) gives a gas (*B*) which is a constituent of air. This gas when treated with H_2 in the presence of a catalyst gives another gas (*C*) which is basic in nature.

(*A*) should not be **[2020, 2 Sep Shift-I]**

(a) NH_4NO_2	(b) $(NH_4)_2Cr_2O_7$
(c) NaN_3	(d) $Pb(NO_3)_2$

Ans. ***(d)***

(*A*) can be NH_4NO_2 or $(NH_4)_2Cr_2O_7$ or NaN_3 but not $Pb(NO_3)_2$ because each option a, b, c on heating liberates N_2 gas (*B*).

$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$$

$$2NaN_3 \xrightarrow{\Delta} 3N_2 + 2Na$$

But, $Pb(NO_3)_2$ on heating liberates NO_2 and O_2.

$$2Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + 4NO_2 + O_2$$

N_2 is a constituent of air ($N_2 = 78\%, O_2 = 21\%$ by volume). It reacts with H_2 in presence of a catalyst to give ammonia NH_3(*C*) gas which is basic in nature.

$$N_2 + 3H_2 \xrightarrow[\text{Fe (catalyst)}]{\text{200 atm, 773 K}} 2NH_3$$

12 If you spill a chemical toilet cleaning liquid on your hand, your first aid would be **[2020, 2 Sep Shift-II]**

(a) vinegar	(b) aqueous NaOH
(c) aqueous $NaHCO_3$	(d) aqueous NH_3

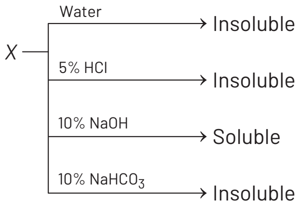
Ans. ***(c)***

Toilet cleaning liquid contains mainly HCl and surfactants like classical ATX. HCl is corrosive to our skin. So, it should be removed immediately.

The first aid for removal of HCl should be basic in nature. But NaOH is a hard base whereas NH_4OH is a very soft base. So, the best substance to remove the spill (HCl) is $NaHCO_3$.

$$HCl + NaHCO_3 \longrightarrow NaCl + CO_2\uparrow + H_2O$$

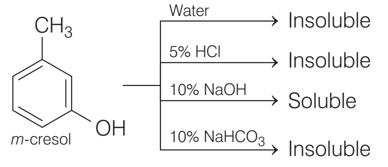
13 An organic compound *X* showing the following solubility profile is **[2019, 8 April Shift-I]**



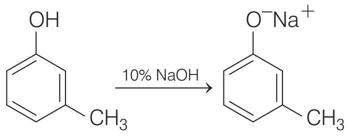
(a) *o*-toluidine	(b) oleic acid
(c) *m*-cresol	(d) benzamide

Ans. ***(c)***

m-cresol is the organic compound that shows the following solubility profile.



m-cresol on reaction with 10% NaOH forms 3-methyl sodiumphenoxide ion.



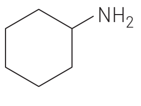
It does not react with H_2O, 5% HCl and 10% $NaHCO_3$.

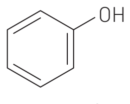
Oleic acid ($C_{18}H_{34}O_2$) is soluble in 10% NaOH and 10% $NaHCO_3$ due to the presence of COOH group.

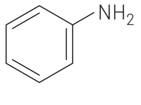
Benzamide ($C_6H_5\overset{\overset{O}{||}}{C}NH_2$) is insoluble in 5% HCl, 10% NaOH and 10% $NaHCO_3$ due to the presence —$CONH_2$ group. *o*-toluidine is soluble in 5%. HCl due to presence of basic group (—NH_2) attached to ring.

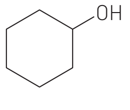
14 The organic compound that gives following qualitative analysis is **[2019, 9 April Shift-I]**

Test	Inference
(i) Dil. HCl	Insoluble
(ii) NaOH solution	Soluble
(iii) Br_2 /water	Decolourisation

(a) 

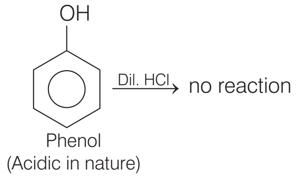
(b) 

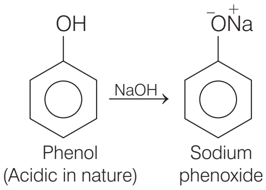
(c) 

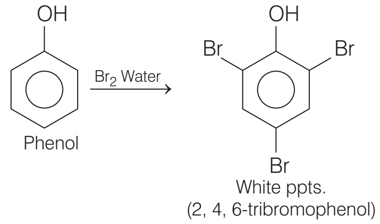
(d) 

Ans. ***(b)***

Phenol (ArOH) is insoluble in dil. HCl and readily soluble in NaOH solution. It reacts with Br_2/water to give 2, 4, 6-tribromophenol. It readily decolourises the yellow colour of Br_2 water. Reactions involved are as follows :

- 

- 

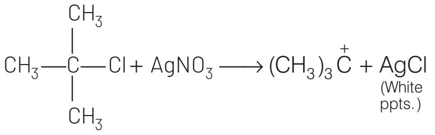
- 

15 Which one of the following is likely to give a precipitate with $AgNO_3$ solution? **[2019, 9 April Shift-II]**

(a) $CH_2=CH—Cl$ (b) CCl_4
(c) $CHCl_3$ (d) $(CH_3)_3CCl$

Ans. ***(d)***

$(CH_3)_3CCl$ gives a precipitate with $AgNO_3$ solution because it forms stable carbocation. (i.e. tertiary) that readily combines with $AgNO_3$ to give precipitates of AgCl.



$$CH_3—\underset{CH_3}{\overset{CH_3}{C}}—Cl + AgNO_3 \longrightarrow (CH_3)_3\overset{+}{C} + \underset{\text{(White ppts.)}}{AgCl}$$

$CH_2=CH—Cl$ forms unstable carbocation.

Hence, it does not readily react with $AgNO_3$.

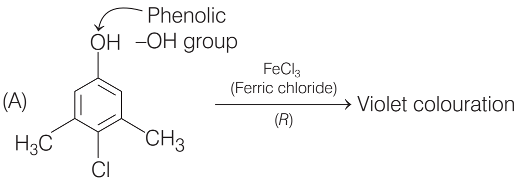
16 The correct match between Item-I and Item-II is

	Item-I (Drug)		**Item- II** (Test)
A.	Chloroxylenol	P.	Carbylamine test
B.	Norethindrone	Q.	Sodium hydrogen carbonate test
C.	Sulphapyridine	R.	Ferric chloride test
D.	Penicillin	S.	Bayer's test

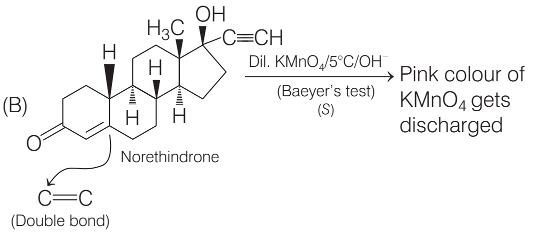
[2019, 9 Jan Shift-I]

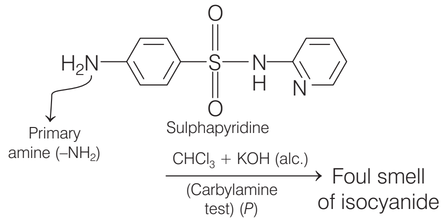
(a) A → R ; B → P ; C → S ; D → Q
(b) A → R ; B → S ; C → P ; D → Q
(c) A → Q ; B → P ; C → S ; D → R
(d) A → Q ; B → S ; C → P ; D → R

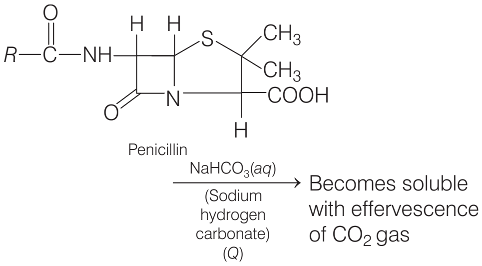
Ans. ***(b)***

(A) 

Chloroxylenol (Dettol)

(B) 

(C) 

(D) 

Thus, the correct match is :

A → R; B → S; C → P; D → Q

17 The correct match between item 'I' and item 'II' is

	Item 'I' (Compound)		**Item 'II'** (Reagent)
(A)	Lysine	(P)	1-naphthol
(B)	Furfural	(Q)	Ninhydrin
(C)	Benzyl alcohol	(R)	$KMnO_4$
(D)	Styrene	(S)	Ceric ammonium nitrate

[2019, 10 Jan Shift-II]

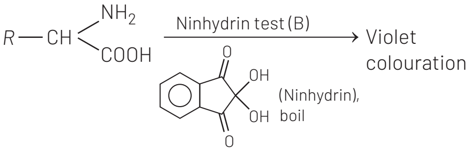
Codes

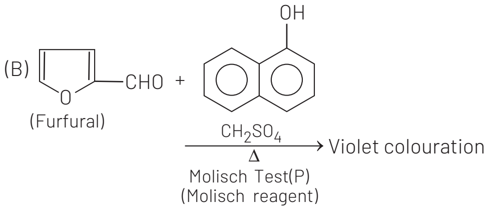
	A	B	C	D		A	B	C	D
(a)	Q	R	S	P	(b)	R	P	Q	S
(c)	Q	P	S	R	(d)	Q	P	R	S

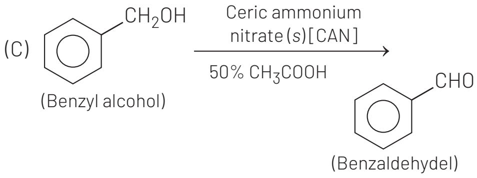
Ans. ***(c)***

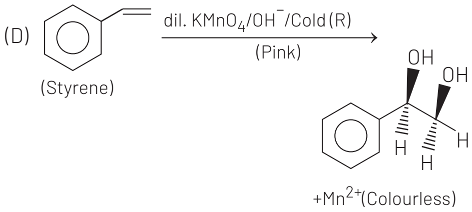
(A) → Q; B → (P) ; C → (S), D → (R)

(A) Lysine (R=$-(CH_2)_4-NH_2$)









18 The compound formed in the positive test for nitrogen with the Lassaigne solution of an organic compound is **[AIEEE 2004]**

(a) $Fe_4[Fe(CN)_6]_3$ (b) $Na_3[Fe(CN)_6]$
(c) $Fe(CN)_3$ (d) $Na_4[Fe(CN)_5NOS]$

Ans. ***(a)***

If nitrogen is present in organic compound, then sodium extract contains NaCN.

$$Na + C + N \xrightarrow{\text{Fuse}} NaCN$$

$$FeSO_4 + 6NaCN \longrightarrow \underset{(A)}{Na_4[Fe(CN)_6]} + Na_2SO_4$$

A changes to Prussian blue $Fe_4[Fe(CN)_6]_3$ on reaction with $FeCl_3$.

$$4FeCl_3 + 3Na_4[Fe(CN)_6] \longrightarrow Fe_4[Fe(CN)_6]_3 + 12NaCl$$

TOPIC 3

Chemistry Involved in Titrimetric Exercise

19 When 10 mL of an aqueous solution of $KMnO_4$ was titrated in acidic medium, equal volume of 0.1 M of an aqueous solution of ferrous sulphate was required for complete discharge of colour.

The strength of $KMnO_4$ in g/L is .... $\times 10^{-2}$. (Nearest integer)

[Atomic mass of K = 39, Mn = 55, O = 16]

[2021, 27 Aug Shift-I]

Ans. ***(316)***

Let molarity of $KMnO_4 = x$

$$\underset{n=5}{KMnO_4} + \underset{n=1}{FeSO_4} \longrightarrow Fe(SO_4)_3 + Mn^{2+}$$

(Equivalent of $KMnO_4$ reacted) = (Equivalent of $FeSO_4$ reacted)

$\Rightarrow \quad 5x \times 10 = 1 \times 0.1 \times 10$

$x = 0.02$ M

Molar mass of $KMnO_4 = 158$ g / mol

Strength $= x \times 158 = 0.02 \times 158 = 3.16$ g / L

$= 316 \times 10^{-2}$ g /L

$\therefore \quad x \approx 316.$

20 The OH^- concentration in a mixture of 5.0 mL of 0.0504 M NH_4Cl and 2 mL of 0.0210 M NH_3 solution is $x \times 10^{-6}$ M. The value of *x* is .... (Nearest integer)

[Given, $K_w = 1 \times 10^{-14}$ and $K_b = 1.8 \times 10^{-5}$]

[2021, 26 Aug Shift-I]

Ans. ***(3)***

Number of moles of NH_4Cl = concentration of NH_4Cl × volume of NH_4Cl

$= 0.0504$ M × 5 mL = 0.2520 millimoles

Total volume of solution in mixture

= Volume of NH_4Cl solution + volume of NH_3 solution

$= 5 + 2 = 7$ mL.

Concentration of NH_4Cl in mixture

$$= \frac{\text{Number of moles of } NH_4Cl}{\text{Total volume}}$$

$$= \frac{0.2520 \text{ millimole}}{7 \text{ mL}} = 0.036 \text{ M}$$

Number of moles of NH_3 = concentration of NH_3 × volume of NH_3

$= 0.0210 \times 2 = 0.042$ millimole

$$\text{Concentration of } NH_3 \text{ in mixture} = \frac{\text{Number of moles of } NH_3}{\text{Total volume}}$$

$$= \frac{0.042}{7} = 0.006 \text{ M}$$

According to Handerson's equation

$$pOH = pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$[\text{Salt}] = [NH_4Cl]$$

$$[\text{Base}] = [NH_3]$$

$$pOH = -\log K_b + \log \frac{0.036}{0.006}$$

$$pOH = -\log(1.8 \times 10^{-5}) + 0.7782$$

$$pOH = 5.523$$

$\because \quad pOH = -\log[OH^-]$

So, $\quad [OH^-] = 2.9 \times 10^{-6} \approx 3 \times 10^{-6}$

$\therefore \quad x = 3$

21 Given below are two statements.

Statement I In the titration between strong acid and weak base methyl orange is suitable as an indicator.

Statement II For titration of acetic acid with NaOH phenolphthalein is not a suitable indicator.

In the light of the above statements, choose the most appropriate answer from the options given below.

[2021, 26 Aug Shift-I]

(a) Statement I is false but statement II is true.
(b) Statement I is true but statement II is false.
(c) Both statement I and statement II are true.
(d) Both statement I and statement II are false.

Ans. ***(b)***

In the titration of strong acid with the weak base methyl orange is an suitable indicator. Initially, pH of weak base is high, as acid is added pH falls slowly and equivalence point is attained. (Equivalence point is point when chemical equivalent quantities of acid and base are mixed). After equivalence point pH falls sharply. So, methyl orange having pH range 3.2 - 4.4 will work as suitable indicator. Methyl orange shows red colour in acidic medium and yellow colour in basic medium.

Hence, statement I is true.

In titration of weak acid and strong base initially pH of weak acid is below 7. As strong base is added pH increases slowly and equivalence point is attained. After equivalence point pH abruptly increases. So, phenolphthalein having pH range 8.2–10.0 will work as suitable indicator. Phenolphthalein is colourless in acidic solution whereas pink in basic solution. Hence, statement II is false.

22 Consider titration of NaOH solution *versus* 1.25 M oxalic acid solution. At the end point following burette readings were obtained.

(i) 4.5 mL (ii) 4.5 mL (iii) 4.4 mL
(iv) 4.4 mL (v) 4.4 mL

If the volume of oxalic acid taken was 10.0 mL, then the molarity of the NaOH solution is .... M. (Rounded off to the nearest integer) **[2021, 25 Feb Shift-II]**

Ans. ***(6)***

Average burette reading = Volume of NaOH solution (V_1)

$$= \frac{4.5 + 4.5 + 4.4 + 4.4 + 4.4}{5}$$

$$= 4.44 \text{ mL}$$

Strength of NaOH solution $= S_1(\text{M})\,(\text{say}) = S_1(\text{N})$

Volume of oxalic acid solution $(V_2) = 10$ mL

Strength of oxalic acid solution $(S_2) = 1.25$ M 3= 1.25×2 N

So, $V_1S_1 = V_2S_2$ (∵ Law of equivalence)

$$\Rightarrow \quad S_1 = \frac{V_2S_2}{V_1} = \frac{10 \times (1.25 \times 2)}{4.44} = 5.63 \text{ N}$$

$$\simeq 6 \text{ M} = 6 \text{ M}$$

Note n-factor of NaOH = 1

n-factor of $H_2C_2O_4 = 2$ (oxalic acid)

$$N = M \times n$$

23 0.4 g mixture of NaOH, Na_2CO_3 and some inert impurities was first titrated with $\frac{N}{10}$ HCl using phenolphthalein as an indicator, 17.5 mL of HCl was required at the end point. After this methyl orange was added and titrated. 1.5 mL of same HCl was required for the next end point. The weight percentage of Na_2CO_3 in the mixture is .... (Rounded off to the nearest integer). **[2021, 25 Feb Shift-I]**

Ans. ***(4)***

As given, NaOH and Na_2CO_3 is titrated with N/10 HCl.

For NaOH,

Equivalents of NaOH = Equivalents of HCl

Equivalents of HCl = Normality × Volume (L)

$$= 0.1 \times \frac{17.5}{1000}$$

Equivalent of HCl $= 1.75 \times 10^{-3}$

Equivalents of NaOH $= 1.75 \times 10^{-3}$

Weight of NaOH = Equivalent of NaOH × equivalent weight of NaOH

$$= 40 \times 1.75 \times 10^{-3} = 0.07 \text{ g}$$

Now, weight % of NaOH

$$= \frac{0.07}{0.4} \times 100 = \frac{70}{4} = 17.5\%$$

Similarly for Na_2CO_3,

Equivalent of HCl = Equivalent of Na_2CO_3

Equivalent of $Na_2CO_3 = 0.1 \times \frac{1.5}{1000} = 0.15 \times 10^{-3}$

Weight of Na_2CO_3 = Equivalent of Na_2CO_3 × equivalent weight of Na_2CO_3

$$= 0.15 \times 10^{-3} \times 106 = 15.9 \times 10^{-3} \text{ g}$$

Weight % of $Na_2CO_3 = \frac{15.9 \times 10^{-3}}{0.4} \times 100$

$$= 0.039 \times 100 = 3.9\% \simeq 4\%$$

24 While titrating dilute HCl solution with aqueous NaOH, which of the following will not be required? **[2020, 2 Sep Shift-I]**

(a) Pipette and distilled water
(b) Burette and porcelain tile
(c) Bunsen burner and measuring cylinder
(d) Clamp and phenolphthalein

Ans. ***(c)***

Titration (neutralisation) of dil. HCl solution with aqueous NaOH will require the following steps and apparatus. NaOH solution made with distilled water and solid NaOH is taken in a burette and then it is fitted with a clamp.

A given volume of standard HCl solution (dilute) is then pipetted out and taken in a conical flask for titration. Then, few drops of phenolphthalein indicator is added in this HCl solution. So, we do not require measuring cylinder and bunsen burner as the titration takes place at room temperature.

25 The volume strength of 8.9 M H_2O_2 solution calculated at 273 K and 1 atm is .... ($R = 0.0821$ L atm K^{-1} mol^{-1}) (rounded off to the nearest integer). **[2020, 3 Sep Shift-I]**

Ans. ***(100.00)***

$$\text{“x vol”} \, H_2O_2 = \frac{x}{11.2} \text{ M } H_2O_2$$

So, $\frac{x}{11.2} = 8.9$

$\Rightarrow$ $x = 11.2 \times 8.9 = 99.68 \simeq 100$

So, at NTP volume strength of 8.9 M H_2O_2 solution is 100 vol.

26 A 20.0 mL solution containing 0.2g impure H_2O_2 reacts completely with 0.316 g of $KMnO_4$ in acid solution. The purity of H_2O_2 (in%) is .... (molecular weight of $H_2O_2 = 34$; molecular weight of $KMnO_4 = 158$). **[2020, 4 Sep Shift-I]**

Ans. ***(85)***

Given, volume of solution $= 20.0$ mL

Impure sample of $H_2O_2 = 0.2$ g

Mass of $KMnO_4 = 0.316$ g

Impure H_2O_2 react with $KMnO_4$ (acidic)

$$K\overset{+7}{Mn}O_4 + H_2\overset{-1}{O_2} \longrightarrow \overset{+2}{Mn} + \overset{0}{O_2}$$

$KMnO_4$ acts as an oxidising agent,

$$\overset{+7}{Mn} + 5e^- \longrightarrow \overset{+2}{Mn}$$

(valency factor $= 5$)

$$\overset{-1}{O_2} \longrightarrow \overset{0}{O_2} + 2e^-$$

(valency factor $= 2$)

We have to compare both $KMnO_4$ and H_2O_2.

$$(\text{Mass equivalent})_{H_2O_2} = (\text{Mass equivalent})_{KMnO_4}$$

$$\frac{\text{Weight}}{\text{molecular weight/valence factor}} \times 1000$$

$$= \frac{\text{weight}}{\text{molecular weight/valence factor}} \times 1000$$

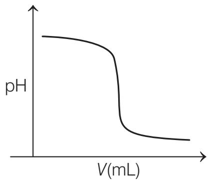
$$\frac{(\text{weight})_{H_2O_2}}{34/2} \times 1000 = \frac{0.316}{158/5} \times 1000$$

$$(\text{weight})_{H_2O_2} = \frac{0.316}{158} \times 5 \times \frac{34}{2} = \frac{26.86}{158}$$

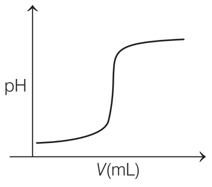
$$(\text{weight})_{H_2O_2} = 0.17 \text{ g}$$

$$(\text{Purify})_{H_2O_2} = \frac{(\text{Pure})_{H_2O_2}}{(\text{Impure})_{H_2O_2}} \times 100 = \frac{0.17}{0.2} \times 100 = 85\%$$

27 In an acid-base titration, 0.1 M HCl solution was added to the NaOH solution of unknown strength. Which of the following correctly shows the change of pH of the titration mixture in this experiment? **[2019, 9 April Shift-II]**



(A)



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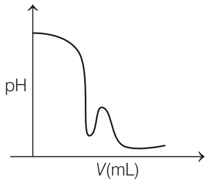
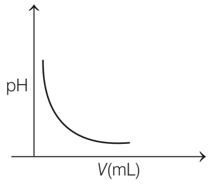


(C)

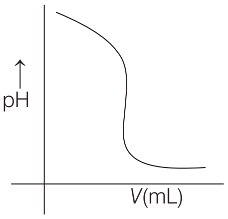


(D)

(a) (*D*) (b) (*A*) (c) (*B*) (d) (*C*)

Ans. ***(b)***

The graph that shows the correct change of pH of the titration mixture in the experiment is



In this case, both the titrants are completely ionised.

$$HCl + NaOH \rightleftharpoons \overset{+}{Na}\overset{-}{Cl} + H_2O$$

As $\overset{\oplus}{H}$ is added to a basic solution, $[OH^{\ominus}]$ decreases and $[H^+]$ increases. Therefore, pH goes on decreasing. As the equivalence point is reached, $[OH^{\ominus}]$ is rapidly reduced. After this point $[OH^{\ominus}]$ decreases rapidly and pH of the solution remains fairly constant. Thus, there is an inflexion point at the equivalence point.

The difference in the volume of NaOH solution between the end point and the equivalence point is not significant for most of the commonly used indicators as there is a large change in the pH value around the equivalence point. Most of them change their colour across this pH change.

28 25 mL of the given HCl solution requires 30 mL of 0.1 M sodium carbonate solution. What is the volume of this HCl solution required to titrate 30 mL of 0.2 M aqueous NaOH solution? **[2019, 11 Jan Shift-II]**

(a) 75 mL (b) 25 mL
(c) 12.5 mL (d) 50 mL

Ans. ***(b)***

The reaction of HCl with Na_2CO_3 is as follows:

$$2HCl + Na_2CO_3 \longrightarrow 2NaCl + H_2O + CO_2$$

We know that, M_{eq} of HCl $= M_{eq}$ of Na_2CO_3

$$\frac{25}{1000} \times 1 \times M_{HCl} = \frac{30}{1000} \times 0.1 \times 2$$

$$M_{HCl} = \frac{30 \times 0.2}{25} = \frac{6}{25} \text{ M}$$

The reaction of HCl with NaOH is as follows:

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

Also, M_{eq} of HCl $= M_{eq}$ of NaOH

$$\frac{6}{25} \times 1 \times \frac{V}{1000} = \frac{30}{1000} \times 0.2 \times 1$$

$$V = 25 \text{ mL}$$

29 50 mL of 0.5 M oxalic acid is needed to neutralise 25 mL of sodium hydroxide solution. The amount of NaOH in 50 mL of the given sodium hydroxide solution is **[2019, 12 Jan Shift-I]**

(a) 40 g (b) 80 g (c) 20 g (d) 10 g

Ans. ***(*)***

The reaction takes place as follows,

$$H_2C_2O_4 + 2NaOH \longrightarrow Na_2C_2O_4 + 2H_2O$$

Now, 50 mL of 0.5 M $H_2C_2O_4$ is needed to neutralize 25 mL of NaOH.

$\therefore$ Meq of $H_2C_2O_4$ = Meq of NaOH

$$50 \times 0.5 \times 2 = 25 \times M_{NaOH} \times 1$$

$$M_{NaOH} = 2M$$

Now, $\text{molarity} = \dfrac{\text{Number of moles}}{\text{Volume of solution (in L)}}$

$$= \frac{\text{Weight/molecular mass}}{\text{Volume of solution (in L)}}$$

$$2 = \frac{w_{NaOH}}{40} \times \frac{1000}{50}$$

$$w_{NaOH} = \frac{2 \times 40 \times 50}{1000} = 4g$$

Thus, (*) none option is correct.

30 29.5 mg of an organic compound containing nitrogen was digested according to Kjeldahl's method and the evolved ammonia was absorbed in 20 mL of 0.1M HCl solution. The excess of the acid required 15 ML of 0.1 M NaOH solution for complete neutralization. The percentage of nitrogen in the compound is **[AIEEE 2010]**

(a) 59.0 (b) 47.4 (c) 23.7 (d) 29.5

Ans. ***(c)***

Mass of organic compound = 29.5 mg

mmoles of HCl = $20 \times 0.1 = 2$ mmoles

mmoles of NaOH = $15 \times 0.1 = 1.5$ mmole

Involved reactions are

$$NH_3 + \underset{\substack{\text{(2 mmoles}\\ \text{initially taken)}}}{HCl} \longrightarrow NH_4Cl$$

$$\underset{\text{(Lewis acid)}}{HCl} + \underset{\substack{\text{(1.5 mmoles}\\ \text{initially taken)}}}{NaOH} \longrightarrow NaCl + H_2O$$

From the above equation, it is clear that

mmoles of HCl reacted with NaOH = $2 - 1.5 = 0.5$ mmol

m moles of NH_3 reacted in first equation with HCl = 0.5×17 mg

Mass of $NH_3 = 0.5 \times 17 \text{ mg} = 8.5$ mg

Mass of N contained in $NH_3 = 8.5 \text{ mg} \times \dfrac{14}{17} = 7$ mg

Thus, % of N present in OC $= \dfrac{7}{29.5} \times 100 = 23.7\%$

TOPIC 4

Qualitative Salt Analysis

31 To an aqueous solution containing ions such as Al^{3+}, Zn^{2+}, Ca^{2+}, Fe^{3+}, Ni^{2+}, Ba^{2+} and Cu^{2+} conc. HCl, was added followed by H_2S. The total number of cations precipitated during this reaction is/are **[2021, 27 July Shift-II]**

(a) 1 (b) 3 (b) 4 (d) 2

Ans. ***(a)***

Only Cu^{2+} get precipitated when HCl followed by H_2S was added. Al^{3+} and Fe^{3+} sulphides hydrolyse in water. Ni^{2+} and Zn^{2+} require basic medium with H_2S to form ppt. Ca^{2+} and Ba^{2+} sulphides are soluble.

Hence, we will recieve ppt. of only CuS.

32 Which one of the following set of elements can be detected using sodium fusion extract ? **[2021, 27 July Shift-II]**

(a) Sulphur, nitrogen, phosphorus, halogens
(b) Phosphorus, oxygen, nitrogen, halogens
(c) Nitrogen, phosphorus, carbon, sulphur
(d) Halogens, nitrogen, oxygen, sulphur

Ans. ***(a)***

By sodium fusion extract we can detect sulphur, nitrogen, phosphorus and halogens. The elements present in the compound are converted from covalent into ionic form by fusing the compound with sodium metal. Following reactions take place :

$$Na + C + N \xrightarrow{\Delta} NaCN$$

$$2Na + S \xrightarrow{\Delta} Na_2S$$

$$Na + X \xrightarrow{\Delta} NaX \ (X = Cl, Br \text{ or } I)$$

$$3Na + PO_4^{3-} \xrightarrow{\Delta} Na_3PO_4$$

33 In Tollen's test for aldehyde, the overall number of electron(s) transferred to the Tollen's reagent formula $[Ag(NH_3)_2]^+$ per aldehyde group to form silver mirror is .... (Round off to the nearest integer). **[2021, 18 March Shift-II]**

Ans. ***(2)***

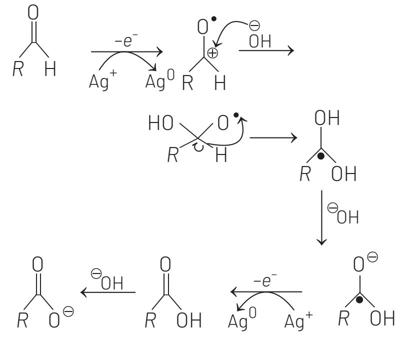
When an aldehyde is heated with freshly prepared Tollen's reagent i.e. $[Ag(NH_3)_2]^+$, a bright silver mirror of Ag is formed.

$$AgNO_3 + NaOH \longrightarrow AgOH + NaNO_3$$

$$2AgOH \longrightarrow Ag_2O + H_2O$$

$$Ag_2O + 4NH_3 + H_2O \longrightarrow \underset{\text{Tollen's reagent}}{2Ag(NH_3)_2^+} + 2OH^-$$

Reaction of aldehyde with Tollen's reagent take place as follows



Total $2e^-$ transfer to Tollen's reagent.

34. If Fe^{3+} and Cr^{3+} both are present in group III of qualitative analysis, then distinction can be made by **[AIEEE 2002]**

(a) addition of NH_4OH in the presence of NH_4Cl when only $Fe(OH)_3$ is precipitated
(b) addition of NH_4OH in presence of NH_4Cl when $Cr(OH)_3$ and $Fe(OH)_3$ both are precipitated and on adding Br_2 water and NaOH, $Cr(OH)_3$ dissolves

(c) precipitate of $Cr(OH)_3$ and $Fe(OH)_3$ as obtained in (b) are treated with conc. HCl when only $Fe(OH)_3$ dissolves

(d) both (b) and (c)

Ans. ***(b)***

If Fe^{3+} and Cr^{3+} both are present, then very first solid ammonium chloride and ammonium hydroxide is added slowly till the solution smells of ammonia. Fe^{3+} and Cr^{3+} precipitates in the hydroxide form.

For identification, precipitate is treated with NaOH and Br_2 water, yellow colouration confirms Cr^{3+} ion.

$$2NaOH + Br_2 \longrightarrow NaBrO + NaBr + H_2O$$
$$NaBrO \longrightarrow NaBr + [O]$$
$$2Cr(OH)_3 + 4NaOH + 3[O] \longrightarrow 2Na_2CrO_4 + 5H_2O$$

Solution is acidified and treated with lead acetate solution.

$$Na_2CrO_4 + Pb(CH_3COO)_2 \longrightarrow \underset{\text{(Yellow ppt)}}{PbCrO_4} + 2CH_3COONa$$

TOPIC 5

Experiments Involving Enthalpy

35 When silver nitrate solution is added to potassium iodide solution then the sol produced is **[2021, 22 July Shift-II]**

(a) AgI/I^- (b) AgI/Ag^+

(c) KI/NO_3^- (d) $AgNO_3/NO_3^-$

Ans. ***(a)***

Since, $AgNO_3$ solution was passed to KI solution, the AgI/I^- sol was produced. (Here, the KI solution through which $AgNO_3$ passed, was considered to be in excess).

As we know that, colloids can be prepared from precipitate by using suitable electrolytes. Colloids may be positively or negatively charged depend on electrolyte we adding.

If we add $AgNO_3$ and KI, it gives AgI and KNO_3.

$$AgNO_3 + KI \rightarrow AgI + KNO_3$$

and thus AgI adsorb I^- ion as KI is in excess.

If KNO_3 added, then $AgNO_3$ will be in excess, so AgI adsorb Ag^+ ion.

Hence, AgI produce the I^- ion.

36 The reaction of cyanamide, $NH_2CN(s)$ with oxygen was run in a bomb calorimeter and ΔU was found to be $-742.24\ kJ\ mol^{-1}$. The magnitude of ΔH_{298} for the reaction

$$NH_2CN(s) + \frac{3}{2}O_2(g) \longrightarrow N_2(g) + O_2(g) + H_2O(l)$$

is ……… kJ (Rounded off to the nearest integer).
[Assume ideal gases and $R = 8.314\ J\ mol^{-1}\ K^{-1}$]

[2021, 25 Feb Shift-I]

Ans. ***(741)***

$$\Delta U = -742.24\ kJ\ mol^{-1}$$

Δn_g = [Number of gaseous molecules of products − Number of gaseous molecules of reactants]

$$NH_2CN(s) + \frac{3}{2}O_2(g) \longrightarrow N_2(g) + O_2(g) + H_2O(l)$$

$$\Delta n_g = 2 - \frac{3}{2} = \frac{1}{2}$$

$$\Delta H = \Delta U + \Delta n_g RT$$
$$= -742.24 + \frac{1}{2} \times \frac{8.314}{1000} \times 298 = -741\ kJ/mol$$

Hence, answer is 741.