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Purification and Characterisation of Organic Compounds

TOPIC 1

Methods of Purification

01 The most suitable method of separation of 1:1 mixture of *ortho* and *para*-nitrophenols is **[NEET 2017, CBSE AIPMT 99, 94]**

(a) sublimation
(b) chromatography
(c) crystallisation
(d) steam distillation

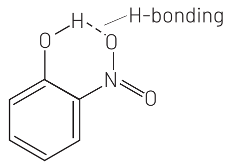
Ans. ***(d)***

Steam distillation is used to purify the substances which

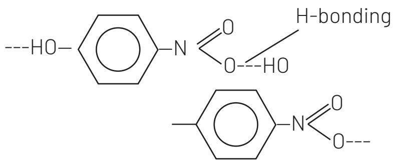
(i) are volatile in steam but are immiscible with water.
(ii) possess sufficiently high vapour pressure at the boiling point of water.
(iii) contain non- volatile impurities.

The process of steam distillation can also be used to separate a mixture of two organic compounds one of which is steam volatile while the other is not.

In *ortho* and *para*-nitrophenol, *ortho*-nitrophenol has intramolecular H-bonding. So, it has lower boiling point. Intermolecular H-Bonding more strong then intramolecular H-bonding. Whereas *para*-nitrophenol has intermolecular H-bonding. So, it has higher boiling point. Due to difference in boiling points *ortho* and *para*-nitrophenol can be separated from each other by distillation.



Intramolecular H-bonding in o-nitrophenol



Intermolecular H-bonding in p-nitrophenol

02 Which of the statements is not true? **[CBSE AIPMT 2012]**

(a) On passing H_2S through acidified $K_2Cr_2O_7$ solution, a milky colour is observed
(b) $Na_2Cr_2O_7$ is preferred over $K_2Cr_2O_7$ in volumetric analysis
(c) $K_2Cr_2O_7$ solution in acidic medium is orange
(d) $K_2Cr_2O_7$ solution becomes yellow on increasing the pH beyond 7

Ans. ***(b)***

Being hygroscopic, sodium dichromate, $Na_2Cr_2O_7$ cannot be used in volumetric analysis.

All other given statements are true.

03 The best method for the separation of naphthalene and benzoic acid from their mixture is

(a) chromatography **[CBSE AIPMT 2005]**
(b) crystallisation
(c) distillation
(d) sublimation

Ans. ***(d)***

The best method for the separation of naphthalene and benzoic acid from their mixture is sublimation because it is applicable for those organic compounds which pass directly from solid to vapour state on heating and *vice versa* on cooling. In these compounds naphthalene is volatile and benzoic acid is non-volatile due to the formation of dimer *via* hydrogen bonding (intermolecular).

04 Camphor is often used in molecular mass determination because **[CBSE AIPMT 2004]**

(a) it is readily available
(b) it has a very high cryoscopic constant
(c) it is volatile
(d) it is solvent for organic substances

Ans. ***(c)***

Camphor is used in molecular mass determination due to its volatile nature. The method is called Rast's camphor method. Camphor acts as a solid solvent which is volatile, hence can be removed easily.

05 In steam distillation of toluene, the pressure of toluene in vapour is **[CBSE AIPMT 2001]**

(a) equal to the pressure of barometer
(b) less than the pressure of barometer
(c) equal to vapour pressure of toluene in simple distillation
(d) more than vapour pressure of toluene in simple distillation

Ans. *(b)*

In steam distillation of toluene, the pressure of toluene in vapour is less than pressure of barometer, because it is carried out when a solid or liquid is insoluble in water and is volatile with steam but the impurities are non-volatile.

06 Which of the following techniques is most suitable for purification of cyclohexanone from a mixture containing benzoic acid, isoamyl alcohol, cyclohexane and cyclohexanone? **[CBSE AIPMT 1997]**

(a) Crystallisation (b) IR spectroscopy
(c) Sublimation (d) Evaporation

Ans. *(b)*

IR spectroscopy is used for the purification of cyclohexanone from a mixture of benzoic acid, isoamyl alcohol, cyclohexane and cyclohexanone because in IR spectroscopy each functional group appears at a certain peak. IR spectroscopy exploits the fact that molecules absorb specific frequencies that are characteristic of their structure.

07 *A* is a lighter phenol and *B* is an aromatic carboxylic acid. Separation of a mixture of *A* and *B* can be carried out easily by using a solution of **[CBSE AIPMT 1992]**

(a) sodium hydroxide
(b) sodium sulphate
(c) calcium chloride
(d) sodium bicarbonate

Ans. *(d)*

Carboxylic acids are soluble in sodium bicarbonate but phenol are not dissolve in it, so they are separated because carboxylic acid react with $NaHCO_3$ and form sodium carboxylate.

$$R\text{—COOH} + NaHCO_3 \longrightarrow R\text{—COO}^-Na^+ + H_2CO_3$$

08 Prussian blue is formed when **[CBSE AIPMT 1989]**

(a) ferrous sulphate reacts with $FeCl_3$
(b) ferric sulphate reacts with $Na_4[Fe(CN)_6]$
(c) ferrous ammonium sulphate reacts with $FeCl_3$
(d) ammonium sulphate reacts with $FeCl_3$

Ans. *(b)*

When the sodium fusion extract is added with $FeCl_3$ and then the resulting solution is acidified with dilute hydrochloric acid, the appearance of Prussian blue colouration confirms the presence of nitrogen in the organic compound.

$$Na + C + N \longrightarrow NaCN$$
$$FeSO_4 + 2NaCN \longrightarrow Fe(CN)_2 + Na_2SO_4$$
$$Fe(CN)_2 + 4NaCN \longrightarrow Na_4[Fe(CN)_6]$$
$$3Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$$

TOPIC 2
Qualitative Analysis

09 The Lassaigne's extract is boiled with conc. HNO_3 while testing for halogens. By doing so it **[CBSE AIPMT 2011]**

(a) helps in the precipitation of AgCl
(b) increases the solubility product of AgCl
(c) increases the concentration of NO_3^- ions
(d) decomposes Na_2S and NaCN, if formed

Ans. *(d)*

Na_2S and NaCN, if present in the extract, will be decomposed to H_2S and HCN by HNO_3.

$$NaCN + HNO_3 \longrightarrow NaNO_3 + HCN$$
$$Na_2S + 2HNO_3 \longrightarrow 2NaNO_3 + H_2S$$

These will escape from the solution and will not interfere with the test for halogens.

10 Lassaigne's test for the detection of nitrogen fails in **[CBSE AIPMT 1994]**

(a) $NH_2CONHNH_2 \cdot HCl$
(b) $NH_2NH_2 \cdot HCl$
(c) NH_2CONH_2
(d) $C_6H_5NHNH_2 \cdot HCl$

Ans. *(b)*

Lassaigne's test is given by only those compounds which contain both carbon and nitrogen. When compounds containing C and N heated with sodium, then it form NaCN which is easily detected by $FeCl_3$.

Or

Some compounds live hydrazine $(NH_2 \cdot NH_2)$ although contain nitrogen but they do not respond Lassaigne's test because they do not have any carbon and hence, NaCN is not formed.

11 In sodium fusion test of organic compounds, the nitrogen of the organic compound is converted into **[CBSE AIPMT 1991]**

(a) sodamide (b) sodium cyanide
(c) sodium nitrite (d) sodium nitrate

Ans. *(b)*

When the nitrogen containing compound is heated with sodium, then nitrogen and carbon of organic compound converted into sodium cyanide.

$$Na + \underbrace{C + N}_{\text{From organic compound}} \longrightarrow NaCN$$

12 Lassaigne's test is used to detect **[CBSE AIPMT 1990]**

(a) nitrogen (b) sulphur
(c) chlorine (d) All of these

Ans. *(d)*

The detection of chlorine, sulphur and nitrogen in organic compounds is done by Lassaigne's test.

TOPIC 3
Quantitative Analysis

13 In Duma's method for estimation of nitrogen, 0.25g of an organic compound gave 40 mL of nitrogen collected at 300 K temperature and 725 mm pressure. If the aqueous tension at 300 K is 25 mm, the percentage of nitrogen in the compound is **[CBSE AIPMT 2015]**

(a) 17.36 (b) 18.20 (c) 16.76 (d) 15.76

Ans. *(c)*

Mass of the substance taken = 0.25 g
Volume of nitrogen collected = 40 mL
Atmospheric pressure = 725 mm

Room temperature = 300 K

Aqueous tension at 300 K = 25 mm

Actual pressure of the gas

$= (725 - 25)$ mmHg = 700 mm

To convert the volume at experimental conditions to volume at STP.

Experimental value	**At STP**
$p_1 = 700$ mm	$p_2 = 760$ mm
$V_1 = 40$ ml	$V_2 = ?$
$T_1 = 300$ k	$T_2 = 273$ k

Substituting these values in the gase eq.

$$\frac{p_2V_2}{T_2} = \frac{p_1V_1}{T_1}$$

we get, $$\frac{760 \times V_2}{273} = \frac{700 \times 40}{300}$$

$$V_2 = \frac{700 \times 40}{300} \times \frac{273}{760}$$

$$= 33.53 \text{ mL}$$

To convert volume at STP into mass

22400 ml of nitrogen at STP weigh = 28 g

$\therefore$ 33.53 ml of nitrogen at STP will

weigh $= \dfrac{28 \times 33.53}{22400 \times 0.25}$

To calculate percentage of nitrogen

$$= \frac{28 \times 33.53}{22400 \times 0.25} \times 100$$

$$= 16.76\ \%$$

14 In Duma's method of estimation of nitrogen 0.35g of an organic compound gave 55 ml of nitrogen collected at 300K temperature and 175 mm pressure. The percentage composition of nitrogen in the compound would be (Aqueous tension at 300 K = 15mm) **[CBSE AIPMT 2011]**

(a) 16.45 (b) 17.45
(c) 14.45 (d) 15.45

Ans. ***(a)***

According to combined gas equation,

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

Where, p_2 = pressure of N_2 at STP

= 760 mm

T_2 = Temperature of N_2 at STP = 273 K

$V_2 = ?$

Volume of N_2 at STP (By gas equation)

$$\left(\frac{\rho - \rho_1}{t + 273}\right) V_1 \times \frac{273}{760} = V_2$$

Where, $p_1 = \rho - \rho_1$

$\rho = 715$ mm (pressure at which N_2 collected)

ρ_1 = aqueous tension of water = 15 mm

$T_1 = t + 273 = 300$ K

$V_1 = 55$ mL = volume of moist nitrogen in nitrometer

$$\therefore \quad V_2 = \frac{(715 - 15) \times 55}{300} \times \frac{273}{760}$$

$$= 46.098 \text{ mL}$$

% of nitrogen in given compound

$$= \frac{28}{22400} \times \frac{V_2}{W} \times 100$$

$$= \frac{28}{22400} \times \frac{46.098}{0.35} \times 100$$

$$= 16.45\%$$

15 Kjeldahl's method is used in the estimation of **[CBSE AIPMT 1990]**

(a) nitrogen (b) halogens
(c) sulphur (d) oxygen

Ans. ***(a)***

Kjeldahl's method is simpler and more convenient than Duma's method. This method is largely used for the estimation of nitrogen in food stuff, drugs, fertilisers and many other organic compounds. However, this method cannot be used for organic compounds containing nitrogen in the ring such as pyridine, quinoline and organic compounds containing nitro ($-NO_2$) and diazo ($-N=N-$) groups.