Unit-2 Decomposition techniques in Analysis

(a) Inorganic compounds

*** Principle of decomposition :-**

The process of conversion of solid or liquid or gas sample into the solution from which is readily available for analysis is called "decomposition".

Decomposition is a dissolution technique. since the substance can be analysed easily in the sol. form.

In this technique, solids & complex materials are brought into solution form by using different dissolution techniques

complex (solid) $\xrightarrow{\text{Decompose}}$ solution

Not only solids, but also liquids & gases can also be in the form of solution during decomposition.

we use liquid form of sample for classical methods of analysis.

solid must be made to soluble form for analysis. Gases must be made to dissolved form for analysis.

Eg:- solid 5%, liquid 90%, Gas 5%

Decomposition techniques are generally employed for 1) ores 2) Alloys 3) slags 4) Metals 5) Minerals 6) Refractory materials.

Eg:

Siliceous ores are dissolved in conc. HCl, or a mixture of HCl + HNO_3 or aqua regia (3:1)

(Hcl : HNO_3)

2) In case of metals & alloys dissolved in conc HNO_3

3) for slag, fusion methods the sample is treated with fusion mixtures in Pt, Ag, Ni crucible.

(19) Fusion mixture a) $Na_2CO_3 + K_2CO_3$ (2 : 3)

b) $NaNO_3 + KNO_3$ (1 : 1)

c) Na_2O_2

Generally we can use following chemicals for dissolution (or) decomposition i.e. H_2O, HF, Hcl, HI, HNO_3, H_2SO_4, H_3PO_4, $HClO_4$.

Decomposition is of 3 types.

1. Acids (Direct dissolution in Acids)
2. Fusion (following dissolution)
3. Sintering (followed by dissolution)

In dissolution also effects like temp. Pressure which are very important.

Need for decomposition :-

1. Selection of container.
2. High temp of pressure.

Selection solvents depends upon :-

1. Nature of the compound which is to be dissolved.
2. Nature of the study determination.
3. Instrument - technique used.
4. Some metals with chlorides (Cl) are highly volatile at low temp.
5. In microwave digestion system we use the effect of temp & pressure.
6. In ultrasonic - technique digestion use high energy waves & break the substances with sample with.

Selection of containers:

It is very important 3 types.

1. Glass — quartz, Boro silicates.
2. Metal crucibles - Ni, Ag, Co, Au, Pt
3. Teflon (TFE)

→ Boro silicates are not used to estimated Na. since 'Na' forms complex materials with Boro silicates leading to destruction of container.

→ By using HF as decomposition agent we should adopt glass as the container.

since $HF + Si \longrightarrow$ Volatile SiF_4.

So it. cleaning of glass will occurs leading to destruction of container.

→ Also use HF by decomposing agent Teflon containers.

*Principle of Dissolution:-

The process of converting the solids or gases samples into liquid form. some time it may be get destroyed. so it is called dissolution.

Inorganic compounds required acid or base to complete dissolution.

Organic compounds dissolve in suitable reagent. Heat require many samples especially organic samples.

By dissolving the sample the original form is changed so it is better to used decomposition method. so changing the nature of original species.

If there is no change, it is dissolution method.

Eg:

1) H_2S (molecular) + NaOH ⟶ Na_2S (Ionic)

2) Fe_2O_3 (oxide) + HCl ⟶ $FeCl_3$ (Ionic)

Generally decomposition or dissolution two types.

1. Organic compounds
2. Inorganic compounds.

Organic compound :-

Nature of species will not change it abruptly. so it is dissolution. The species is mostly in molecular form and very few in ionic form.

Eventhough, the species not change it may interact. with solvent by

1. Dipole-Dipole (Non-polar)
2. Dipole- induced dipole (weakly polar)
3. Hydrogen bonding (medium polar)
4. Charge transfer (Highly polar)

The ionic form, the molecule is in the ion formation (strong interaction)

Eg:

1) C_6H_6 in cyclohexane has dipole-dipole interaction.

2) Amine in ethanol has interaction by H-B

$H_2N: \longrightarrow H-O-R$

Inorganic compounds:-

Solvents used in 1) H_2O (cold/hot

2) dil. HCl & Conc HCl

Eg: $NaCl + H_2O \longrightarrow \{Na^{+}\}^{aliq} \ldots \{Cl^{-}\}^{aq}$

Selection of solvent depend on
1. Nature of solute compound
2. Nature of study.
3. Availability of the instrument.

other solvents is
1. dil & conc H_2SO_4
2. dil & conc. HNO_3
3. $HCl + HNO_3$ (3:1)

* When dil HCl is added i.e. $Cl^{\ominus}$ ions are added there is a possibility of interfering from $Cl^{\ominus}$ ion & H^{+} ion.
* S^{2-}, CO_3^{2-}, SO_3^{2-}, $OH^{\ominus}$ are soluble in dil HCl
* Inorganic species, the decomposition is also almost dissolution except in case of Acid-Base type of interaction.
Eg:- H_2O - Highly polar.
* Inorganic compounds mostly require decomposition method.
Ex:- H_2O - All salts may dissolve.
* No oxidation power - H^+Cl
Mild oxidation power - $H_2^+SO_4$
Strong oxidation power - H^+NO_3, H^+ClO_4
* H_3PO_4 is not only used for dissolving also used complexing agent.
Similarly 'HF' (SiO_2 is soluble in HF only)
$SiO_2 + HF \longrightarrow SiF_4$ (Volatile) Low B.P

* Differences blw Dissolution & Decomposition

Dissolution	Decomposition
1. The solute particles going into solvent to get a sol. is called dissolution	1. These substances which cannot be dissolved are decomposed.

2. The nature of the sdute species is nearly same as in the case of solid.	2. The nature of the species changes.
3. Temp. is a parameter.	3. H^+ ions conc, nature of the anions are the important parameter.
4. Those are physical in nature.	4. These are chemical in nature.
5. Hydrolysis reactions may be taken place.	5. Hydrolysis reactions may not be taken place.
6. No new compounds are formed.	6. New compounds are formed.

* Decomposition of samples with acids :-

* 1. HF :-

1. In decomposition of minerals & ores. HF has an effects which differs greatly from others mineral acids. It react with SiO_2 & silicates to form unstable H_2SiF_6 which dessociate and gives highly volatile SiF_4.

$$6HF + SiO_2 \xrightarrow{H_2SO_4} H_2SiF_6 + 2H_2O$$

$$H_2SiF_6 \longrightarrow SiF_4 \text{ (low B.P)} + 2HF$$

H_2SiF_6 is not stable at high temp.

SiF_4 can easely removed by boiling.

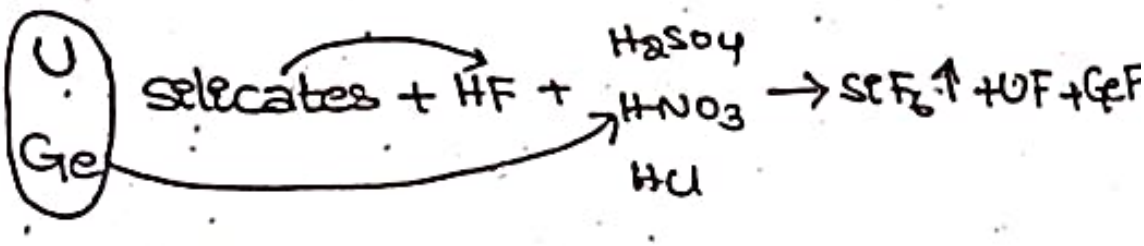
SiF_4 B.P = $-86^\circ C$, exist as vapour.

SiF_8 = $-18^\circ C$

2. HF dissolves to very less extent in water and form $(HF_2^{(-)})$ type of species.

3. The fluoro complexes with several metals some like V, B, Se, Al, Fe, Niobium, Tantalum, Zo, Te, As, Sb, Ge, W, Se, Mo.

4. Certain metal ions also form fluoro complexes like fluoroborate, fluoro Aluminate, fluoro ferrate.
5. For decomposition of chloro peptides, a mixture of HF and $HClO_4$ (1:1) is used at elevated temp. & pressure. The temp increased to 200°C. In a teflon beaker or teflon coated metal system.
6. Dissolution of silicates in HF is generally used for the decomposition of several trace elements.
7. Some of the metal fluorides are volatile the fluorides of Cr, Se, are volatile in presence of $HClO_4$ by taking precautions like
a. suitable minerals acids.
b. Volatility can be reduced.
c. Metals can be determined.
Eg: Analysis of Se in deep sea sediments can be done by decomposing the sediments with HF & HNO_3 in ratio 1:1.
8. for the determination of trace elements in coal fly ash. Best method. is decompose fly ash with a mix HF + HCl.
9. for the determination of 'U' & 'Th' The conc. of 'U' & 'Th' minerals is very low large quantity. of sample must be taken



10, For determination of 'Ti' in silicates decomposition with HF is most suitable method.

11, HF can be stored in polyethylene vessels Because 'HF' reacts with glass very well.

Applications :-

* In the analysis of silicates mixture of HF and mineral acids are used.
* The F^- ions of HF forms complex with many metal atoms such as V, B, Al, Fe, Ti, Ho, W.
* For the determination of 'U' & 'Th'. HF is used. If the conc of 'U' & 'Th' is very low, then large quantity of sample must be used.
* In hydrofluoric acid, H^+ ion conc is 29 N. Its B.P is 112°c.

Hcl :-

- Hcl is basic solvent for dissolution of the compounds. It is highly used in ores & minerals.
1. Dissolution of heavy metal carbonate, chloro carbonates is done by Hcl

Ex:- Ce^{+4}, As^{+3}, Sb^{+3}, Sn^{+3}, Hg^{+2}.

3. It also forms complex with some metals in high acid medium ex:- $[FeCl_6]^{-3}$, $[FeCl_6]^{-4}$
4. Oxides of Fe, Mn are brought into a sol. form using conc Hcl.
5. Sulphides of several metals are also soluble in conc Hcl.

6. ores of Zn, In, Ba, Ca are dissolved in conc Hcl. for the decomposition of ores & minerals in the form of CO_3^{-2} Hcl is best solvent.

Use:- Lime stone, ddanite, Hematite, Azobite,
.. Boral ores are also decomposed using Hcl at elevated temp, under reflux conditions to eliminated volatisation of Boric acid (H_3BO_3).
.. The salt of PO_4^{-3}, $Cl^{\ominus}$, $OH^{\ominus}$ soluble in Hcl.
1. Minerals of U, Th, Rare earths metals are also decomposed by Hcl which are present as phosphates.
2, Vanadates, Tungsten, Arsenates etc soluble by Hcl.
1, ~~Ferro~~ Mo" decomposed by conc Hcl under different conditions like temp, duration of heating time conc of acid.
2, Most of silicates are insoluble, they may decompose as silicic acid (H_4SiO_4) which is insoluble.
3, If heavy metals are associated which silicates like Cu, Zn, Mn the metal ion can be brought into the solution by decomposing with Hcl.
4, Glass or quartz vessels are decomposed by 'Hcl'. If Pt or gold vessels are corroded leading to the dissolution of metals in sol.

Hcl is used in various combinations with HNO_3 for good separations.

3:1 $Hcl + HNO_3 \longrightarrow$ Good oxidant

$Hcl + HNO_3 \longrightarrow Cl_2$ powerful oxidant

$HBr + HNO_3 \rightarrow Br_2$ } Mild oxidant.

$HI + HNO_3 \rightarrow I_2$ }

5. Hcl, H^+ strength in normality is 11.6N

Its B.p is 110°c, It is heavy smell reducing

Powder.

16. Generally decomposition with HCl is carried out in glass vessels. If Pt (or) Gold vessels are used. They may be corroded due to prolonged constant with HCl.

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Applications:

1. Dissolution of heavy metal carbonates & fluoro carbonates is done by HCl.

$Fe_2(CO_3)_3 + 6HCl \rightarrow 2FeCl_3 + 3CO_2 + 3H_2O$.

2. Oxides of Iron, Manganese are brought into sol. using conc. HCl.

3. Oxes of Zn, Fe, Ba, Ca are soluble in conc HCl.

4. Minerals of U, Th. rare earth metals also decomposed by using conc HCl.

5. The salts of phosphate hydroxide chloride ions also soluble in HCl.

* 3 HNO_3:

1. It is powerful solvent for a no. of minerals especially for S^{-2} & PO_4^{-2}.

2. It is a strong acid & strong oxidant oxidises several species to higher oxidant states like S^{-2}, S, SO_4^{-2} arsenate. Arsenite.

3. It is generally stored in polyethylene vessels or glass or Teflon. fuming HNO_3 can be boiled in Teflon vessels.

4. Au, Pt, U, Rh, Ir don't dissolve in HNO_3. Whereas Ag, Pd are easily soluble.

Majority of metals decomposed with conc HNO_3, except Au & Pt.

5. For the analysis of sulphide ores like W, Zn, Cd, HNO_3 is the best solvent.
6. Minerals containing Be, Mo, Sn easily decomposed using HNO_3 at slightly high temp.
7. HNO_3 is generally in combination with HCl. Aquaregia HCl ; HNO_3 (3:1), HCl: HNO_3 (1:3) is inverted aquaregia. This mixture is a powerful chlorinating agent and powerful oxidant.
8. Hot conc. aquaregia completely dissolves Al, Pt, Au and corrodes Na. V is highly resistant, crucible made up of Pt. V alloy or Zn or Teflon can be used for decomposition of minerals using Aquaregia.
9. It is used for the extraction of Au, Pt, gp metals.
10. Decomposition of sulpho salts takes place by oxidation of sulpho salts → sulphates.

$Fe(II) \longrightarrow Fe(III)$ $\quad Sb^{+3} \longrightarrow Sb^{+5}$

$As^{+3} \longrightarrow As^{+5}$ $\quad Cu^{+} \longrightarrow Cu^{+2}$

11. It dissolves polymetallic ores like Cu, Zn, Pb, Mo, Cd, Tl, Be - - - - etc and also uranium oxides and other rare earth metals
12. The inverted aquaregia is powerful oxidant for the quantitative oxidation of $S^{-2} \rightarrow SO_4^{-2}$

*4. H_2SO_4 :-

1. It is efficient solvent for so. of ores and minerals.
2. Conc H_2SO_4 & hot condition is a mild oxidising agent.
3. When H_2SO_4 used at high temp one must keep in mild. The nature of crucible used. Since Pt, Au at very high temp

are not recommended.
4. 'Au' is stable upto 250°c Teflon is stable upto 300°c.
5. H_2SO_4 can be used for the preliminary decomposition of rocks containing Pt group metals.
6. H_2SO_4 can be at high temp is mostly used for the decomposition of S^{2-} ores such as As, Sb, & other metals like are Arsenides & sulphites of Co & Ni.
7. H_2SO_4 used for the decomposition of minerals containing Se, Te. The temp of decomposition must be maintained below 100°c to avoid volatilisation of 'Se' salts.
8. H_2SO_4 used for the decomposition of poly metallic ores. especially for the determination of Tl.
9. Halides. especially F^- can be easily decomposed using H_2SO_4.
10. for the decomposition of Nb, Ta oxides for further estimation H_2SO_4 is used.
11. H_2SO_4 is used for the decomposition of CO_3^{2-}, PO_4^{3-} silicates.
12. SO_2 is main reducing product in Gelther method Nitrogen + H_2SO_4 is used to destroy the organic matter. Its B.P raised by K_2SO_4 the rate of reaction is speed catalyses such as Se, Hg.
13. Many metals dissolution / decomposition, hot conc H_2SO_4 used the B.P is 340°c.

5. $HClO_4$:-

1. It is strong acid & powerful oxidising