

## Quadrant II – Transcript and Related Materials

**Programme: Bachelor of Science**

**Subject: Chemistry**

**Paper Code: CHC 106**

**Paper Title: Inorganic Chemistry**

**Unit: Chemistry of Halogens**

**Module Name: Pseudohalogens: Methods of preparation, Chemical properties and structure**

**Module No: 05**

**Name of the Presenter: Mrs Varsha Virginkar**

**Notes -----**

Pseudohalogens

Introduction:

Inorganic radicals which in the free state possess properties comparable to those of elemental halogens and in the form of anions possess properties comparable to those of halide ions are called Pseudohalogens or Halogenoids

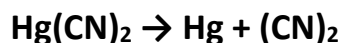
These inorganic radicals exist as neutral dimers in the free state and as monomeric anions in the anionic state .

Pseudohalogens	Neutral Dimers	Pseudohalides	Anion
Cyanogen	$(\text{CN})_2$	Cyanide	$\text{CN}^-$
Thiocyanogen	$(\text{SCN})_2$	Thiocyanate	$\text{SCN}^-$
Selenocyanogen	$(\text{SeCN})_2$	Selenocyanate	$\text{SeCN}^-$
Tellurocyanogen	$(\text{TeCN})_2$	Tellurocyanate	$\text{TeCN}^-$
Oxycyanogen	$(\text{OCN})_2$	Cyanate	$\text{OCN}^-$

Azidocarbonyldisulphide	$(\text{SCSN}_3)_2$	Azidodithiocarbonate	$\text{SCSN}_3^-$
unknown	$(\text{N}_3)_2$	Azide ion	$\text{N}_3^-$

## Cyanogen $(\text{CN})_2$

**Preparation :** By heating cyanides of inactive metals such as Ag, Hg, Au



**Properties:**

Colourless poisonous gas with Smell of bitter almonds

Polymerises to paracyanogen  $(\text{CN})_x$  at  $400 - 500^\circ\text{C}$

Reacts with water producing hydrocyanic acid and cyanic acid



Reacts with alkalis to form cyanide and sodium cyanate



**Structure :** It is a linear molecule



The C-N bond length is  $1.16 \text{ \AA}$ .

The C-C bond length is  $1.37 \text{ \AA}$ .

## Thiocyanogen $(\text{SCN})_2$

**Preparation:** prepared by the action of bromine on a suspension of

lead thiocyanate in ether



**Properties:** Obtained in solid form at  $-70^\circ\text{C}$ .

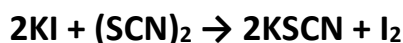
Polymerises at room temperature to red solid

parathiocyanate  $(\text{SCN})_x$

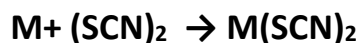
Reacts with water forming thiocyanic acid as one of the products.



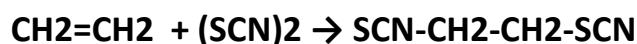
Oxidises iodide to iodine



Reacts directly with divalent metals to form thiocyanates



Like halogens it reacts with unsaturated hydrocarbons like ethylene to give saturated compounds

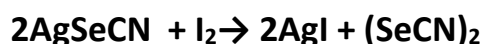


Structure: Thiocyanogen is suggested to have the following structure



Selenocyanogen  $(\text{SeCN})_2$

Preparation: Prepared by action of iodine on silver selenocyanate suspended in ether



Decomposition of lead tetraselenocyanate gives selenocyanogen



Electrolysis of Potassium selenocyanate in methyl alcohol. On evaporation of anode solution selenocyanogen is left behind.

Properties: Yellow coloured powder

Soluble in benzene, chloroform, etc

In water it is hydrolysed to selenious, selenocyanic and hydrocyanic acid.



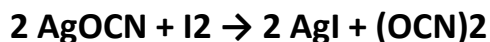
Structure: Similar to that of thiocyanogen



## Cyanogen (OCN)<sub>2</sub>

Preparation: Prepared by the reaction of AgOCN and I<sub>2</sub> in

CS<sub>2</sub> or CCl<sub>4</sub>



Structure:  $\text{N}\equiv\text{C}-\text{O}-\text{O}-\text{C}\equiv\text{N}$

## Azidocarbonyldisulphide (SCSN<sub>3</sub>)<sub>2</sub>

Preparation: Prepared by oxidising KSCSN<sub>3</sub> with I<sub>2</sub> or H<sub>2</sub>O<sub>2</sub>



Properties: White crystalline solid

Unstable and explodes due to autocatalytic reaction



Reacts with alkali



Structure:

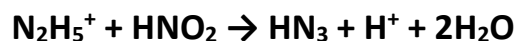


## Azide N<sub>3</sub>

No existence of free azide group

Number of azides containing azide ion N<sup>3-</sup> are known e.g. IN<sub>3</sub>, KN<sub>3</sub> etc.

Free hydrazoic acid is obtained by action of Nitrous acid



Sodium salt is prepared by reaction of sodium nitrate and Sodium amide NaNH<sub>2</sub>



Structure:  $-\text{N}=\text{N}^+=\text{N}-$

