

LECTURE NOTES

ON

**CHM 212: Basic Inorganic Chemistry II**

DEPARTMENT OF CHEMISTRY,  
UNIVERSITY OF AGRICULTURE, ABEOKUTA(UNAAB)

*LECTURERS IN CHARGE*

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**COURSE DESCRIPTION**CHM 212: Basic Inorganic Chemistry II2units

Introduction to study of non-aqueous solvents. Introduction to group theory and symmetry. Inorganic energetic of ionic solids, inorganic application of standard reduction potentials. Concept of hard and Soft acids and bases. Chemistry of Groups VIA and VIIA and treatment of interhalogen.

## INTRODUCTION TO STUDY OF NON-AQUEOUS SOLVENTS.

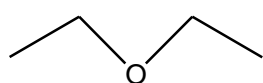
### What are Non-aqueous Solvents?

These are solvents other than water. Their use as solvents is due to the fact that water is not always a good solvent since some reagents may react with water (eg alkali metals) during inorganic reactions.

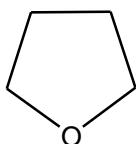
### Classifications and Examples of Non-aqueous Solvents

Examples of Non-aqueous Solvents are;

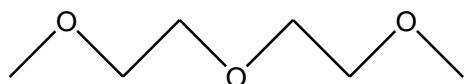
Organic solvents: Dichloromethane, Hexane, Toluene, Ethers(eg diethyl ether, diglyme, tetrahydrofuran-THF)



Diethyl ether



tetrahydrofuran

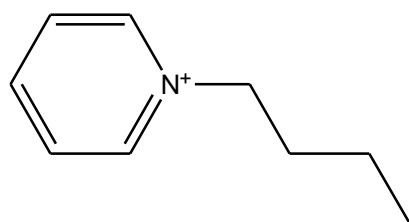


Diglyme

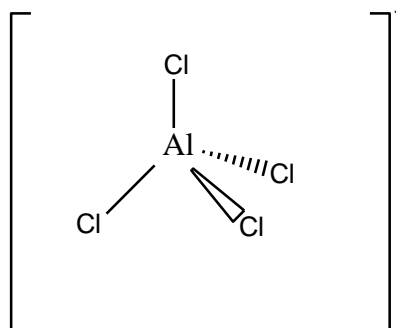
1-(2-methoxyethoxy)-2-methoxyethane

Exotic solvents(Inorganic): Liquid ammonia( $\text{NH}_3$ ), Liquid Sulphur dioxide( $\text{SO}_2$ ), Sulphuric acid( $\text{H}_2\text{SO}_4$ ), Bromine trifluoride( $\text{BrF}_3$ )

Ionic solvents:  $[\text{pyBu}][\text{AlCl}_4]$



N-butylpyridinium ion



Tetrachloroaluminate ion

These solvents can be classified as:

*Protic Solvent:* This is a solvent that undergoes self-ionization and provides protons which are solvated. Examples: HF, MeOH, EtOH,  $\text{H}_2\text{SO}_4$ , Liquid  $\text{NH}_3$  etc

**(NB: Self ionizing is when a pure liquid partially dissociates into ions.)**

**Aprotic Solvent:** This a solvents that undergoes self-ionization without the formation of protons. Examples:  $N_2O_4$ ,  $BrF_3$ , N, N-dimethylformamide, dimethyl sulfoxide, and nitrobenzene

### Definition of Some Terms

**Relative Permittivity:** This is also referred to as dielectric constant. When two charges  $q_1$  and  $q_2$  are separated by a distance  $r$  in a vacuum, the potential energy of their interaction is

$$V = \frac{q_1 q_2}{4\pi\epsilon_0 r}$$

When the same two charges are immersed in a medium such as a liquid(solvent), their potential difference is reduced to

$$V = \frac{q_1 q_2}{4\pi\epsilon r} \quad \text{where } \epsilon \text{ is the permittivity of the medium.}$$

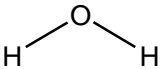
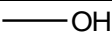
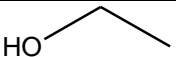
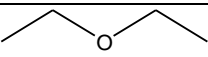
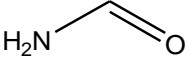
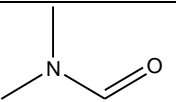
The permittivity is normally expressed in terms of the dimensionless relative permittivity,  $\epsilon_r$ .

$$\epsilon_r = \frac{\epsilon}{\epsilon_0}$$

The relative permittivity of a substance is large if its molecules are polar or highly polarizable

**Dipole moments:** This represents the arrangement of charges in a system or molecule that is oppositely charged at two points or pole. It has a symbol  $\mu$  with a unit Debye, D.

Examples:

Solvent	Formula	Relative permittivity, $\epsilon_r$	Dipole moments, $\mu$
Water		78.7	1.85
Methanol		32.7	1.70
Ethanol		24.3	1.69
Diethyl ether		4.3(293K)	1.15
Formamide		109(293K)	3.73
N,N-dimethylformamide		36.7	3.86

From the table, the values of  $\mu$  follows in value of the  $\epsilon_r$  for solvents of related structures.

Ion-solvent interactions are favoured by using solvents with a large dipole moment, but for maximum effect, the solvent molecule should also be small and both ends of it should be able to interact with the ions in the same way that water interacts with cations through the oxygen atoms and with anions through the hydrogen atoms.

Question: Liquid ammonia has  $\epsilon_r = 25.0$ ,  $\mu = 1.47D$ . Dimethylsulphoxide has  $\epsilon_r = 46.7$ ,  $\mu = 3.96D$  and nitromethane has  $\epsilon_r = 35.9$ ,  $\mu = 3.46D$ . Which one of them is the better solvent for ionic salts.

### **Acid base behavior in Non aqueous solvents.**

#### ***Levelling Effect:***

Levelling effect is exhibited by a solvent when the strength of the dissolved acid cannot exceed that of the protonated solvent. For example, HCl dissolved in acetic acid acts as a weak acid. Non-aqueous solvents like ammonia are good proton acceptors and encourage acids to ionize in them. Liquid  $NH_3$  has a marked levelling effect upon acids; thus, for example, acetic, benzoic, nitric, and hydrochloric acids all give solutions with identical acidic properties, owing to the ion  $NH_4^+$ , although, of course, in water they behave very differently.

#### ***Differentiating Effect:***

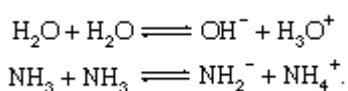
As stated earlier, HCl and also HBr and HI behave as weak acids in acetic acid. But the extent of their ionization varies as follows;  $HI > HBr > HCl$ . These acids are normally classified as strong acids in aqueous solution because they are fully ionized. But acetic acid gives a contrast to this, thus it has a differentiating effect on the acidic behavior of HCl, HBr and HI whereas water does not.

### **Solvent Based definition of Acids and bases.**

Question: What is the Brønsted–Lowry definition of acid and base?

Ans; Acid is a proton donor and Base is a proton acceptor.

In a self ionizing solvent, an acid is described as a substance that produces the cation characteristic of the solvent, and a base is a substance that produces the anion characteristic of the solvent.



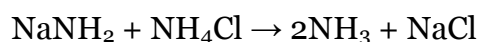
Here, self ionization corresponds to the transfer of a proton from one solvent to another;

Examples:

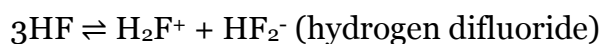
1. Liquid ammonia



Therefore, in liquid ammonia, an acid is described as a substance that produces  $[NH_4]^+$  ions, while a base produces a  $[NH_2]^-$ . Thus  $NaNH_2$  is a base and  $NH_4Cl$  is an acid in liquid ammonia, and they react, producing the salt and the solvent:



2. Liquid Hydrogen fluoride



## 3. Pure Sulphuric acid



## 4. Dinitrogen tetraoxide



In this medium, nitrosyl salts eg  $[\text{NO}][\text{ClO}_4]$  behave as acids and metal nitrate eg  $\text{NaNO}_3$  behave as a base.  $\text{NaNO}_3 + \text{NOCl} \rightarrow \text{N}_2\text{O}_4 + \text{NaCl}$

5.  $2\text{SbCl}_3 \rightleftharpoons \text{SbCl}_2^+ \text{ (dichloroantimonium)} + \text{SbCl}_4^- \text{ (tetrachloroantimonate)}$ 6.  $\text{POCl}_3 \rightleftharpoons \text{POCl}_2^+ + \text{POCl}_4^-$ 

Selected properties of some Non-aqueous solvents

Property/unit	H <sub>2</sub> O	Liquid NH <sub>3</sub>	Liquid SO <sub>2</sub>	Liquid HF	H <sub>2</sub> SO <sub>4</sub>
Melting point/K	273.0	195.3	197.5	Liquefies from 190-292.5K	283.4
Boiling point/K	373.0	239.6	263.0		≈603
Density of liquid/gcm <sup>-3</sup>	1.00	0.77	1.43		1.84
Dipole moment/D	1.85	1.47	1.63		
Relative permittivity	78.7(at 298K)	25.0(at mp)	17.6(at bp)	84(at 273K) 175(at 200K)	110(at 292k)
Self ionization constant	1.0x10 <sup>-27</sup>	5.1x10 <sup>-27</sup>		2.0x10 <sup>-12</sup> (at 273K)	2.7x10 <sup>-4</sup> (at 298K)

bp=boiling point

mp=melting point

## LIQUID AMMONIA

This is the most studied nonaqueous solvent. It is a strong hard base which has the ability to coordinate to *d-block* acids and protons. It undergoes self ionization to produce



### Reactions in Liq NH<sub>3</sub>.

## 1. Neutralisation

In a neutralization reaction involving liq. Ammonia as a solvent, phenolphthalein may be used to detect endpoint.



## 2. Precipitation reaction

### ***Solvent Affinity***

Chemical Characteristics:

1. The metals are very soluble in liquid ammonia
2. Their solutions in liquid ammonia have a conductivity comparable with their pure metal .
3. liquid ammonia solvates the metal ion but is resistant to reduction by the free electrons.
4. The solutions of the metals in liquid ammonia are very good reducing agents because of the presence of the free electrons.

### ***Applications of Solutions of liquid ammonia***

1. Solutions of the ammonium salts are used to clean cooling systems in some nuclear reactors
2. Liquid sodium is used to cool fast breeder nuclear reactors

## **Introduction to group theory and symmetry**

Literally, symmetry means quality of being very similar or exact match in size and shapes of molecules. It is an operation performed on an object which leaves it in a configuration that is indistinguishable from and super imposable on, the original configuration.

### **Symmetry Elements and Symmetry Operations**

Five types of symmetry elements are used to describe the symmetry of molecules:

- 1) Centre of symmetry
- 2) Proper rotation axis
- 3) Mirror plane
- 4) Improper rotation axis
- 5) Identity element

Each of these symmetry elements has associated with it a symmetry operation. They are: the inversion operation, rotation operation, reflection operation and operation of improper rotation respectively



## Inorganic energetic of ionic solids

Lattice Energy of an Ionic crystal/ solid( $\Delta U$ ): This is the amount energy required per mole to separate ions from their positions to an infinite distance in the gas phase of an ionic solids under standard condition. It is the enthalpy change that accompanied the formation of one mole when one mole of an ionic crystal is formed from its constituent ions in the gaseous state under standard conditions.

It is a measure of ionic strength. Lattice energy(ies) cannot be measured directly, but experimentally values are obtained from thermodynamic data using Born- Haber cycle and applying Hess's law. The theoretical values for lattice energy may be calculated using the Born- Lande equation which depends on the product of the ionic charges, on the crystal structure, and on the distance between ions.

Calculations on these concepts will be available as tasks.

- 1) If the enthalpy energy of formation of  $\text{MgCl}_2$  is  $641\text{kJmol}^{-1}$ , with the following data:

$$\Delta H^{\circ}_{\text{atom}}(\text{Mg}) = +150\text{kJ/mol}, \Delta H^{\circ}_{\text{I.E}}(\text{Mg}) = 7,360\text{kJ/mol}, \Delta H^{\circ}_{\text{atom}}(\text{Cl}) = +120\text{kJ/mol},$$

$$\Delta H^{\circ}_{\text{E.A}}(\text{Cl}) = -364\text{kJ/mol}, \text{ determine the } \Delta U(\text{MgCl}_2) ?$$

- 2) If the lattice energy of  $\text{CsCl}$  ionic solid is  $-744\text{kJ/mol}$ , determine the  $\Delta H_f^{\circ}$  for

$\text{CsCl}$  using data below:

$$\Delta H^{\circ}_{\text{atom}}(\text{Cs}) = +76\text{kJ/mol}, \Delta H^{\circ}_{\text{I.E}}(\text{Cs}) = +376\text{kJ/mol}, \Delta H^{\circ}_{\text{atom}}(\text{Cl}) = +120\text{kJ/mol},$$

$$\Delta H^{\circ}_{\text{E.A}}(\text{Cl}) = -3429\text{kJ/mol}$$

- (3) Calculate the lattice energy for  $\text{LiF}$  using the Born- Lande equation with the following data.  $n=6$ ,  $\text{Li-F}$  (internuclear separation) =  $2.8\text{\AA}$ ,  $A = 1.7476$ ,  $\epsilon_0 = 8.85 \times 10^{-12}\text{ Fm}^{-1}$ ,  $N_0 = 6.023 \times 10^{23}\text{mol}^{-1}$ ,  $e = 1.602 \times 10^{-19}\text{ C}$

## Standard Electrode Potentials( $E^{\circ}$ )

This is the potential difference set up between the metal and a one molar solution of its ions at  $25^{\circ}\text{C}$  when coupled with standard hydrogen electrode (SHE) as the reference electrode of  $0.00\text{V}$ . While the cell potential (emf) is the difference between two electrodes potentials, one associated with the cathode and the other associated with the anode. By convention, the

potential associated with each electrode is chosen to be the potential for the reduction to occur at that electrode.

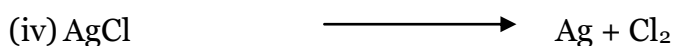
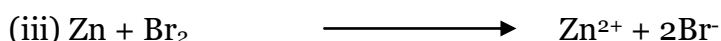
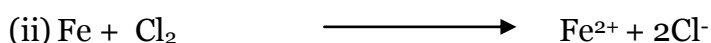
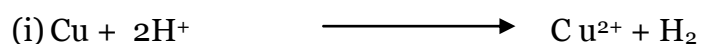
Mathematically, the cell potential,  $E^{\circ}_{\text{cell}}$  is given by the standard reduction of the cathode reaction  $E^{\circ}_{\text{red(cathode)}}$  minus the standard reduction of the anode reaction  $E^{\circ}_{\text{red(anode)}}$

$$\text{i.e. } E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red(cathode)}} - E^{\circ}_{\text{red(anode)}}$$

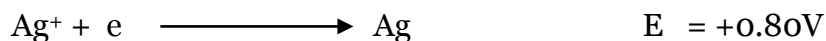
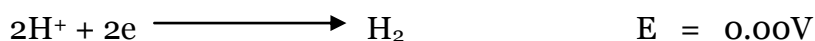
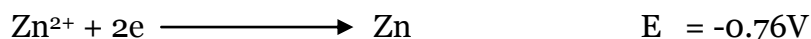
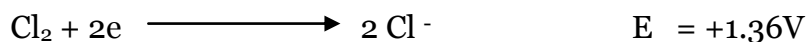
**Note:** The positive overall potential (emf) indicates that the reaction is spontaneous(feasible) and if the potential is negative, it is not spontaneous and the reverse reaction is.

Calculations on these concepts will be available as tasks.

4) Predict whether the following reactions are spontaneously under standard conditions or not?



Given :



### What is a hard and soft acids?

The term hard and soft acid is a qualitative one which refers to the polarizability of the acid (and typically refers only to Lewis acids). Hard acids are either small monocations with a relatively high charge density or are highly charged. A soft acid is the one that is highly polarizable, whereas a hard acid is one that is not polarizable.

Factors that contribute to the strength of the bonds between donor and acceptor are :

- 1) Sizes of the cation and donor atom
- 2) Their Charges
- 3) Their electronegativities
- 4) Their orbital overlap between them

Selected hard and soft metal centers ( Lewis acids) and ligands and those that exhibit intermediate behaviour:

Hard ; class(a)  $F^-$ ,  $Cl^-$ ,  $H_2O$ ,  $ROH$ , :  $Li^+$ ,  $Na^+$ ,  $Rb^+$ ,  $Be^{2+}$  etc

Soft class(b)  $I^-$ ,  $H^-$ ,  $R^-$ ,  $[CN]^-$  : zero oxidation state metal,  $Tl^+$ ,  $Cu^+$ ,  $Ag^+$  etc

Intermediate  $Br^-$ ,  $[N_3]^-$ ,  $Py$  :  $Pb^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$  etc

## CHEMISTRY OF GROUP VIA

### Some Physical Data

Members	Symbol	Atomic No.	Electronic Configuration	Atomic radii (Ionic radii-X <sup>2-</sup> )	Mp°C	Bp°C
Oxygen	O	8	[He]2s <sup>2</sup> 2p <sup>4</sup>	0.074(0.140)	-218.4°C	-183.0° C
Sulphur	S	16	[Ne]3s <sup>2</sup> 3p <sup>4</sup>	0.104(0.184)	*119°C	444.6° C
Selenium	Se	34	[Ar]4s <sup>2</sup> 4p <sup>4</sup>	0.117(0.198)	+217° C	685° C
Tellurium	Te	52	[Kr]5s <sup>2</sup> 5p <sup>4</sup>	0.137(0.221)	450	990
Polonium	Po	84	[Xe]4f <sup>14</sup> 6s <sup>2</sup> 6p <sup>4</sup>	0.140	254	960

\* For monoclinic sulphur

+For grey selenium

### General Characteristics of Group V Elements

- Group 6 elements are often called the chalcogens
- All members other than oxygen are solids under normal conditions.
- Metallic character generally increases down the group with oxygen, sulphur and selenium being non-metals while tellurium is a metalloid and polonium is a metal.
- The group electron configuration is ns<sup>2</sup>p<sup>4</sup>. This suggests a group maximum oxidation number of +6. Oxygen never achieves this but other members do. They can complete their octet by either gaining two electrons to form 2-valent ion or by forming two covalent bonds.. Te and Po can also form the 4-valent cation X<sup>4+</sup> (inert pair effect).

### Oxygen

#### **Properties**

1. It is colourless and odourless diatomic gas
2. It liquefies at -183°C and freezes at -218°C
3. It is chemically very reactive forming compounds with all other elements except noble gases and some unreactive metals.
4. It's molecule is paramagnetic

#### **Ozone**

This is an allotrope of oxygen.

#### **Properties**

1. It boils at -112°C
2. It is explosive and highly reactive blue gas which is thermodynamically unstable.
3. It decomposes to the dioxygen
4. It has a pungent characteristic smell
5. It is diamagnetic

6. When pure, it is a pale blue gas. Liquid ozone is darker blue(or blue-black) and solid ozone is violet-blue.
7. It absorb strongly in the 220-290nm region of the spectrum which is vital on preventing the harmful UV rays of the sun from getting to the Earth's surface
8. Ozone reacts with unsaturated polymers causing undesirable cross-linking and degradation.

## **Sulphur**

### ***Occurrence***

Sulphur occurs naturally in deposits around volcanoes and hot springs and sulphur containing minerals include iron pyrites(fool's gold)-FeS<sub>2</sub>., galena(PbS), sphalerite or zinc blende(ZnS), cinnabar(HgS), realgar (As<sub>4</sub>S<sub>4</sub>), or piment (As<sub>2</sub>S<sub>3</sub>) , molybdenite(MoS<sub>2</sub>) and chalcocite(Cu<sub>2</sub>S).

They can be extracted by Frasch process or Claus process.

*Clauss process:* This involves the extraction from natural gas and crude oil. Here hydrogen sulphide is first oxideized in air at 1000-1400°C. Some SO<sub>2</sub> is produced which reacts with the remaining H<sub>2</sub>S at 200-350°C over a catalyst (activated carbon or alumina) to produce the Sulphur

### ***Allotropes of Sulphur***

Sulphur can exhibit allotropy. Two common allotropes are rhombic(α-form) and monoclinic (β-form) sulphurs. Rhombic are yellow, transparent and have a density of 2.00g/cm<sup>3</sup>. Monoclinic are amber-yellow, transparent and have a density of 1.96g/cm<sup>3</sup>.

The temperature 95.6°C is the transition temperature of the allotropes(α- and β-form). Below this temperature rhombic Sulphur is more stable. Above it, monoclinic Sulphur is more stable. This type of allotropy in which a definite point exists where two forms becomes equally stable is called ENANTIOTROPY.

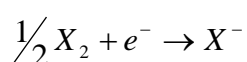
## CHEMISTRY OF GROUP VIIA AND TREATMENT OF INTERHALOGEN

### Some Physical Data

Members	Symbol	Atomic No.	Electronic Configuration	Atomic radii (Ionic radii)	Mp <sup>o</sup> C	Bp <sup>o</sup> C
Fluorine	F	9	[He]2s <sup>2</sup> 2p <sup>5</sup>	0.072(0.136)	-220	-188
Chlorine	Cl	17	[Ne]3s <sup>2</sup> 3p <sup>5</sup>	0.099(0.181)	-101	-34.7
Bromine	Br	35	[Ar]4s <sup>2</sup> 4p <sup>5</sup>	0.114(0.195)	-7.2	58.8
Iodine	I	53	[Kr]5s <sup>2</sup> 5p <sup>5</sup>	0.133(0.216)	114	184
Astatine	At	85	[Xe]4f <sup>14</sup> 6s <sup>2</sup> 6p <sup>5</sup>			

### General Properties

- All halogens exist as diatomic molecules linked by a covalent bond.
- F and Cl exist as gases, Bromine as liquid and Iodine as solid. They are all non-metallic, although there is the usual increase in metallic character with increasing atomic number eg dipyrindine iodine nitrate can be written as [I(pyridine)<sub>2</sub>]<sup>+</sup>NO<sub>3</sub><sup>-</sup> containing I<sup>+</sup> ion as part of the complex.
- Their melting point and boiling point increasing down the group while the volatility decreases down the group. This is due to the increasing strength of Van der Waal's forces with increasing relative molar mass.
- They are all coloured, the depth of the colour increasing with increase in atomic number.  
Fluorine=pale yellow  
Chlorine=pale green  
Bromine=red brown  
Iodine=Shiny black
- All halogens except fluorine dissolve slightly in water and colour it. Fluorine is a strong oxidizing agent that converts water to oxygen. Halogens are non-polar simple molecules, hence are more soluble in organic solvents eg in tetrachloromethane [Cl is colourless, Br is red and I is violet]
- They react with metals to form ionic compounds containing halide ion (X<sup>-</sup>). With non-metals and some metals with high oxidation states, they tend to form simple molecular compounds with covalent bond(X<sub>n</sub>).
- They act as strong oxidizing agents. The order of decreasing power as oxidizing agents is  
F<sub>2</sub>>Cl<sub>2</sub>> Br<sub>2</sub>> I<sub>2</sub>



$F_2$ ,  $Cl_2$  and  $Br_2$  will oxidise  $Fe^{2+}$  to  $Fe^{3+}$  but not  $I_2$ . The electrode potential becomes less positive from fluorine to iodine, reflecting decreasing oxidizing power.

### FLUORINE

Fluorine is different from other halogen because of

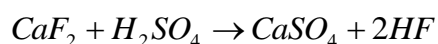
1. Inability of F to exhibit oxidation state other than -1 in its compounds.
2. Relatively small size of F atom and  $F^-$  ion
3. Low dissociation energy of  $F_2$ .
4. High electronegativities of fluorine

### Occurrence

It occurs naturally as fluorspar ( $CaF_2$ , calcium fluoride or fluorite), cryolite ( $Na_3[AlF_6]$ ), fluorapatite ( $Ca_5F(PO_4)_3$ )

### Extraction/Preparation

Most fluorine containing compounds are made using HF which is prepared from fluorite by reaction.



HF is also recycled from aluminum manufacturing processes, petroleum alkylation processes.

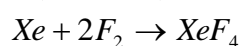
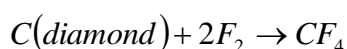
$F_2$  is prepared industrially by electrolytic oxidation of  $F^-$  ion. (The electrolyte is a mixture of anhydrous molten KF and HF, the electrolysis cell is a steel or Cu cathode, ungraphitized carbon anode, a Mond metal (Cu/Ni) diaphragm.

### Uses of Fluorine

1. Added to some water supplies and toothpaste as Fluoride ions to prevent tooth decay.
2. Used as  $UF_6$  in the nuclear power industry for separation of isotopes of uranium
3. HF used to etch glass
4. Used as a non-aqueous solvent.

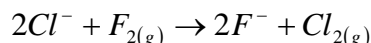
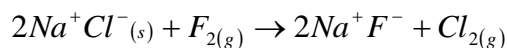
### Properties of F

1. It is a pale yellow gas with irritating smell
2. It is extremely poisonous
3. It liquefies at  $-188^\circ C$  and at  $-220^\circ C$
4. Fluorine is the most chemically reactive non-metal. It reacts with diamond and xenon on heating



5. Most metals catch fire fluorine and even gold and platinum are attacked if heated in a stream of the gas. Elements generally attain their highest valency state in combination with fluorine. E.g.  $SF_6$ ,  $AgF_2$  (with Cl is 1-valent)

6. It is the most electronegative of elements and will displace all other halogens from their ionic halides eg



7. It's synthesis cannot be carried out in aqueous media because  $F_2$  decomposes  $H_2O$ , liberating ozonized oxygen ( $O_2$  containing  $O_3$ ).

## CHLORINE, BROMINE AND IODINE

### Occurrence

Chlorine occurs in combination with Na and K. The most common compound of chlorine is NaCl which occurs in sea water and in rock salt. Also occurs in sylvite (KCl) and carnallite( $KCl \cdot MgCl_2 \cdot 6H_2O$ ).

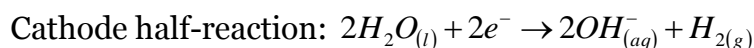
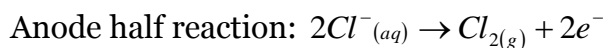
Bromides and iodides occur in much smaller amounts than either fluorides or chlorides. Sea water contains only small concentration of bromine( $Br_2$ ) but significantly higher concentrations of  $Br^-$  are present in salt lakes and natural brine wells.

The natural abundance of iodine is less than that of the lighter halogens. It occurs as iodide ion ( $I^-$ ) in sea water and is taken up by seaweed from which it may be extracted. The main source of iodine is sodium iodate(V) ( $NaIO_3$ ) found in Chile (impure Chile saltpeter (caliches)).

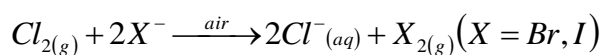
### Extraction

All the dihalogens are produced commercially on a large scale, with chlorine production by far the greatest followed by fluorine. This is done by electrolysis of the halides.

Most commercial chlorine is produced by the electrolysis of aqueous sodium chloride solution in a chloralkali cell. Half reactions are



Bromine is obtained by the chemical oxidation of  $Br^-$  ions in sea water. A similar process is used to recover iodine from certain natural brines that are rich in  $I^-$ . Chlorine is used as oxidizing agent in both processes(since it is a stronger oxidizing halogen). The resulting  $Br_2$  and  $I_2$  are driven from the solution in a stream of air;



### Uses

#### Chlorine

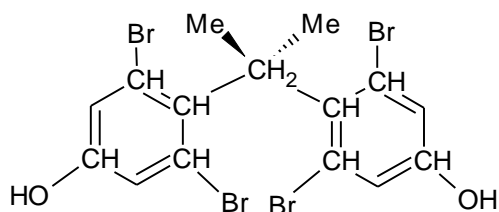
1. Used for the manufacture of organic chemicals such as



- a. Tetrachloromethane
  - b. 1,2-dichloroethene and vinyl chloride are used in the polymer industry (a monomer used in the production of plastic PVC)
  - c. As antiseptic: TCP, dettol
  - d. As pesticides eg bhc(benzene hexachloride).
2. Dichlorine  $\text{Cl}_2$  is used widely as a bleach in the paper and pulp industry. However due to environmental legislation, chloride dioxide  $\text{ClO}_2$  (an elemental –chlorine free bleaching agent) is favoured over  $\text{Cl}_2$  because it does not produce toxic effluents.
  3.  $\text{ClO}_2$  is used in the treatment of drinking water. (but it is however unstable as a compressed gas).

### *Bromine*

1. Also used in the manufacture of organic compounds such a 1,2- dibromomethane which is added to petrol to remove lead as volatile leadbromide. This is the primary application of this halogen
2. Also used in the production of AgBr for photographic films.
3. Some bromine based organic compounds are used as flame retardants eg tetrabromobisphenol A(TBBPA)



Others include octabromodiphenyl ether (octa-BDE), perbrominated diphenyl ether ( $\text{C}_6\text{Br}_5$ )<sub>2</sub>O [deca-BDE].

### *Iodine*

1. It is used in the production of some organic compounds which is the primary application eg in the manufacture of alkyl halides
2. It is converted to AgI and used in the manufacture of the photographic films
3. Used in the preparation of iodized salt.
4. Used as iodine tincture for medicinal purpose. It is prepared by making a solution of  $\text{I}_2$  in EtOH
5. Iodine is an essential element in humans lack of which causes goiter.
6. Used as a medical radioisotope ( $^{131}\text{I}$ )
7. Some dyes contain high iodine content eg erythrosine B (food red-colour additive E127) which is added to carbonated soft drinks, gelatins and cake icing.

## Differences of Chlorine Bromine and Iodine in terms of colour, odour and solubility

	Chlorine	Bromine	Iodine
Colour/odour	Greenish-yellow poisonous gas with an extremely irritating smell. TA room temperature under pressure(7atm), it liquefies to a yellow liquid	Dark red liquid with unpleasant and poisonous vapour	A dark shiny solid which produces purple vapour on heating
Solubility	Moderately soluble in water but soluble in organic solvent	Moderately soluble in water but soluble in organic solvent	Sparingly soluble in water but soluble in organic solvent

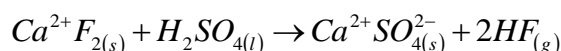
## COMPOUNDS OF THE HALOGENS

### Hydrides-

#### Hydrogen fluoride

Preparation:

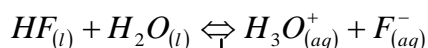
It is formed by action of concentrated  $H_2SO_4$  on calcium fluoride.



When dry, it is known as anhydrous hydrofluoric acid available as a liquid which is stored in mild steel cylinders.

Properties:

1. It is a colourless gas and has a boiling point of  $19.5^\circ C$  which is higher than  $HCl(g)$  ( $-84^\circ C$ ). This is because individual HF units are associated into larger aggregates by means of hydrogen bonding because F is more electronegative than Cl.
2. It behaves as a weak acid in water compared to other aqueous solution of the other hydrogen halides



Equilibrium well over to the left

3. An aqueous solution of hydrofluoric acid attacks most metal with the formation of the metallic fluoride.
4. It forms acidic salts eg  $K^+HF_2^-$  unlike other hydrogen halides.

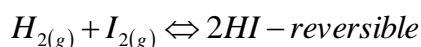
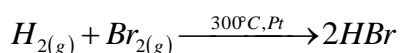
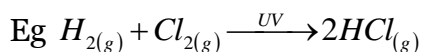
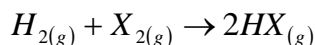
Uses:

An important reagent for the introduction of F into organic and other compounds. Eg in the production of CFCs.

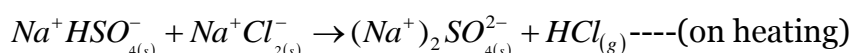
#### Hydrides of Chlorine, Bromine and Iodine

Preparation:

1. By direct synthesis(under appropriate conditions)

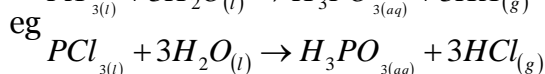
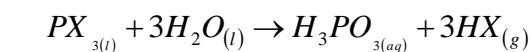


2. Reaction of an ionic halide with conc.  $H_2SO_4$ .



This method cannot be used for HBr and HI because they are reducing agents and are readily oxidized by conc.  $H_2SO_4$  to the free halogens.

3. Action of water on phosphorous trihalides



Properties:

All are colourless gases.

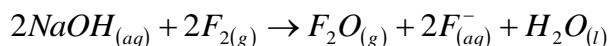
	HCl	HBr	HI
Mp/k	159	186	222
Bp/k	188	207	237.5

## Oxides

### **Oxides of fluorine**

#### Oxygen difluoride- $F_2O$

It is obtained by the reaction of the fluorine gas with sodium hydroxide.

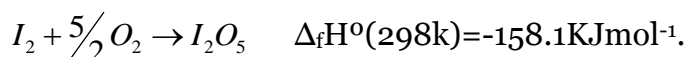


#### Oxygen monofluoride $F_2O_2$

It is obtained by the action of a silent electrical discharge on a fluorine/oxygen mixture at low temperature and pressure. It decomposes into its elements above  $-95^{\circ}C$ .

### **Oxides of Chlorine, Bromine and Iodine**

The oxides of chlorine, bromine and iodine and in some of their compounds, halogen atoms are in an oxidation state of +3, +5 or +7. Only iodine form an oxide which is thermodynamically stable with respect to decomposition into its elements.

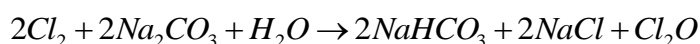
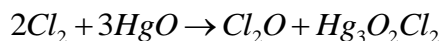


The Cl and Br oxides are hazardous materials with tendency to explode Very difficult to prepare and are all liable to decompose explosively.

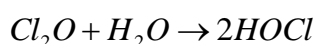
### Chlorine Oxides

Dichlorine monoxide- $\text{Cl}_2\text{O}$ .

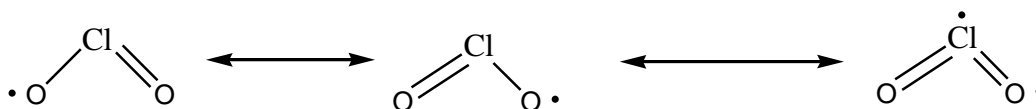
- A yellow-brown (or orange gas) obtained by action of  $\text{Cl}_2$  on mercury (II) oxide or moist  $\text{Na}_2\text{CO}_3$ .



- Liquefies at  $\approx 277\text{K}$
- Hydrolyses to hypochlorous acid



Chlorine dioxide- $\text{ClO}_2$ .

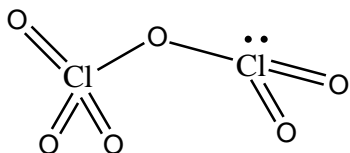


- $\text{ClO}_2$  is a yellow gas with boiling point  $283\text{K}$ .
  - It is produced in the highly dangerous reaction between potassium reaction between potassium chloride  $\text{KClO}_3$  and conc  $\text{H}_2\text{SO}_4$ . A safer method is using  $\text{H}_2\text{Cr}_2\text{O}_4$ .
- $$2\text{KClO}_3 + 2\text{H}_2\text{Cr}_2\text{O}_4 \rightarrow \text{K}_2\text{Cr}_2\text{O}_4 + 2\text{ClO}_2 + 2\text{CO}_2 + 2\text{H}_2\text{O}$$
- It dissolves uncharged in water but is slowly hydrolysed to  $\text{HCl}$  and  $\text{HClO}_3$ .

### Uses.

1. Used to bleach flour and wood pulp
2. Used for water treatment

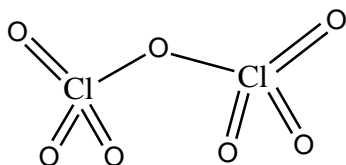
Chlorine Hexoxide  $\text{Cl}_2\text{O}_6$



- It is a dark red liquid
  - Prepared by reaction of ozone with  $\text{ClO}_2$  at  $273\text{K}$  or by this reaction:
- $$\text{ClO}_2\text{F}^- + \text{HClO}_4 \rightarrow \text{Cl}_2\text{O}_6 + \text{HF}$$
- Its solid contains  $[\text{ClO}_2]^+$  and  $[\text{ClO}_4]^-$  ions.
  - It is unstable with respect to decomposition into  $\text{ClO}_2$ ,  $\text{ClClO}_3$  and  $\text{O}_2$ . With  $\text{H}_2\text{O}$ , the following occurs,  $\text{Cl}_2\text{O}_6 + \text{H}_2\text{O} \rightarrow \text{HClO}_4 + \text{HClO}_3$

### Chlorine Heptoxide $\text{Cl}_2\text{O}_7$

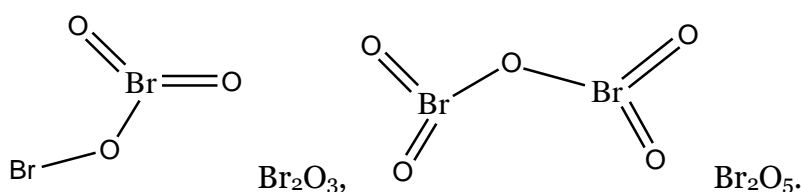
- ◆ It is an oily colourless explosive liquid with boiling point  $\approx 353\text{K}$ .
- ◆ It is made by dehydrating  $\text{HClO}_4$  using phosphorous (V) oxide at low temperatures.



### Bromine Oxides

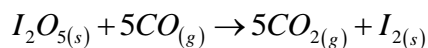
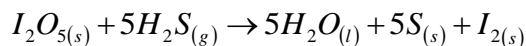
Examples are  $\text{Br}_2\text{O}$ ,  $\text{Br}_2\text{O}_3$ ,  $\text{Br}_2\text{O}_5$ ,  $\text{Br}_3\text{O}_8$ ,  $\text{BrO}_2$  and  $\text{Br}_2\text{O}_7$ .

They are highly unstable and still under study. Structure of  $\text{Br}_2\text{O}_3$  and  $\text{Br}_2\text{O}_5$  has been studied.



### Iodine Pentoxide, $\text{I}_2\text{O}_5$

- ◆ It is stable at  $573\text{K}$ .
- ◆ It is a white crystalline solid
- ◆ It is an oxidizing agent and liberates iodine when reacted with  $\text{H}_2\text{S}$  and  $\text{CO}$ .

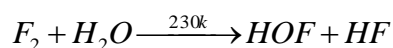


## Oxyacids or Oxoacids

### Oxoacids of Fluorine

#### Hypofluorous acid $\text{HOF}$

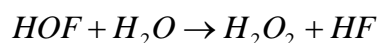
Production: It is obtained by passing  $\text{F}_2$  over ice at  $230\text{K}$  and condensing the gas produced.



#### General Properties

1. It is unstable and no salt of it is known
2.  $\text{HOF}$  decomposes rapidly at  $298\text{K}$   

$$2\text{HOF} \rightarrow \text{O}_2 + 2\text{HF}$$
3. Does not ionize in water but reacts as follows



### Oxoacids of Chlorine

1. Hypochlorous acid  $\text{HOCl}$ . The salt is  $\text{NaOCl}$  which is used as parazone(bleach), Milton etc

2. Chlorous acid HOClO (HClO<sub>2</sub>)
3. Chloric acid HOClO<sub>2</sub> (HClO<sub>3</sub>)
4. Perchloric acid HOClO<sub>3</sub> (HClO<sub>4</sub>)

### ***Oxoacids of Bromine***

1. Hypobromous acid HOBr.
2. Bromic acid HOBrO<sub>2</sub> (HBrO<sub>3</sub>)
3. Perbromic acid HOBrO<sub>3</sub> (HBrO<sub>4</sub>)

### ***Oxoacids of Iodine***

1. Hypoiodous acid HOI.
2. Iodic acid HOIO<sub>2</sub> (HIO<sub>3</sub>)
3. Periodic acid HOIO<sub>3</sub> (HIO<sub>4</sub>)
4. Orthoperiodic acid (HO)<sub>5</sub>IO (H<sub>5</sub>IO<sub>6</sub>)

## **INTERHALOGENS**

Here, halogens form compounds among themselves. These binary interhalogens are molecular compounds with formula XY, XY<sub>3</sub>, XY<sub>5</sub> and XY<sub>7</sub> where the heavier, less electronegative halogen X is the central atom.

### **Preparation:**

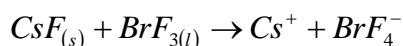
All interhalogens are prepared by direct combination of elements and where more than 2 one product is possible, the outcome of the reaction is controlled by temperature and relative proportion of the halogens.

### **Physical Properties**

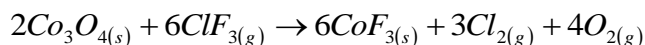
1. XY are made for all combinations of the elements but not all survive for long
2. Most of the higher interhalogens are fluorides. The only neutral interhalogen with the central atom in a +7 oxidation state is IF<sub>7</sub> but ClF<sub>6</sub><sup>+</sup>, a compound of Cl(VII) is known.
3. see table for other properties

### **Chemical properties**

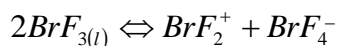
1. Fluorine –containing interhalogens are typically Lewis acids and strong oxidizing agents, though all interhalogens are oxidizing agent.



2. Both ClF<sub>3</sub> and BrF<sub>3</sub> react vigorously (often explosively) with organic matter, burn asbestos and expel oxygen from many metal oxides.



3.  $\text{BrF}_3$  autoionises in the liquid state



### Uses

$\text{ClF}$  (Chlorine monofluoride) acts as a powerful fluorinating and oxidizing agent

### Examples of Interhalogens

Compounds	Appearance at 298K	Melting point/K	Boiling point/K
${}^1\text{ClF}$	Colourless gas	117	
$\text{BrF}$	Pale brown gas	$\approx 240$	
$\text{BrCl}$	Exist only in equilibrium with dissociation products $2\text{BrCl} \rightarrow \text{Br}_2 + \text{Cl}_2$	$\sim$	$\sim$
${}^1\text{ICl}$	Red solid	300( $\alpha$ ) 287( $\beta$ )	$\approx 373^*$
$\text{IBr}$	Black solid	313	289*
$\text{ClF}_3$	Colourless gas	197	285
$\text{BrF}_3$	Yellow liquid	282	399
$\text{IF}_3$	Yellow solid	245	$\sim$
$\text{I}_2\text{F}_6$	Orange solid	337	$\sim$
$\text{ClF}_5$	Colourless gas	170	260
$\text{BrF}_5$	Colourless liquid	212.5	314
$\text{IF}_5$	Colourless liquid	282.5	373
$\text{IF}_7$	Colourless gas	278(sublimation)	-
* dissociates [ $2\text{IX} \rightarrow \text{I}_2 + \text{X}_2 \{X = \text{Cl}, \text{Br}\}$ ]		${}^1$ Most stable diatomic	

### ASTATINE

This is the heaviest member and it is radioactive. It is only known in form of its radioisotopes which all have shortlives.

#### About the Radioisotopes:

- The longest lived isotope is  ${}^{210}\text{At}$  ( $t_{1/2} = 8.1\text{h}$ ) present as transient products of the decay of uranium and thorium minerals.
- ${}^{218}\text{At}$  is formed from  $\beta$ -decay of  ${}^{218}\text{Po}$  but the path competes with decay to  ${}^{214}\text{Pb}$  (the dominant decay).
- ${}^{211}\text{At}$  is artificially prepared from nuclear reaction of  ${}^{209}\text{Bi}(\alpha, 2n){}^{211}\text{At}$  and separated by vacuum distillation. It is an  $\alpha$ -emitter.

Properties of Astatine

1. It is chemically similar to iodine.
2.  $\text{At}_2$  is less volatile than  $\text{I}_2$ .
3.  $\text{At}_2$  is soluble in organic solvents
4.  $\text{At}_2$  is reduced by  $\text{SO}_2$  to  $\text{At}^-$  which can be coprecipitated with  $\text{AgI}$  or  $\text{TlI}$ .
5. Hypochlorite  $[\text{ClO}]^-$  or peroxydisulphate  $[\text{S}_2\text{O}_8]^{2-}$  oxidises astatine to an anion that is carried by  $[\text{IO}_3]^-$  (eg coprecipitation with  $\text{Ag IO}_3$ ) and is therefore probably  $[\text{AtO}_3]^-$ .
6. Less powerful oxidizing agents such as  $\text{Br}_2$  also oxidizes astatine probably to  $[\text{AtO}]^-$  or  $[\text{AtO}_2]^-$ .