ADVANCED CHEMISTRY BLOC

Fluorine, isolation, toxicity and properties

Mukul C. Ray, Odisha

Fluorine was recognized for the first time in fluorspar (CaF_2), a mineral. Toxic properties of fluorine compounds were studied for the first time in animal experiments in 1867. Because of fluorine's tight bonding as well as the toxicity of hydrogen fluoride, the element resisted many attempts to isolate it.

It could not be prepared for a long time from HF and metal fluorides due to the following reasons:

- Generally, we consider by oxidising halides, we can produce elemental halogens, such as production of bromine from HBr using concentrated sulphuric acid. Fluorine, however, being the strongest oxidising agent, no oxidising agent can oxidise fluorides (NaF or KF) to fluorine.
- Fluorine being highly reactive, attacks all materials of the apparatus such as glass, carbon, etc.
- It cannot be prepared by the electrolysis of anhydrous HF, as anhydrous HF is a bad conductor of electricity. Though aqueous solution of HF is good conductor of electricity but it does not give fluorine by electrolysis. This is because fluorine produced in this method reacts with water to produce HF once again. Note that electrolysis of aqueous solution of HCl produces chlorine.

Progress in isolating the element was slowed by the exceptional dangers of generating fluorine; several 19th century experimenters, the "fluorine martyrs", were killed or blinded. The English chemist Davy, as well as French chemist Louis Gay-Lussac and Louis Jacques Thenard, experienced severe pain from inhaling hydrogen fluoride gas; Davy's eyes were damaged. Irish chemist Thomas and George Knox developed fluorite apparatus for working with HF gas, but nevertheless were severely poisoned. Thomas nearly died and George was an invalid for three years. Belgian chemist Paulin Louyet and French chemist Jerome Nickles tried to follow the Knox work, but they died from hydrogen fluoride poisoning even though they were aware of the dangers.

Initial attempts to isolate the element were also hindered by material difficulties: the extreme corrosiveness and reactivity of hydrogen fluoride and fluorine gas as well as non- availability of suitable conducting liquid for electrolysis.

Fluorine was crudely prepared by Scheele, a Swedish, in 1771 and named by Ampere.

Henry Moissan (a French man, was awarded Noble prize for this in 1906) first prepared this gas in 1886. A U-shaped tube fitted with two electrodes (made up of an alloy of platinum and iridium) is used as the cell. Anhydrous HF is used as the electrolyte. To make it good conductor, potassium hydrogen fluoride (KHF_2) is mixed with the hydrofluoric acid. Since fluorine gas attacks the glass vessel, hence to avoid it, the vessel is kept in boiling methyl chloride. Methyl chloride on evaporation lowers the temperature of the vessel to about –23°C.

On electrolysis, fluorine is liberated at the anode.

$KHF_2 \rightleftharpoons K^+ + H^+ + 2F^-$

$HF \rightleftharpoons H^+ + F^-$ (Practically unionized)

At cathode: $2H^+ + 2e^- \longrightarrow H_2$

At anode: $2F^- - 2e^- \longrightarrow F_2$

This method has few limitations such as the platinum-iridium alloy used is costly and the entire system is to be maintained at very low temperature, which is really difficult.

UNSCRAMBLED WORDS

SEPTEMBER 2018

1-d- OLIVINE
2-h- MARGARINE
3-j- JELUTONG
4-a- HUMECTANT
5-j- ELUTRIATION
6-b- AMETTRYST
7-e- PLEOCHROISM
8-c- CYCLONITE
9-g- COACERVATION
10-f- TETRATOGEN

Look at the following reaction:

$K_2MnF_6 + 2SbF_5 \longrightarrow 2KSbF_6 + MnF_3 + 1/2\ F_2$

This is an uncommon reaction giving elemental fluorine. You never find a reaction probably other than this where elemental fluorine is on the product side. As we have discussed early in this section that no oxidising agent can oxidise fluoride to fluorine but here we see preparation of fluorine from a fluoride. The success of this reaction lies in the thermodynamic instability of MnF_4. The SbF_5 is a very strong fluoride acceptor. It snatches fluoride from K_2MnF_6 to break it to MnF_4, which then decomposes to release elemental fluorine.

Physical Properties

It is a pale yellow irritating gas and is highly corrosive. It is non-combustible water soluble gas. Melting point 54.4 K, boiling point 84.9 K, density 1.5 g/cm^3, bond length 143 pm, bond dissociation energy 158.8 kJ/mol. As fluorine is most electronegative, it combines directly with all other elements (except nitrogen) and noble gases (except helium, neon and argon).

Important Chemical Reactions

Fluorine has very powerful oxidising ability, which is clear from its electrode potential.

$F_2 + 2e^- \longrightarrow 2F^- \quad E^\circ = +2.87\ V$

In molecular form, its oxidizing ability can be illustrated by the following partial equation :

$F_2 + H_2O \longrightarrow 2HF + O$

The complete equation for oxidation of bisulphate is

$$\begin{array}{l} F_2 + H_2O \longrightarrow 2HF + O \\ 2KHSO_4 + O \longrightarrow K_2S_2O_8 + H_2O \\ \hline F_2 + 2KHSO_4 + H_2O \longrightarrow K_2S_2O_8 + 2HF + H_2O \end{array}$$

Similarly, for chlorate:

$$\begin{array}{l} F_2 + H_2O \longrightarrow 2HF + O \\ KClO_3 + O \longrightarrow KClO_4 \\ \hline F_2 + KClO_3 + H_2O \longrightarrow KClO_4 + 2HF \end{array}$$

Oxidation of chromic salts can be written as:

$$\begin{array}{l} [F_2 + H_2O \longrightarrow 2HF + O] \times 3 \\ Cr_2(SO_4)_3 + 4H_2O + 3O \longrightarrow H_2Cr_2O_7 + 3H_2SO_4 \\ \hline 3F_2 + Cr_2(SO_4)_3 + 7H_2O \longrightarrow H_2Cr_2O_7 + 3H_2SO_4 + 6HF \end{array}$$

With dilute alkali, OF_2 is formed :

$2NaOH + 2F_2 \longrightarrow OF_2 + 2NaF + H_2O$

With concentrated alkali, oxygen is formed :

$4NaOH + 2F_2 \longrightarrow 4NaF + 2H_2O + O_2$

◆ ◆

Exam Alert

The schedule of JEE Main and NEET examinations to be conducted by the National Testing Agency (NTA) till May 2019.

Examination: JEE Main I	
Mode of examination: Computer based	
Registration dates	1st to 30th Sept 2018
Downloading of admit cards	17th Dec 2018
Dates of examinations	6th to 20th Jan 2019
Date for announcing results	31st Jan 2019

Examinations will be organised on the weekends (Saturdays and Sundays) during the period of 6th to 20th January, 2019.

Examination: JEE Main II	
Mode of examination: Computer based	
Registration dates	8th Feb to 7th March 2019
Downloading of admit cards	18th March 2019
Dates of examinations	6th to 20th April 2019
Date for announcing results	30th April 2019

Examination: NEET (UG)	
Mode of examination: Pen & Paper exam (in single session)	
Registration dates	1st Nov to 30th Nov 2018
Downloading of admit cards	15th April 2019
Date of examination	5th May 2019
Date for announcing result	5th June 2019

The NEET exam pattern will now be a single exam in pen-and-paper mode and in the same number of languages as has been conducted last year.

National Testing Agency (NTA) established a countrywide network of test practice centres (TPCs) for students of rural areas so that everyone will have an opportunity to practice before the exam. (2,697) Schools/engineering colleges with computer centres are being made available on every Saturday/Sunday starting from 1st September, 2018 and any student can use the facility free of charge. An App is being developed which will enable the students to choose the nearest TPC.

The TPCs will have a downloaded Computer Based Test (CBT) which will be similar to the actual test to be conducted on the exam day. The practice tests will help the candidates to familiarize themselves with logging into the system, going through the detailed instructions regarding the test, using the mouse or numeric keyboard on screen (virtual) for attempting each question, scrolling down to the next question, navigating between questions, reviewing and editing their options and submit questions.