

## Sodium:

- It is the most abundant element in I-A group.
- Sea water contains 2.0 to 2.9% of NaCl. It occurs only in the combined state.
- The important minerals of sodium are
  1. Rock salt : NaCl,
  2. Chilesalt petre :  $\text{NaNO}_3$
  3. Saji Mitti :  $\text{Na}_2\text{CO}_3$ ,
  4. Mirabilite :  $\text{Na}_2\text{SO}_4$ ,
  5. Borax :  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  known as tincal in India
  6. Cryolite :  $\text{Na}_3\text{AlF}_6$

### Extraction of the sodium:

- Alkali metals cannot be prepared by the thermal reduction of the oxides as they are thermally stable. Electrolysis of the aqueous solutions of their salts will not give alkali metal.
- Chemical reduction methods are not suitable, as they themselves are strong reducing agents.
- They are obtained by the electrolytic reduction of their fused halides or hydroxides.

### Castner's process:

- Anhydrous fused NaOH is electrolyte. Cell is cylindrical iron tank.
- Iron rod is cathode.
- A hollow nickel cylindrical anode surrounds the cathode.
- The two electrodes are separated by a wire gauze.
- The temperature should be maintained about  $330^\circ\text{C}$  to prevent the mixing of Na with fused NaOH.
- During electrolysis sodium is liberated at the cathode and oxygen is liberated at anode. Na is collected on the surface of electrolyte.
- Very little  $\text{H}_2$  may be released at anode due to the reaction of Na with  $\text{H}_2\text{O}$ .

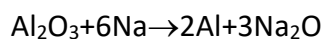
### Down's process:

- Manufacture of Na by Castner's process is costly as NaOH required for this process is first prepared from NaCl.
- Now a days sodium is prepared by the electrolysis of fused NaCl by Down's process.
- The addition of little  $\text{CaCl}_2$  or KCl and KF, to the fused NaCl has the following advantages.
- The melting point of NaCl is decreased from  $803^\circ\text{C}$  to  $600^\circ\text{C}$  and the fuel wastage is prevented.

- At low temperature the vapourisation of Na is less, so the possibility of burning of Na in air is minimised.
- At lower temperature dissolution of Na in fused NaCl is prevented
- The electrolytic process is smooth and the yield is good.
- In Down's process the electrolysis is carried in an iron or steel tank.
- A graphite rod acts as anode.
- The anode is surrounded by a ring shaped iron cathode.
- A wire gauze separates the anode from the cathode.
- The wire gauze prevents the passage of Na liberated at cathode to anode and reaction with  $\text{Cl}_2$ .

### Physical properties of Na:

- Sodium is silvery white soft metal.
- When placed in air it is tarnished.
- It is stored in inert solvents like kerosene.
- It gives the characteristic  $D_1$  ( $5890 \text{ \AA}$ ) and  $D_2$  ( $5896 \text{ \AA}$ ) lines (yellow lines) in the visible region of the spectrum.
- Na forms amalgam with mercury.  
Ex:  $\text{NaHg}$ ,  $\text{Na}_2\text{Hg}$ ,  $\text{Na}_3\text{Hg}$  or  $\text{Na}_x\text{Hg}$
- Sodium in liquid  $\text{NH}_3$  is i) good conductor ii) stronger reducing agent iii) blue colored. The above properties of Na in liquid  $\text{NH}_3$  are due to solvated electron.
- The presence of impurities or catalysts like Fe it reacts with  $\text{NH}_3$  to liberate  $\text{H}_2$  and forms sodamide ( $\text{NaNH}_2$ ).
- Na loses its metallic luster when exposed to moist air due to the formation of oxide, hydroxide and finally to carbonate.
- When heated in limited amount of air or oxygen  $\text{Na}_2\text{O}$  is formed.
- With excess of air or oxygen at  $300^\circ\text{C}$  it gives  $\text{Na}_2\text{O}_2$ .
- Na vigorously reacts with water liberating  $\text{H}_2$  and forming  $\text{NaOH}$ .
- When heated with  $\text{H}_2$ ,  $\text{Cl}_2$ , S, P it forms  $\text{NaH}$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{S}$ ,  $\text{Na}_3\text{P}$  respectively.
- Sodium is a powerful reducing agent.
- It reduces  $\text{CO}_2$  to carbon.  
$$4\text{Na} + 3\text{CO}_2 \rightarrow 2\text{Na}_2\text{CO}_3 + \text{C}$$
- It reduces  $\text{SiO}_2$  to Si  
$$\text{SiO}_2 + 4\text{Na} \rightarrow 2\text{Na}_2\text{O} + \text{Si}$$
- It reduces  $\text{BeCl}_2$  and  $\text{Al}_2\text{O}_3$  to the corresponding metals.  
$$\text{BeCl}_2 + 2\text{Na} \rightarrow \text{Be} + 2\text{NaCl}$$



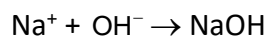
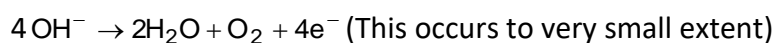
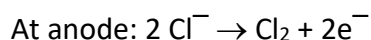
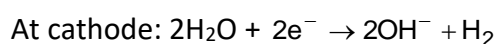
- It liberates hydrogen from compounds containing active hydrogen like  $\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{NH}_3$ ,  $\text{HC} \equiv \text{CH}$  and acids.

### Uses of sodium:

- It is used in the preparation of compounds like  $\text{Na}_2\text{O}_2$ ,  $\text{NaNH}_2$ ,  $\text{NaCN}$  etc.
- Na-Pb alloy is used in the preparation of tetraethyl lead (TEL) which is used as antiknock agent in petrol.
- It is used as a catalyst in the manufacture of rubber.
- It is used in sodium vapour lamps.
- It is used in the detection of elements in organic compounds by Lassaigne's test.
- It is used as a reducing agent.

### Sodium hydroxide or caustic soda:

- It is manufactured by
  1. Causticising process
  2. Electrolytic process
- 1. **Causticising process:** It is also known as Gossage process.
  - In this process milk of lime is added to 10%  $\text{Na}_2\text{CO}_3$  solution and heated to 80 to 85°C.
 
$$\text{Na}_2\text{CO}_3 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 \downarrow + 2\text{NaOH}$$
  - NaOH produced in this process is about 98% pure.
  - It contains NaCl,  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{CO}_3$  as impurities.
- 2. **Electrolytic process:**
  - In this process NaOH is produced by the electrolysis of aqueous NaCl solution or brine
  - $\text{H}_2$  and  $\text{Cl}_2$  are the bi products at cathode and anode respectively.
  - i. **Nelson's process:**
    - The electrolysis is carried out in a U shaped perforated steel vessel which acts as cathode
    - It is lined inside with asbestos which separates the electrodes and prevents loss of heat.
    - Brine solution is the electrolyte.
    - Graphite rod dipped in the electrolyte acts as anode.
    - During the electrolysis  $\text{H}_2$  is liberated at the cathode and  $\text{Cl}_2$  is liberated at the anode.
    - NaOH is collected at the bottom.
    - Approximately 50% of NaCl is converted into NaOH.
    - The resulting solution contains about 11% NaOH and 16% NaCl.
    - The solution is further concentrated on steam evaporators to get 50% NaOH solution with 1% NaCl and 1%  $\text{NaClO}_3$
    - Reactions during electrolysis:



Other possible reactions which may take place when products come in contact with each other:

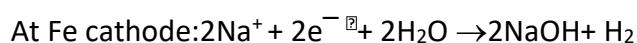
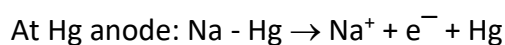
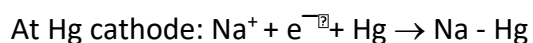
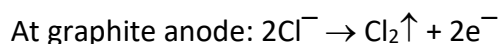


The possible impurities are NaCl, NaClO<sub>3</sub>, NaOCl.

## ii. Castner-Kellner process or Mercury cathode process:

- NaOH is obtained by the electrolysis of brine solution.
- A rectangular iron tank, divided into three compartments by slate partitions is the electrolytic cell.
- The bottom of the tank is covered with mercury and partitions do not touch the bottom.
- NaCl solution is taken in the outer compartments and dil. NaOH is taken in the central compartment.
- Two graphite electrodes are placed in the outer compartments.
- Hg acts as cathode in the outer compartments and anode in the central compartment. Thus Hg is the intermediate electrode.
- A series of iron rods suspended in the central compartment acts as cathode.
- In the outer compartments Cl<sup>-</sup> ions are oxidised and Cl<sub>2</sub> is liberated at the graphite electrodes.
- Na<sup>+</sup> ions gain the electrons at the Hg cathode to form Na metal and forms a amalgam with Hg.
- After reaching the central compartment sodium amalgam reacts with H<sub>2</sub>O to produce NaOH and H<sub>2</sub> which is liberated at Fe cathode.
- 20% NaOH is formed in the central compartment.

## Reactions during electrolysis:



Instead of H<sub>2</sub> gas, sodium is formed in the outer compartments because the discharge potential of sodium is lowered in presence of Hg cathode.

iii. **Castner-Solvay cell:** It is modified form of castner - kellner cell.

- There are no compartments in the cell.
- The principle and the reactions are similar to those of castner kellner cell.
- Mercury flows at the bottom of the tank acts as cathode.
- 50% NaOH is produced along with H<sub>2</sub>.
- About 20-150 graphite rods act as anode.
- Now a days platinum or titanium coated steel rods are used as anode.

**Properties of NaOH:**

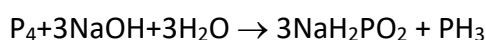
- It is white crystalline solid with soapy touch.
- It is highly deliquescent.
- It dissolves in water with the liberation of heat due to the formation of hydrates. NaOH.nH<sub>2</sub>O (n = 1, 2 or 7)
- It decomposes the body proteins and makes a paste. Hence it is called caustic soda.

**Chemical properties:**

- It is a strong monoacidic base and forms salts with acids.
- Amphoteric metals like Be, Al, Zn, Sn and Pb liberate H<sub>2</sub>. On reaction with NaOH.
- $\text{Zn} + 2\text{NaOH} \rightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2$
- With conc. NaOH solution Al gives sodium aluminate.
- $2\text{Al} + 6\text{NaOH} \rightarrow 2\text{Na}_3\text{AlO}_3 + 3\text{H}_2$
- With dil. NaOH solution Al gives sodium meta aluminate.
- $2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} \rightarrow 2\text{NaAlO}_2 + 3\text{H}_2$
- With dil. NaOH solution Sn gives sodium stannate.
- $\text{Sn} + 2\text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SnO}_3 + 2\text{H}_2$

**Reactions with non metals:**

- Si when heated with conc. NaOH liberates H<sub>2</sub>
- $\text{Si} + 2\text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2$
- Carbon reduces fused NaOH to Na.
- $6\text{NaOH} + \text{C} \rightarrow 2\text{Na} + 2\text{Na}_2\text{CO}_3 + 3\text{H}_2$
- White P when heated with NaOH solution liberates PH<sub>3</sub>.



sodium hypophosphite

- When heated with sulphur NaOH gives  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{Na}_2\text{S}$  or  $\text{Na}_2\text{S}_5$ .  
 $6\text{NaOH} + 4\text{S} \rightarrow 2\text{Na}_2\text{S} + \text{Na}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O}$  or  
 $6\text{NaOH} + 12\text{S} \rightarrow 2\text{Na}_2\text{S}_5 + \text{Na}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O}$
- $\text{Cl}_2$  reacts with cold and dilute NaOH solution to give NaCl & NaClO. (Na hypochlorite)  
 $\text{Cl}_2 + 2\text{NaOH} \rightarrow \text{NaCl} + \text{NaClO} + \text{H}_2\text{O}$
- $\text{Cl}_2$  reacts with hot and concentrated NaOH solution to give NaCl &  $\text{NaClO}_3$ . (Na Chlorate)
- $3\text{Cl}_2 + 6\text{NaOH} \rightarrow 5\text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O}$
- Ammonium salts when heated with NaOH solution liberate  $\text{NH}_3$ .
- $\text{NH}_4\text{Cl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{NH}_3$
- With  $\text{CuSO}_4$  solution NaOH gives blue precipitate of  $\text{Cu}(\text{OH})_2$ .
- With  $\text{FeSO}_4$  solution it gives light green precipitate of  $\text{Fe}(\text{OH})_2$ .
- With  $\text{FeCl}_3$  solution it gives red brown precipitate of  $\text{Fe}(\text{OH})_3$ .
- Silver and mercuric salts give their oxides.  
 $\text{AgNO}_3 + \text{NaOH} \rightarrow \text{NaNO}_3 + \text{AgOH}$   
 $2\text{AgOH} \rightarrow \text{Ag}_2\text{O}(\text{brown}) + \text{H}_2\text{O}$   
 $\text{Hg}(\text{OH})_2 \rightarrow \text{HgO}(\text{red}) + \text{H}_2\text{O}$
- The salts of Zn, Al and Sn give white gelatinous precipitates but these precipitates dissolve in excess of NaOH solution.  
 i)  $\text{ZnSO}_4 + 2\text{NaOH} \rightarrow \text{Zn}(\text{OH})_2 \downarrow + \text{Na}_2\text{SO}_4$   
 $\text{Zn}(\text{OH})_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{ZnO}_2 + 2\text{H}_2\text{O}$   

Sodium zincate

  
 ii)  $\text{AlCl}_3 + 3\text{NaOH} \rightarrow \text{Al}(\text{OH})_3 \downarrow + 3\text{NaCl}$   
 $\text{Al}(\text{OH})_3 + \text{NaOH} \rightarrow \text{NaAlO}_2 + 2\text{H}_2\text{O}$   

sod. meta aluminate
- Acidic oxides like  $\text{CO}_2$  and  $\text{SO}_2$  are absorbed by NaOH solution and form salts.  
 $\text{CO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$   
 $\text{SO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O}$
- Industrially KOH is used in place of NaOH as the potassium salts are more soluble in water.
- Alkalies are not stored in porcelain or glass containers as they slowly form silicates.  
 $\text{SiO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O}$

#### Uses of NaOH:

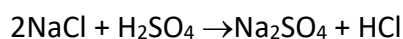
- It is used in soap, paper and textile industries
- used in the preparation of NaClO,  $\text{NaClO}_3$ ,  $\text{Na}_2\text{CO}_3$  etc.

- It is used in the petroleum refining.
- It used for mercerising of cotton.
- It is used in the preparation of alumina, phosphates and silicate glass etc.
- It is used to absorb SO<sub>2</sub> from atmosphere near power generators.
- It is used in cleaning glassware in the laboratory.

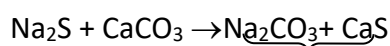
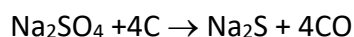
### Sodium carbonate:

- Decahydrated sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O) is called washing soda or salt soda.
- Anhydrous sodium carbonate is called soda ash or soda.
- It is prepared by
  1. Le. Blanc process,
  2. Solvay or ammonia soda process,
  3. Electrolytic process

- **Le-Blanc process:** The raw materials used in this process are Brine, sulphuric acid limestone and coke. The following reactions occur in the Le-Blanc process.



salt cake



black ash

- CaS is the by product. The mixture of Na<sub>2</sub>CO<sub>3</sub> and CaS is called black ash.

### Solvay process or Ammonia soda process:

Raw materials : Brine, limestone, little NH<sub>3</sub>

By - product : CaCl<sub>2</sub>

Intermediate product : NaHCO<sub>3</sub>

Recycled products : NH<sub>3</sub> and CO<sub>2</sub>

Impurities in Brine

solution: Calcium & Magnesium salts.

These are removed in the form of carbonate precipitates.

Precipitation of NaHCO<sub>3</sub> in Carbonation tower

is due to Common ion effect.

Solution from carbonation tower.

consists of : NaHCO<sub>3</sub> and NH<sub>4</sub>Cl.

Recovery of NH<sub>3</sub>: Ca(OH)<sub>2</sub> + NH<sub>4</sub>Cl → CaCl<sub>2</sub> + H<sub>2</sub>O + NH<sub>3</sub>

Reactions:  $\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{HCO}_3$

$\text{NH}_4\text{HCO}_3 + \text{NaCl} \rightarrow \text{NaHCO}_3 + \text{NH}_4\text{Cl}$

$2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$

- It is suitable method to prepare  $\text{Na}_2\text{CO}_3$  because of low solubility of  $\text{NaHCO}_3$ .
- $\text{K}_2\text{CO}_3$  can not be manufactured by Solvay's process because  $\text{KHCO}_3$  is more soluble in water.

**Electrolytic process:**

- $\text{CO}_2$  and steam at high pressures are passed through  $\text{NaOH}$  solution which is obtained by the electrolysis of brine solution.
- Pure  $\text{Na}_2\text{CO}_3$  is obtained by this process.

$2\text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$

**Properties of  $\text{Na}_2\text{CO}_3$ :**

- It is a white crystalline solid.