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 : $NaNO_3$
  3. Saji Mitti : Na_2CO_3,
  4. Mirabilite : Na_2SO_4,
  5. Borax : $Na_2B_4O_7.10H_2O$ known as tincal in India
  6. Cryolite : Na_3AlF_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 330^0C 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 H_2 may be released at anode due to the reaction of Na with H_2O.

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 $CaCl_2$ or KCl and KF, to the fused NaCl has the following advantages.
- The melting point of NaCl is decreased from 803^0C to $600^0C$and the fuel wastage is prevented.

- At low temperature the vapourisation of Na is less, so the possibillity 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 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 A°) and
  D_2 (5896 A°) lines (yellow lines) in the visible region of the spectrum.
- Na forms amalgam with mercury.
  Ex: NaHg, Na_2Hg, Na_3Hg or Na_x Hg
- Sodium in liquid NH_3 is i) good conductor ii) stronger reducing agent iii) blue colored. The above properties of Na in liquid NH_3 are due to solvated electron.
- The presence of impurities or catalysts like Fe it reacts with NH_3 to liberate H_2 and forms sodamide ($NaNH_2$).
- 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 Na_2O is formed.
- With excess of air or oxygen at 300^0C it gives Na_2O_2.
- Na vigorously reacts with water liberating H_2 and forming NaOH.
- When heated with H_2, Cl_2, S, P it forms NaH, NaCl, Na_2S, Na_3P respectively.
- Sodium is a powerful reducing agent.
- It reduces $CO_2$to carbon.
  $4Na + 3CO_2 \rightarrow 2Na_2CO_3 + C$
- It reduces SiO_2 to Si
  $SiO_2 + 4Na \rightarrow 2Na_2O + Si$
- It reduces $BeCl_2$ and Al_2O_3 to the corresponding metals.
  $BeCl_2 + 2Na \rightarrow Be + 2NaCl$

$Al_2O_3 + 6Na \rightarrow 2Al + 3Na_2O$

- It liberates hydrogen from compounds containing active hydrogen like H_2O, C_2H_5OH, NH_3, $HC \equiv CH$ and acids.

Uses of sodium:

- It is used in the preparation of compounds like Na_2O_2, $NaNH_2$, 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% Na_2CO_3 solution and heated to 80 to 85^{0}C.

  $Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3\downarrow + 2NaOH$
- NaOH produced in this process is about 98% pure.
- It contains NaCl, Na_2SO_4 and Na_2CO_3 as impurities.

2. Electrolytic process:

- In this process NaOH is produced by the electrolysis of aqueous NaCl solution or brine
- H_2 and 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 H_2 is liberated at the cathode and 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% $NaClO_3$
- Reactions during electrolysis:

Ionisation: $NaCl \rightleftharpoons Na^+ + Cl^-$

At cathode: $2H_2O + 2e^- \rightarrow 2OH^- + H_2$

At anode: $2Cl^- \rightarrow Cl_2 + 2e^-$

$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$ (This occurs to very small extent)

$Na^+ + OH^- \rightarrow NaOH$

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

$NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O$

$6NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$

The possible impurities are NaCl, $NaClO_3$, 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 donot 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^- ions are oxidised and Cl_2 is liberated at the graphite electrodes.
- Na^+ ions gain the electrons at the Hg cathode to form Na metal and forms a malgam with Hg.
- After reaching the central compartment sodium amaglam reacts with H_2O to produce NaOH and H_2 which is liberated at Fe cathode.
- 20% NaOH is formed in the central compartment.

Reactions during electrolysis:

Ionisaton of brine: $NaCl \rightarrow Na^+ + Cl^-$

At graphite anode: $2Cl^- \rightarrow Cl_2\uparrow + 2e^-$

At Hg cathode: $Na^+ + e^- + Hg \rightarrow Na - Hg$

At Hg anode: $Na - Hg \rightarrow Na^+ + e^- + Hg$

At Fe cathode: $2Na^+ + 2e^- + 2H_2O \rightarrow 2NaOH + H_2$

Instead of H_2 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 caster - 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_2.
- 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 deliquiscent.
- It dissolves in water with the liberation of heat due to the formation of hydrates. $NaOH.nH_2O$ (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_2. On reaction with NaOH.
- $Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$
- With conc.NaOH solution Al gives sodium aluminate.
- $2Al + 6NaOH \rightarrow 2Na_3AlO_3 + 3H_2$
- With dil. NaOH solution Al gives sodium meta aluminate.
- $2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$
- With dil. NaOH solution Sn gives sodium stannate.
- $Sn + 2NaOH + H_2O \rightarrow Na_2SnO_3 + 2H_2$

Reactions with non metals:

- Si when heated with conc. NaOH liberates H_2
- $Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + H_2$
- Carbon reduces fused NaOH to Na.
- $6NaOH + C \rightarrow 2Na + 2Na_2CO_3 + 3H_2$
- White P when heated with NaOH solution liberates PH_3.

  $P_4 + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$

  sodium hypophosphite

- When heated with sulphur NaOH gives $Na_2S_2O_3$ and Na_2S or Na_2S_5.

  $6NaOH + 4S \rightarrow 2Na_2S + Na_2S_2O_3 + 3H_2O$ or

  $6NaOH + 12S \rightarrow 2Na_2S_5 + Na_2S_2O_3 + 3H_2O$
- Cl_2 reacts with cold and dilute NaOH solution to give NaCl & NaClO. (Na hypochlorite)

  $Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$
- Cl_2 reacts with hot and concentrated NaOH solution to give NaCl & $NaClO_3$. (Na Chlorate)
- $3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$
- Ammonium salts when heated with NaOH solution liberate NH_3.
- $NH_4Cl + NaOH \rightarrow NaCl + H_2O + NH_3$
- With $CuSO_4$ solution NaOH gives blue precipitate of $Cu(OH)_2$.
- With $FeSO_4$ solution it gives light green precipitate of $Fe(OH)_2$.
- With $FeCl_3$ solution it gives red brown precipitate of $Fe(OH)_3$.
- Silver and mercuric salts give their oxides.

  $AgNO_3 + NaOH \rightarrow NaNO_3 + AgOH$

  $2AgOH \rightarrow Ag_2O(\text{brown}) + H_2O$

  $Hg(OH)_2 \rightarrow HgO(\text{red}) + H_2O$
- The salts of Zn, Al and Sn give white gelatinous precipitates but these precipitates dissolve in excess of NaOH solution.

  i) $ZnSO_4 + 2NaOH \rightarrow Zn(OH)_2\downarrow + Na_2SO_4$

  $Zn(OH)_2 + 2NaOH \rightarrow Na_2ZnO_2 + 2H_2O$

  Sodium zincate

  ii) $AlCl_3 + 3NaOH \rightarrow Al(OH)_3\downarrow + 3NaCl$

  $Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O$

  sod. meta aluminate
- Acidic oxides like CO_2 and SO_2 are absorbed by NaOH solution and form salts.

  $CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O$

  $SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O$
- 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.

  $SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$

Uses of NaOH:

- It is used in soap, paper and textile industries
- used in the preparation of NaClO, $NaClO_3$, Na_2CO_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_2 from atmosphere near power generators.
- It is used in cleaning glassware in the laboratory.

Sodium carbonate:

- Decahydrated sodium carbonate ($Na_2CO_3.10H_2O$) 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.

$$2NaCl + H_2SO_4 \rightarrow \underset{\text{salt cake}}{Na_2SO_4} + HCl$$

$$Na_2SO_4 + 4C \rightarrow Na_2S + 4CO$$

$$Na_2S + CaCO_3 \rightarrow \underbrace{Na_2CO_3 + CaS}_{\text{black ash}}$$

- CaS is the by product. The mixture of Na_2CO_3 and CaS is called black ash.

Solvay process or Ammonia soda process:

Raw materials : Brine, limestone, little NH_3

By - product : $CaCl_2$

Intermediate product : $NaHCO_3$

Recycled products : NH_3 and CO_2

Impurities in Brine

solution: Calcium & Magnesium salts.

These are removed in the form of carbonate precipitates.

Precipitation of $NaHCO_3$ in Carbonation tower

is due to Common ion effect.

Solution from carbonation tower.

consists of : $NaHCO_3$ and NH_4Cl.

Recoveryof NH_3: $Ca(OH)_2 + NH_4Cl \rightarrow CaCl_2 + H_2O + NH_3$

Reactions: $NH_3 + CO_2 + H_2O \rightarrow NH_4HCO_3$

$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$

$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

- It is suitable method to prepare Na_2CO_3 because of low solubility of $NaHCO_3$.
- K_2CO_3 can not be manufactured by Solvay's process because $KHCO_3$ is more soluble in water.

Electrolytic process:

- CO_2 and steam at high pressures are passed through NaOH solution which is obtained by the electrolysis of brine solution.
- Pure Na_2CO_3 is obtained by this process.

  $2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$

Properties of Na_2CO_3:

- It is a white crystalline solid.