Alkali Metals - Overview

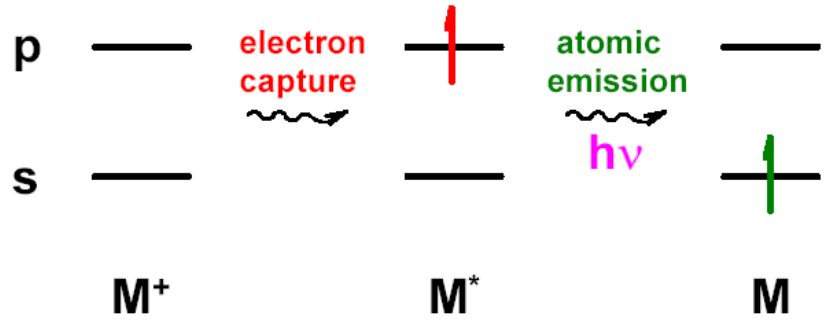
- Silvery, soft metals with a low melting point.
- Very reactive – powerful reducing agents.
- The reactivity increases from Li → Cs

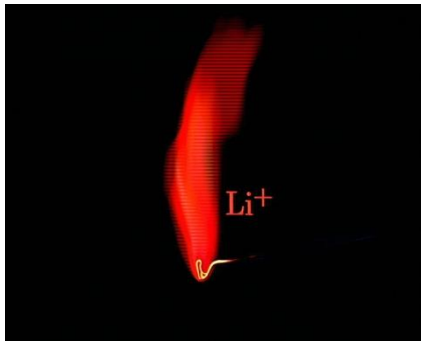
Alkali Metals - History

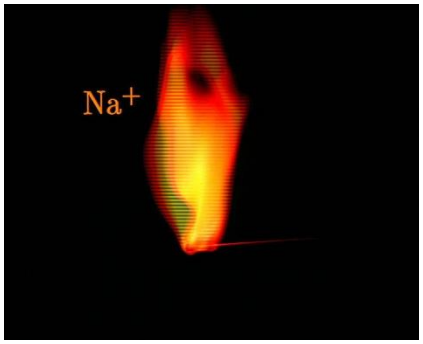
Humphrey Davy
(1778 – 1829)

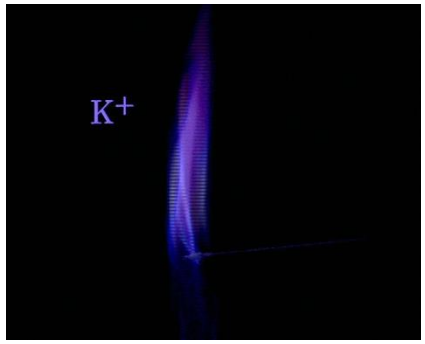
English chemist. He discovered, **by electrolysis**, the metallic elements **sodium** and **potassium** in 1807, and calcium, boron, magnesium, strontium, and barium in 1808. In addition, he established that chlorine is an element and proposed that hydrogen is present in all acids. He invented the safety lamp for use in mines where methane was present, enabling miners to work in previously unsafe conditions. He also discovered the anaesthetic properties of laughing gas. He was knighted for his work in 1812 and made baronet in 1818.

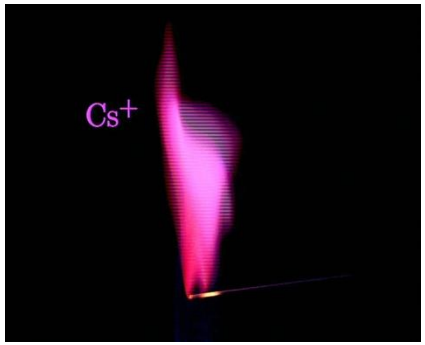
Flame Test for Alkali Metals





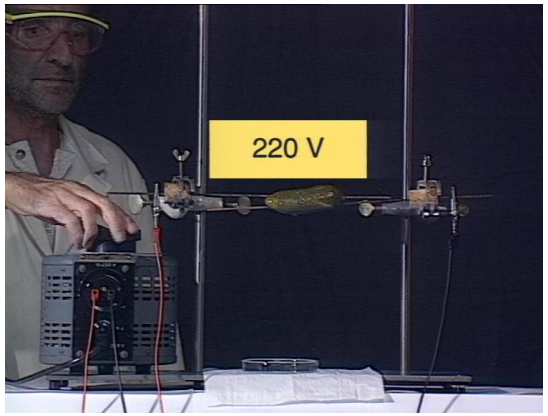


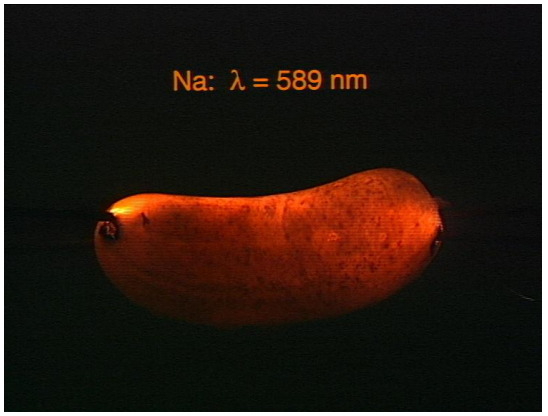




The heating of alkali metals in a Bunsen flame imparts a characteristic flame emission colour, as the outer electrons are easily promoted to a higher energy level. The analytical determination of the alkali metals through flame photometry, atom emission spectroscopy (AES) or atom absorption spectroscopy (AAS) is based on this phenomenon.

The Glowing Cucumber

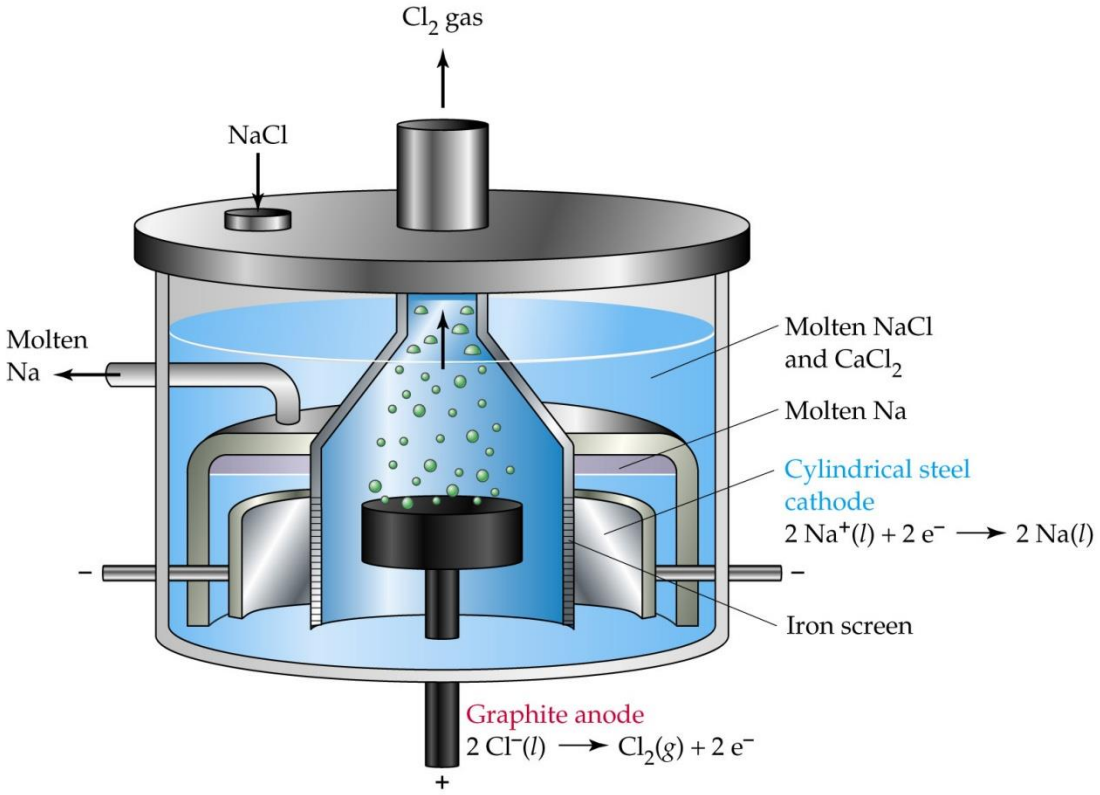




The characteristic flame coloration of alkali metal salts is due to the most intensive spectral lines, which, in the case of sodium are two yellow lines. Gherkins contain sodium chloride and, as the current passes there is strong local heating which vaporizes the sap in the gherkin tissue which contains a high concentration of sodium chloride. Sodium atoms which have been thermally excited emit the intense yellow color as they return to the ground state.

Technical Production of Sodium

- Sodium is produced by electrolysis of NaCl.
- To reduce the melting temp. of NaCl (808 °C), 60 % $CaCl_2$ is added (~ 600 °C).
- The cell design keeps the sodium and chlorine apart so that they can't react with each other.

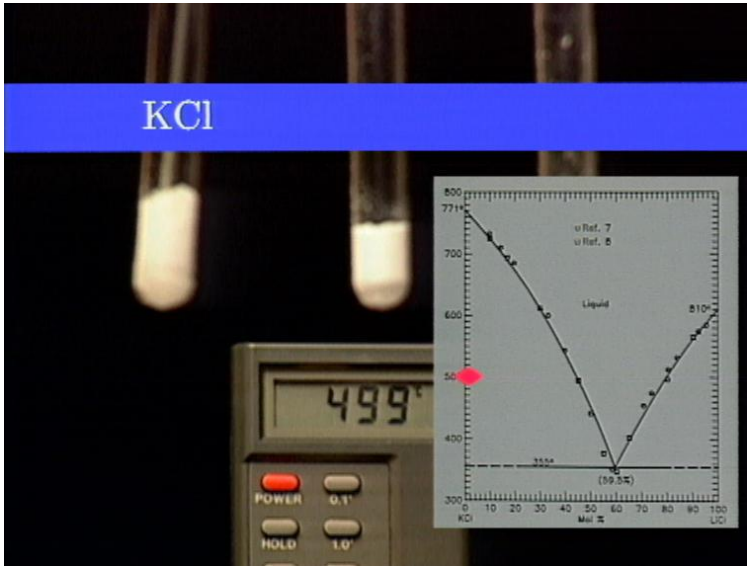


'Downs Cell'

Technical Production of Lithium and Kalium

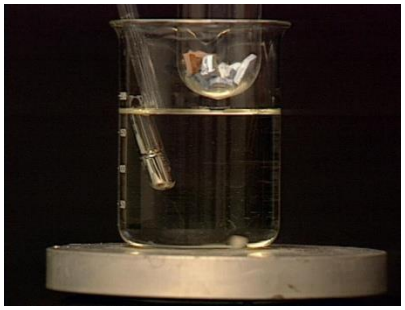
- **Lithium** is produced by electrolysis of an eutectic mixture of LiCl and KCl at 450 °C.

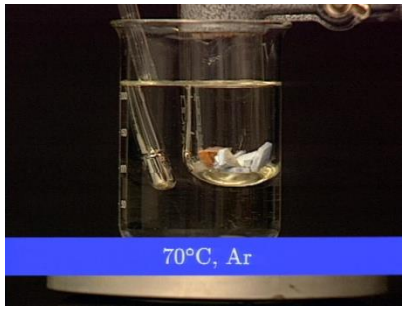
- **Kalium** is produced by reduction of molten KCl with metallic Na. First, a Na-K alloy is obtained from which K is obtained by distillation.

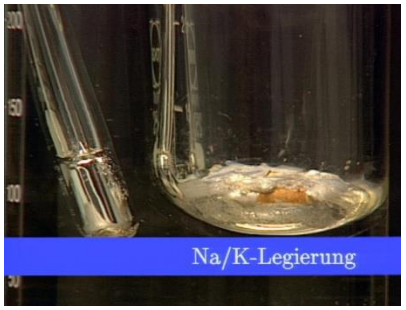


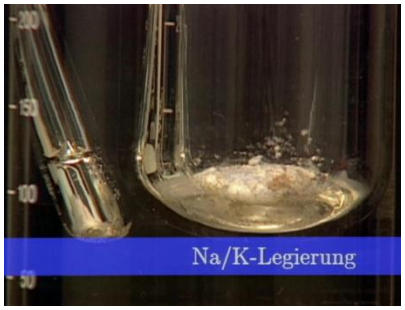
KCl : Mp.: 776°C; LiCl : Mp.: 613°C;
KCl (60 mol%) / LiCl (40 mol%): Mp.: 384°C.

Alkali Metal Alloys





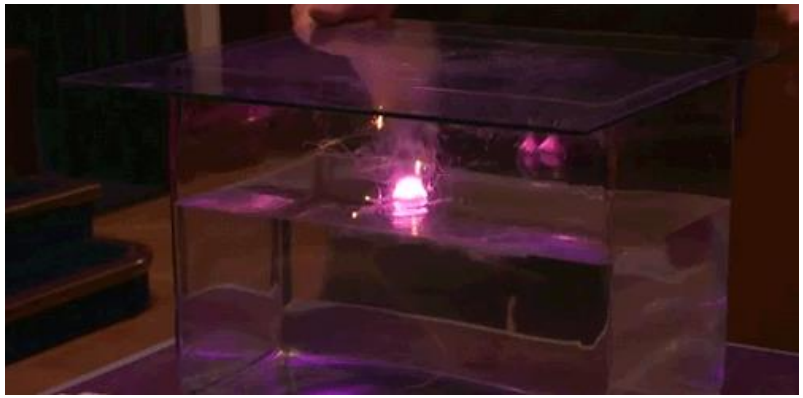




(Video: http://www.cci.ethz.ch)

Chemistry: With the exception of lithium, alloys of alkali metals can be made up at any ratio. The ternary alloy, 12% Na, 47% K and 41% Cs, exhibits the lowest known melting point of any metallic system (Mp: **-78 °C**). The binary alloy 23% Na and 77% K has a melting point of **-12 °C** (eutectic mixture) and is of enormous value in synthetic chemistry as it is a highly effective reductant. This alloy is a far more powerful reductant than either of the pure parent metals.

Alkali Metals and Water



Potassium and water.

$$2\ M + 2\ H_2O \longrightarrow 2\ M^+ + 2\ OH^- + H_2$$

Lithium reacts with water without melting and without ignition of the hydrogen; sodium melts in the reaction, without ignition of the hydrogen (for small pieces). Potassium (as well as the heavier alkali metals) reacts so violently that the hydrogen is ignited and burns producing a violet flame.

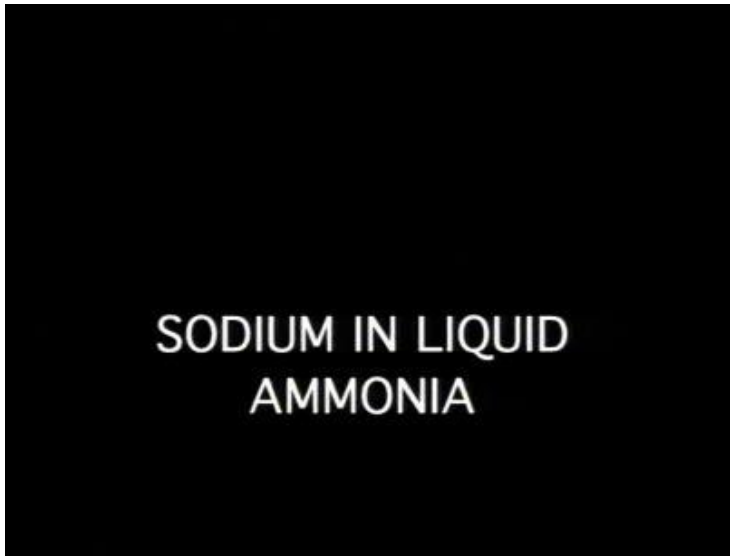
Alkali Metals and Water

brainiac alkaline metals

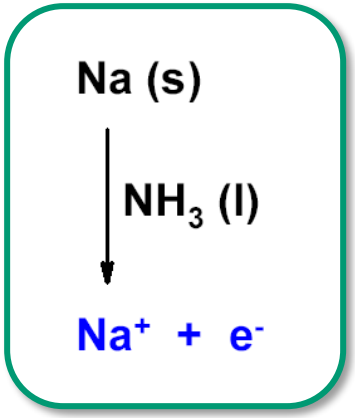
http://www.youtube.com/watch?v=gRuoWkOlaHM

http://www.youtube.com/watch?v=HY7mTCMvpEM/

Alkali Metals and Liquid NH_3



Alkali metals dissolve in liquid NH_3 to give a ‘solvated electron’ solution that is blue when dilute and bronze when concentrated.



Alkali Metal Hydrides

- Alkali metals react with hydrogen to form stoichiometric hydrides (MH). They are salts (NaCl structure) with a lattice energy between MF and MCl.

- **LiH** is obtained form the elements at 600 °C. With water, hydrogen is generated.

$$Li + 0.5\ H_2 \longrightarrow LiH$$

$$LiH + H_2O \longrightarrow LiOH + H_2$$

- **NaH** is obtained form the elements at 300 °C. With water, it reacts stronger than LiH (drying agent).

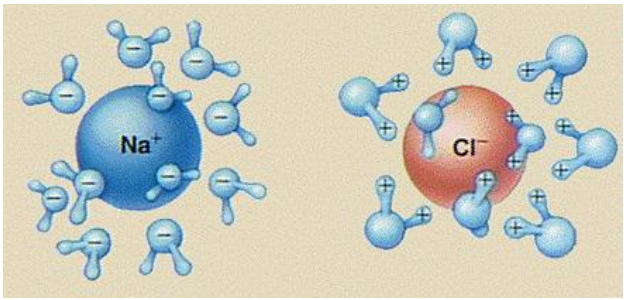
$$Na + 0.5\ H_2 \longrightarrow NaH$$

Solubility – Alkali Metal Halides

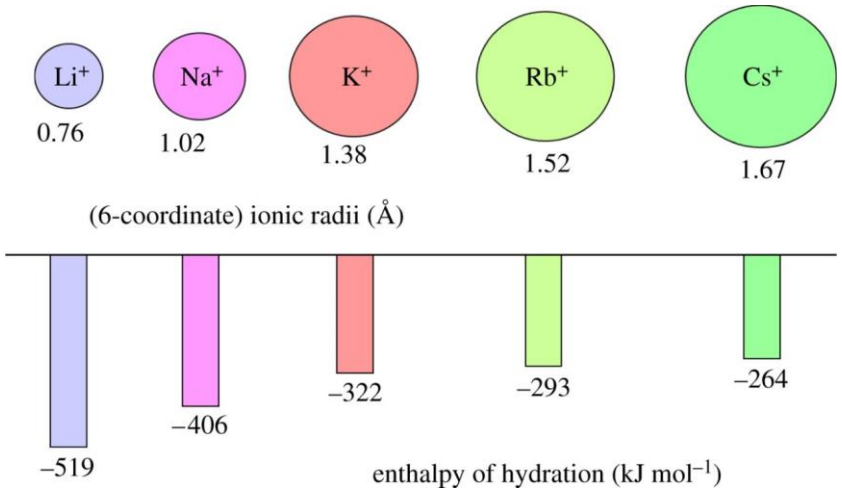
Solubility product:

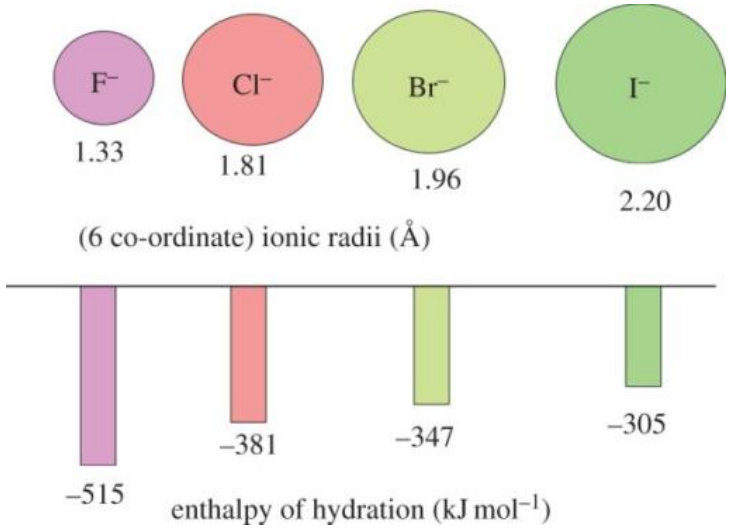
$$M_yX_z \xrightleftharpoons{H_2O} y\,M^{z+}(aq) + z\,X^{y-}(aq)$$

$$K_{sp} = [M^{z+}]^y\,[X^{y-}]^z$$



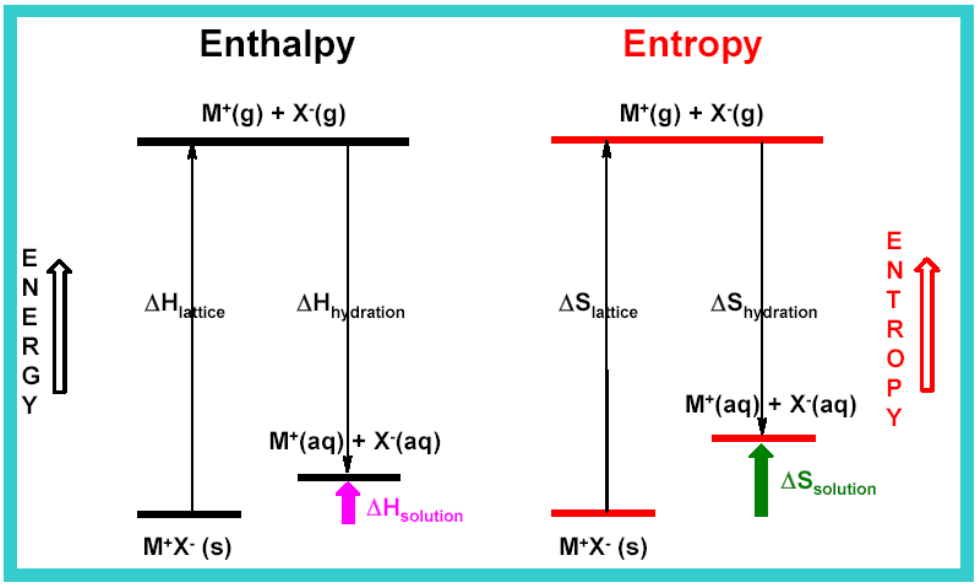
~ 370 g/l

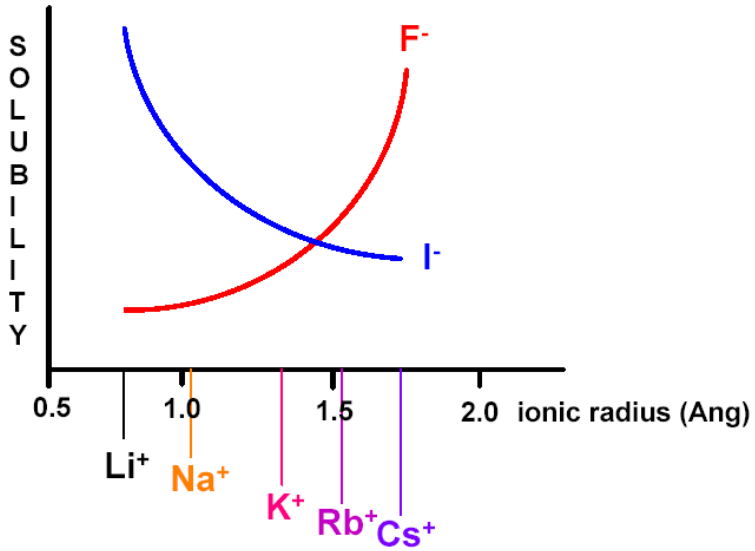


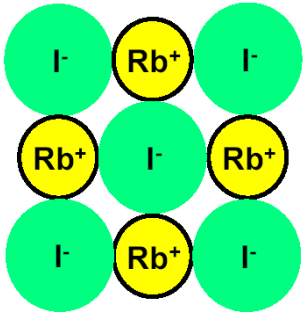


Solubility – Alkali Metal Halides

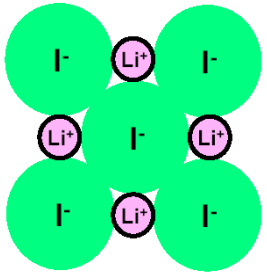
Alkali metal halide salts generally show good solubility in water. Lattice enthalpy effects are important when comparing the solubilities: a mismatch between cation and anion size leads to an increased repulsion between like-charged ions, decreasing lattice enthalpy.







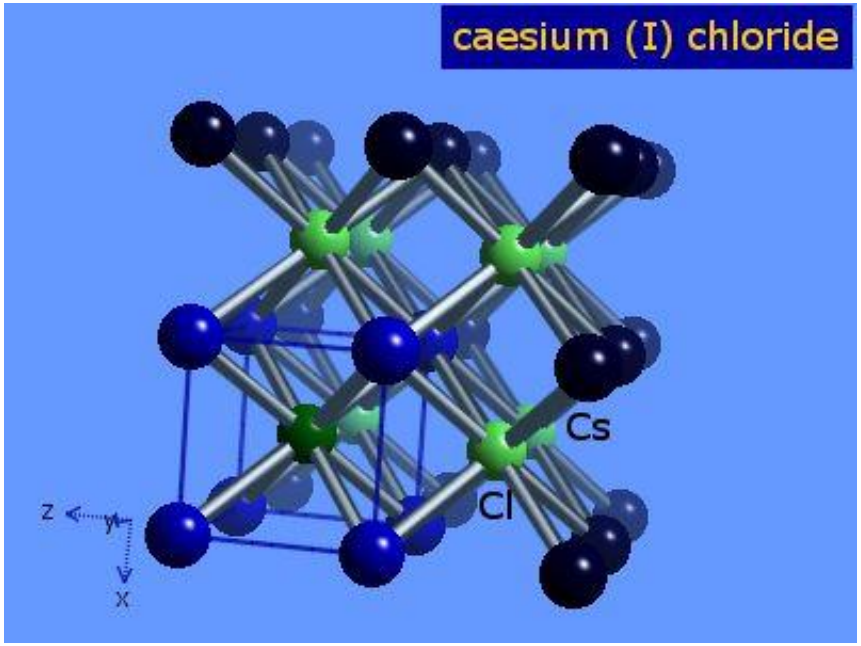
RbI



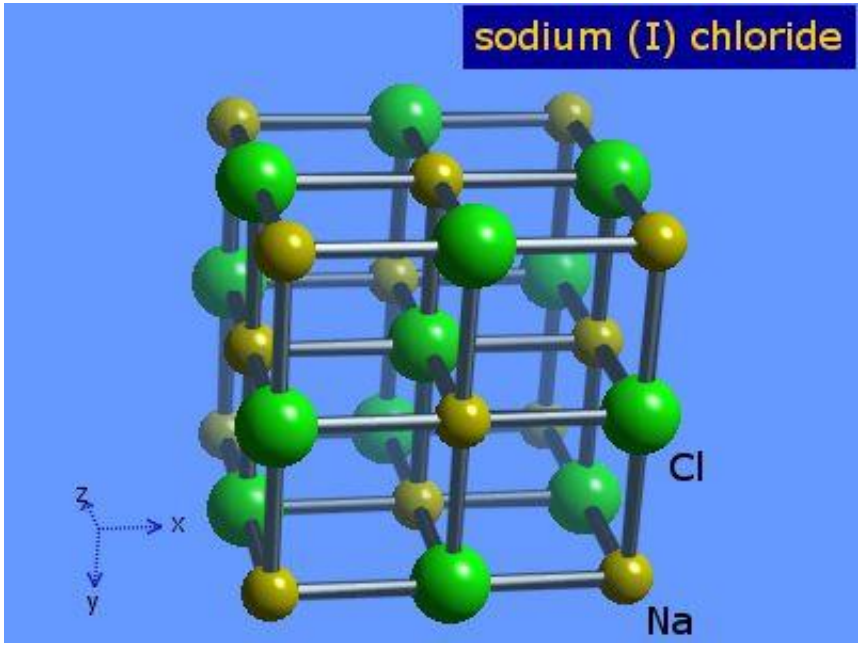
LiI

(both adopt the NaCl structure with 6-coordinate anion and cation sites)

CsCl vs. NaCl



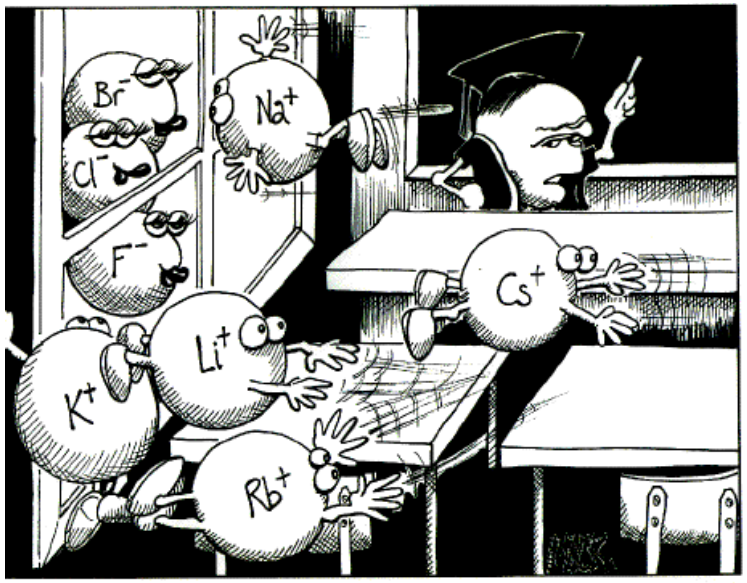
Each Cs^+ is coordinated to 8 Cl^- and each Cl^- is coordinated to 8 Cs^+.



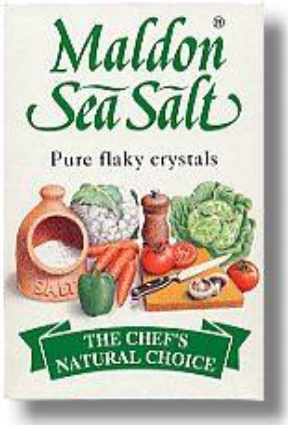
Each Na^+ is coordinated to 6 Cl^- and each Cl^- is coordinated to 6 Na^+.

Sodium Chloride

- Mostly mined, extracted with water from underground salt deposits or obtained by evaporation of sea water.
- Industrially important for the production of Cl_2 and NaOH.
- Food additive (3 g per day required).
- NaCl is not hydroscopic. If food-salt becomes ‘wet’ it is due to impurities of $MgCl_2$.



“Perhaps one of you gentlemen would mind telling me just what it is outside the window that you find so attractive...?”



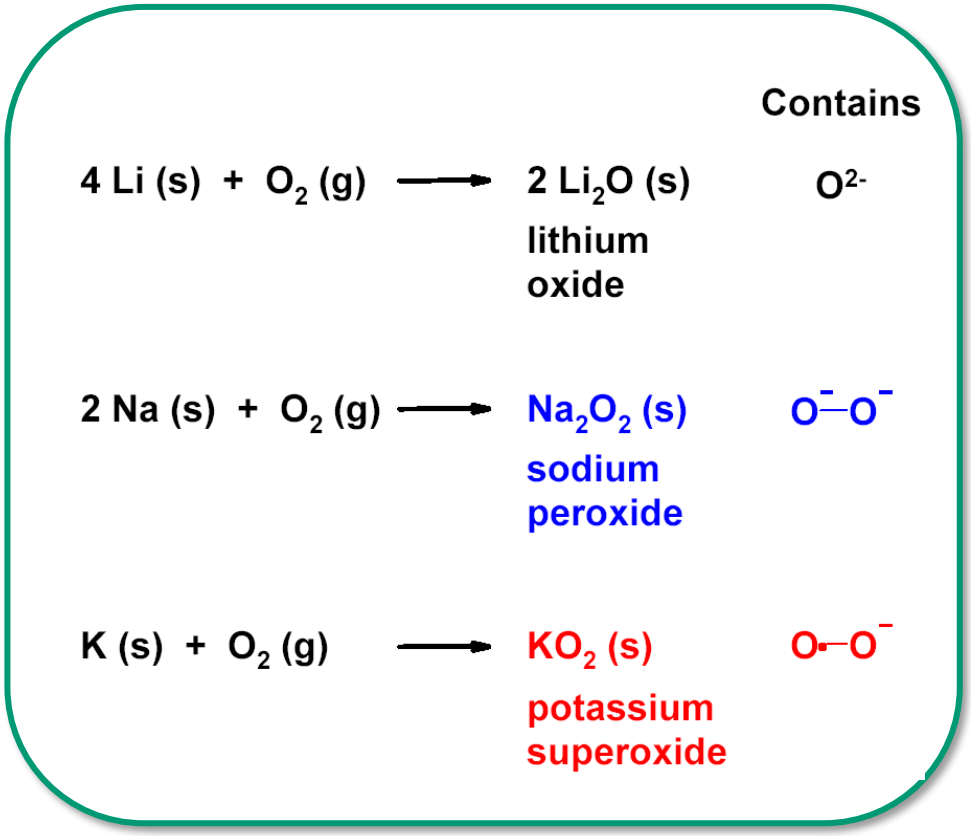
Sodium Chloride

Reaction of Sodium with Chlorine (subtitled)

http://www.youtube.com/watch?v=VBReOjo3ri8

Alkali Metal Oxides

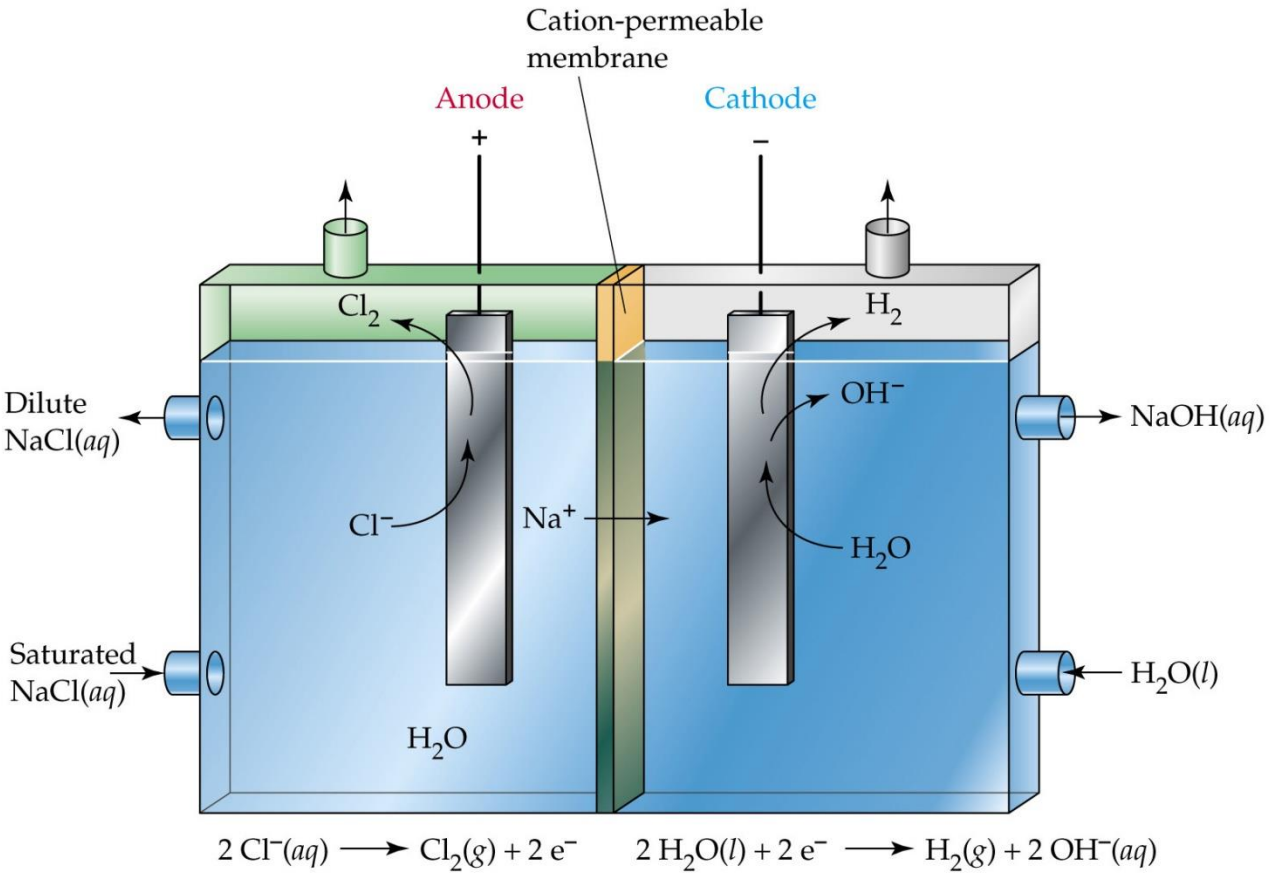
All alkali metals react directly with oxygen, the product obtained varies with cation size. Diamagnetic peroxide and paramagnetic superoxide are reduction products of O_2 with bond orders of 1.0 and 1.5, respectively.



Sodium Hydroxide

- Caustic soda (sodium hydroxide) is an important inorganic chemical produced by the electrolysis of NaCl. The world production of caustic soda is about 45 million tonnes.
- About 70 % is used as a reagent in chemical plants (aluminium production; NaOCl production).
- Active ingredient in cleaning products (e.g. Drano®).
- Widely used in the food industry (soften and remove skins of potatoes; softens olives; the ‘glue’ to stick NaCl on pretzels).

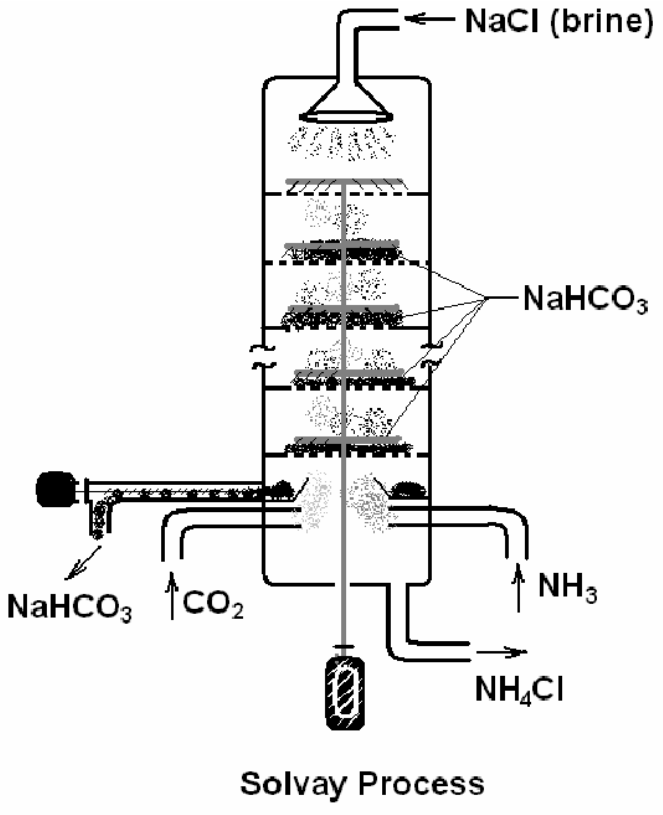
Technical Production of NaOH



A membrane cell for **electrolytic production of Cl_2 and NaOH**. Chloride ion is oxidized to Cl_2 gas at the anode, and water is converted to H_2 gas and OH^- ions at the cathode. Sodium ions move from the anode compartment to the cathode compartment through a cation-permeable membrane. Reactants enter the cell, and products (Cl_2 gas, H_2 gas, aqueous NaOH) leave through appropriately placed pipes .

Sodium Carbonate (Na_2CO_3)

- Important in chemical industry. 70 % are produced synthetically in the Solvay process but the USA has large natural sources.
- Primarily used to make sodium-containing glass.



Solvay Process

precipitates

$$NaCl + NH_3 + H_2O + CO_2 \longrightarrow NaHCO_3 + NH_4Cl$$

$$2\ NaHCO_3 \xrightarrow{200\ °C} Na_2CO_3 + CO_2 + H_2O$$

re-used

Sodium Bicarbonate ($NaHCO_3$)

Utilization:

- As an additive in food and drinks.
- As a baking powder (+ $Ca(H_2PO_4)_2$).
- As a drug (antiacid).
- As a component of personal care products such as toothpaste.
- To blow foams such as expanded polystyrene.

$$NaHCO_3 + H^+ \rightarrow Na^+ + CO_2 + H_2O$$

Li_2CO_3

- 1949: Lithium was reported to calm guinea pigs and to lessen manic symptoms in humans.
- 1970: approval by the Food and Drug Administration (FDA).
- One of the most frequently used drugs for manic depression.
- Drug: simply $Li_2(CO_3)$.
- Suicide rate is reduced by a factor of eight.
- Mode of action not clear.