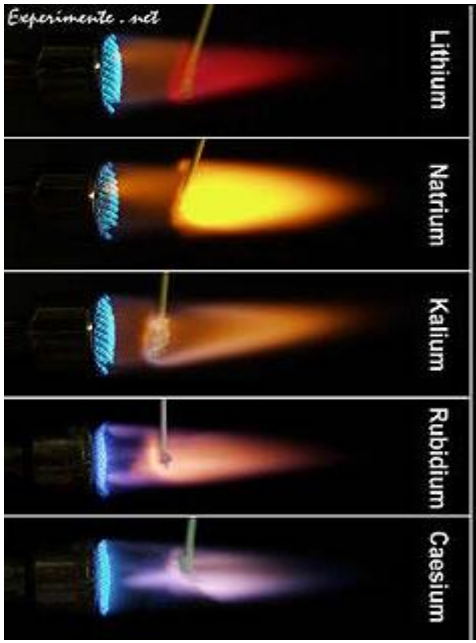
1. Alkali Metals

Content

Group
I or IA



3 Li	*1817*
11 Na	*1807*
19 K	*1807*
37 Rb	*1861*
55 Cs	*1861*
87 Fr	*1871*

„Alkali metals“

1.1 Occurrence

Abundance

Li: $2.0 \cdot 10^{-3}$%, Na: 2.7%, K 2.4%, Rb: $9.0 \cdot 10^{-3}$%, Cs: $3.0 \cdot 10^{-4}$%

Lithium (lithos)	$LiAl[SiO_3]_2$	Spodumene: chain silicate
Greek: stone	$LiAl[Si_2O_5]_2$	Petalite: phyllosilicate
Sodium (neter)	NaCl	Rock salt
Egypt.: soda	$NaNO_3$	Chile saltpetre
	Na_2SO_4	Glauber's salt
	$Na[AlSi_3O_8]$	Albite
Potassium (potasse)	KCl	Sylvite
French: potash	$KMgCl_3 \cdot 6H_2O$	Carnallite
Rubidium (rubidus)	Accompanies the other alkali metals	
Greek: deep red		
Caesium (caesius)	Accompanies the other alkali metals	
Greek: sky blue	$CsAl[SiO_3]$	Pollux

1.2 Properties

All Members of the Group are Highly Reactive Metals and Exhibit an Oxidation State of +I

	Li	Na	K	Rb	Cs
Atomic number	3	11	19	37	55
Electronic configuration	[He] $2s^1$	[Ne] $3s^1$	[Ar] $4s^1$	[Kr] $5s^1$	[Xe] $6s^1$
Electronegativity	1.0	1.0	0.9	0.9	0.9
Ionisation energy [eV]	5.4	5.1	4.3	4.2	3.9
Ionic radius Me^+ for CN 6 [pm]	90	116	152	166	181
Melting point T_m [°C]	181	98	63	39	28
Boiling point T_b [°C]	1347	883	759	688	668
Density [g/cm^3]	0.53	0.97	0.86	1.53	1.87
Flame colouring	crimson red 671 nm	yellow 589,3 nm	pale violet 770/404 nm	red violet 780/422 nm	blue violet 697/495 nm

- Combustion of metals leads to oxides, peroxides, or superoxides, depending on cation size
- Lithium forms Li_3N together with N_2
- The alkaline character of the hydroxides increases with increasing atomic number
- All alkali metals crystallise in a body-centred cubic crystal structure (CN 8)

1.3 Synthesis

By Means of Fused-Salt Electrolysis or by Chemical Reduction via Extremely Strong Reducing Agents

Lithium

Fused-salt electrolysis of LiCl/KCl (eutectic blend)

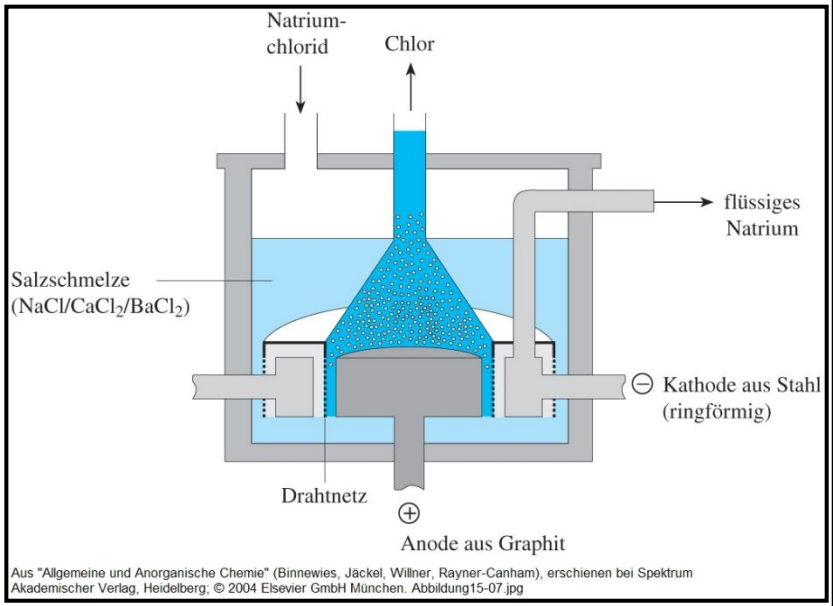
$Li^+ + e^- \rightarrow Li(l)$ (E^0 = - 3.04 V Lithium possesses the most negative standard potential of all elements)

Sodium

Fused-salt electrolysis of NaCl (Downs-cell) →

Cathode: $Na^+(dissolved) + e^- \rightarrow Na(s)$

Anode: $2\ Cl^-(dissolved) \rightarrow Cl_2(g) + 2\ e^-$



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Potassium

Reduction of molten KCl with Na

Rubidium, Caesium

By chemical reduction

$Cs_2Cr_2O_7(s) + Zr(s) \rightarrow 2\ Cs(g) + 2\ ZrO_2(s) + Cr_2O_3(s)$

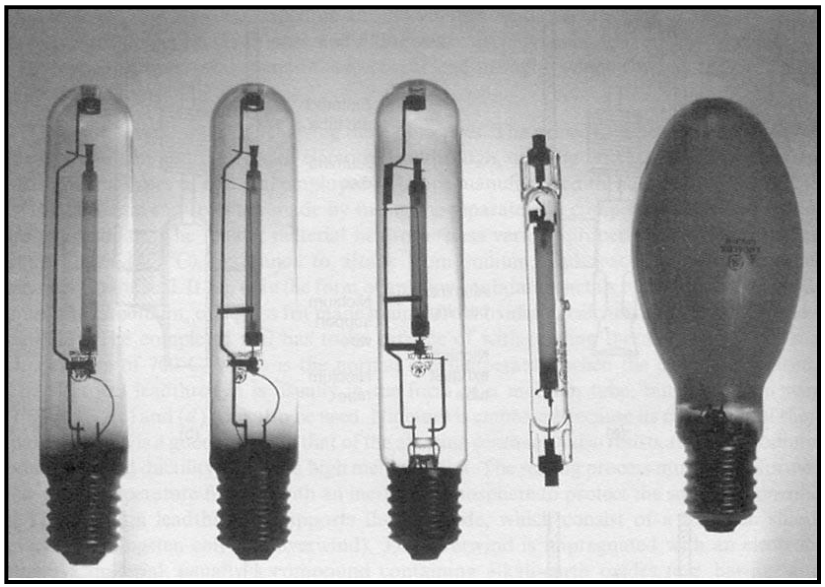
1.4 Application

Lithium

- Li-salts are important reagents in medicine
- $^{6}Li^{2}H$ and ^{6}LiD serve as explosive core in fusion weapons
- Element of alloys to harden Pb, Al and Mg
- Li-ion batteries

Sodium

- Important reducing agent
- Starting material for the synthesis of Na_2O_2, $NaNH_2$, NaH, NaCN, Na/Pb…..
- Cooling agent in fast breeder reactors
- Low and high pressure Na discharge lamps (589.0 + 589.6 nm)



Potassium

- KCl, K_2SO_4 and KNO_3 as fertilizer

Caesium

- Photoelectric effect ⇒ photocell
- ^{137}Cs ($t_{1/2}$ = 30 a) is a ß-radiator (512 keV)

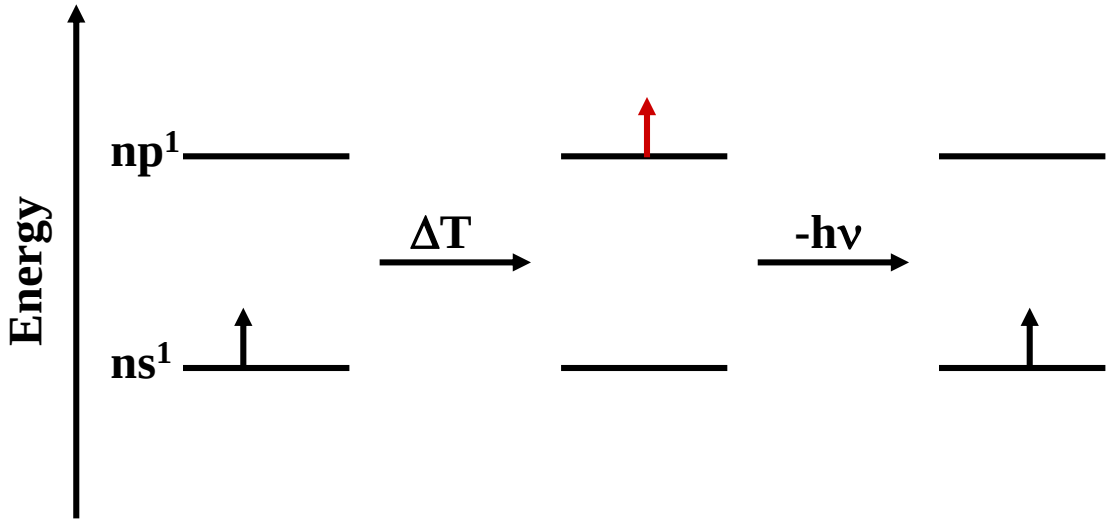
⇒ radiation source in medicine

⇒ ^{133}Cs in atomic clocks (ν = 9.19263177 GHz)

1.5 Flame Colouration

Thermal Excitation of Electrons Can Lead to the Emission of Visible Light and Thus to a Coloured Flame

Element	Colour of Flame
Li	Crimson red
Na	Yellow
K	Pale violet
Rb	Red violet
Cs	Blue violet
Ca	Brick red
Sr	Red
Ba	Pale green
B	Green
Pb	Pale blue
As	Pale blue
Sb	Pale blue
Cd	Red
Cu	Green to blue
Y	Red



In case of alkali metals, the outer electron ns^1 is thermally excited. Upon relaxation to the ground state a photon (hν) is emitting which energy corresponds to the difference between the first excited and the ground state.

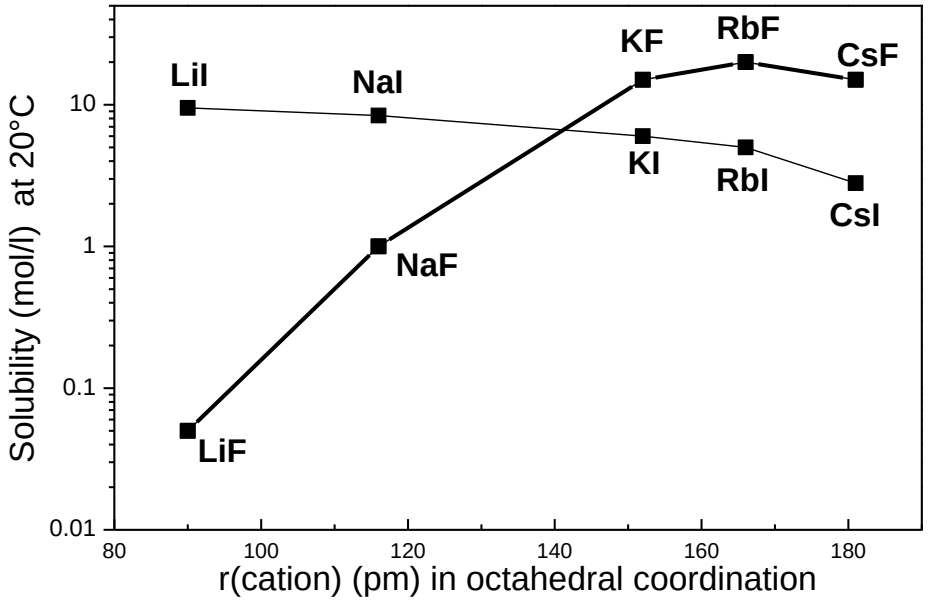
1.6 Solubility of the Salts

The Solubility of the Alkali Metal Salts Is Dependent on the Ratio of $r(K^+)/r(A^-)$

Equilibrium reaction:	**LiI(s)**	**+**	**CsF(s)**	**⇌**	**LiF(s)**	**+**	**CsI(s)**
Lattice enthalpy [kJ/mol]	**-759**		**-756**		**-1047**		**-608**

ΔH^0 = -140 kJ/mol

Solubility of alkali metal fluorides and iodides
($r_{okt.}(F^-)$ = 119 pm, $r_{okt.}(I^-)$ = 206 pm)

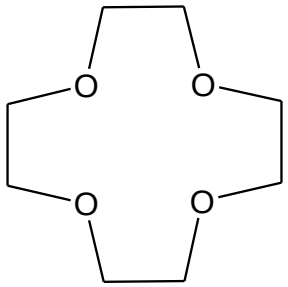


Poorly soluble salts of the larger alkali metals (Me = K, Rb, Cs) are those composed of big anions:

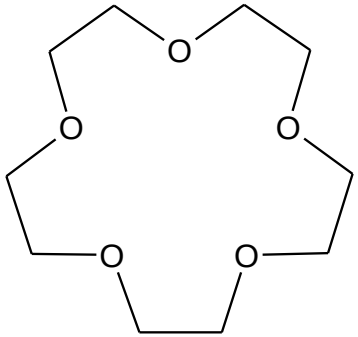
Perchlorate	**$MeClO_4$**
Tetraphenylborate	**$Me[B(C_6H_5)_4]$**
Hexanitrocobaltate	**$Me_3[Co(NO_2)_6]$**

1.7 Complexes with Crown Ethers

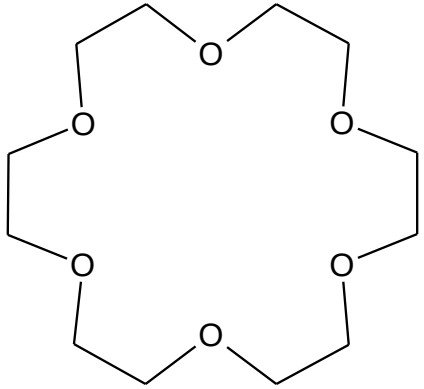
The Solubility of Alkali Metal Salts in Organic Solvents Can Notably Be Increased Through the Addition of Complexing Agents ⇒ Crown Ethers



12-crown-4

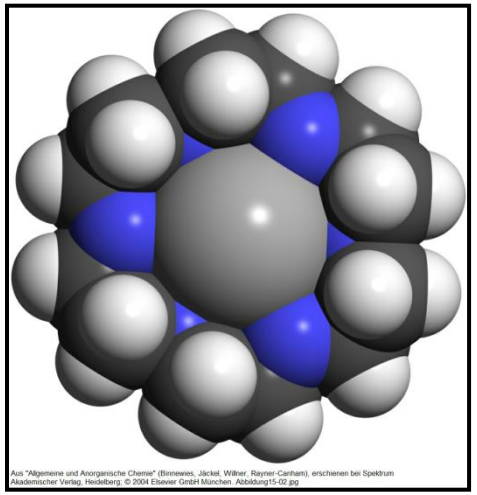


15-crown-5



18-crown-6

Complex of potassium ion with 18-crown-6



- These cyclic polyethers form highly stable complexes with alkali metal cations
- Alkali metal salts, such as $KMnO_4$, dissolve in non-polar solvents, e.g. $CHCl_3$ (trichloromethane), as soon as small amounts of crown ether are added.
- Even elemental Na can be dissolved using 18-crown-6, whereby Na anions(!) are formed:
  $2\ Na(s) + C_{20}H_{36}O_6(l) \rightarrow [Na(C_{20}H_{36}O_6)]^+Na^-(s)$

1.8 Compounds Formed with Oxygen

The Weakly Polarising Alkali Metal Cations Are Able to Stabilise Even Large Anions, f.i. Oxygen. The Reaction Therewith Leads to the Formation of Peroxides and Superoxides, with the Exception of Lithium

Metal	Product of reaction with O_2	Magnetism	Colour
Li	Li_2O	diamagnetic	white
Na	Na_2O_2	diamagnetic	white
K, Rb, Cs	KO_2, RbO_2, CsO_2	paramagnetic	orange

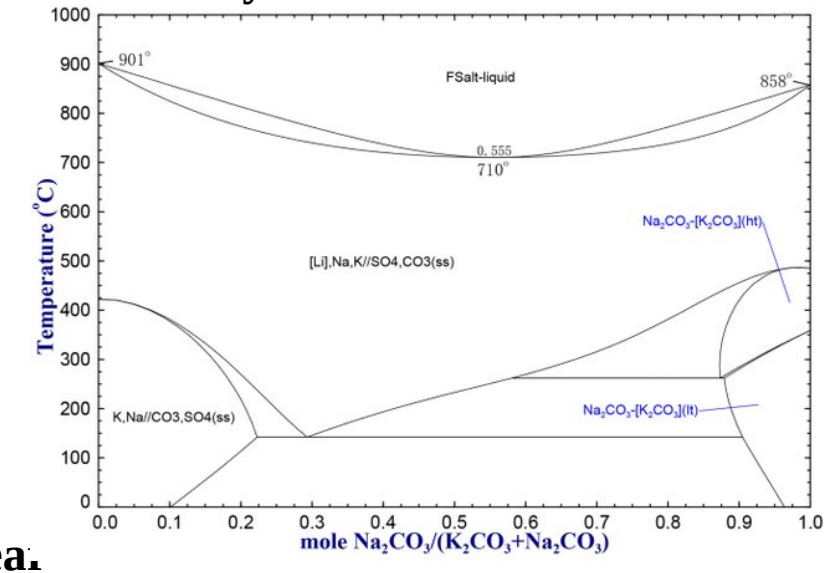
All oxo compounds react violently with H_2O under formation of hydroxides:

$$Li_2O(s) + H_2O(l) \rightarrow 2\ LiOH(s)$$
$$Na_2O_2(s) + 2\ H_2O(l) \rightarrow 2\ NaOH(s) + H_2O_2(l)$$
$$2\ KO_2(s) + 2\ H_2O(l) \rightarrow 2\ KOH(s) + H_2O_2(l) + O_2(g)$$

Reaction with CO_2 leads to carbonates:

$$Li_2O(s) + CO_2(g) \rightarrow Li_2CO_3(s)$$
$$2\ Na_2O_2(s) + 2\ CO_2(g) \rightarrow 2\ Na_2CO_3(s) + O_2(g)$$
$$4\ KO_2(s) + 2\ CO_2(g) \rightarrow 2\ K_2CO_3(s) + 3\ O_2(g)$$
$$K_2CO_3(s) + H_2O(l) + CO_2(g) \rightarrow 2\ KHCO_3(s)$$

$\Rightarrow$ **KO_2 is used as CO_2 and H_2O absorber in diving gear.**



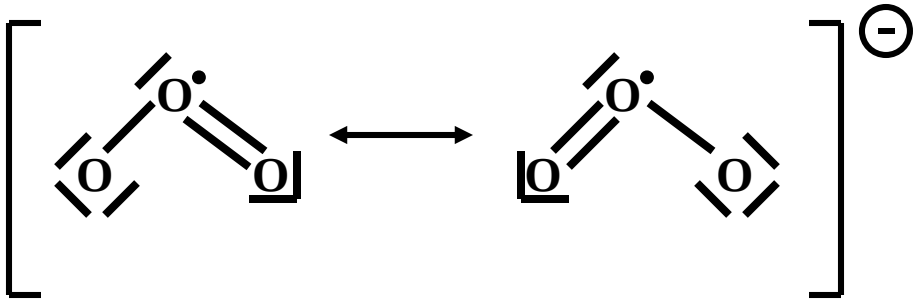
1.8 Compounds Formed with Oxygen

Ozonides Are Formed Upon the Reaction of Superoxides With Ozone O_3

Synthesis: $2\ MeO_2 + O_3 \rightarrow 2\ MeO_3 + O_2$ (Me = K, Rb, Cs)

Decomposition: $2\ MeO_3 \rightarrow 2\ MeO_2 + O_2$ (Me = K, Rb, Cs)

The O_3^- anion possesses 19 valence electrons an is thus paramagnetic!



The bond order of the O-O bond is 1.5

1.9 Salts of the Oxoacids

Salts of Carbonic Acid (Carbonates and Hydrogen Carbonates)

Me_2CO_3 $2\ Li^+(aq) + CO_2(g) + H_2O(l) \rightarrow 2\ H^+(aq) + Li_2CO_3(s)$ "insoluble"

Na_2CO_3 "soda"

K_2CO_3 "potash"

$MeHCO_3$ $2\ NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(l) + CO_2(g)$

$\Rightarrow$ sherbet powder and baking soda

Salts of Phosphoric Acid (Phosphates, Hydrogen Phosph. and Dihydrogen Phosph.)

Me_3PO_4 "alkaline salts"

Me_2HPO_4 "neutral salts"

MeH_2PO_4 "acidic salts"

Salts of Nitric Acid (Nitrates)

$MeNO_3$ $NaNO_3$ "Chile saltpetre"

KNO_3 "saltpetre"

Salts of Sulphuric Acid (Sulphates and Hydrogen Sulphates)

Me_2SO_4 $Na_2SO_4 \cdot 10H_2O$ "Glauber's salt" $\Rightarrow$ laxative

$MeHSO_4$ "acidic salts"

1.10 Biological Aspects

Lithium

Treatment of mental illnesses (e.g. bipolar disorder)

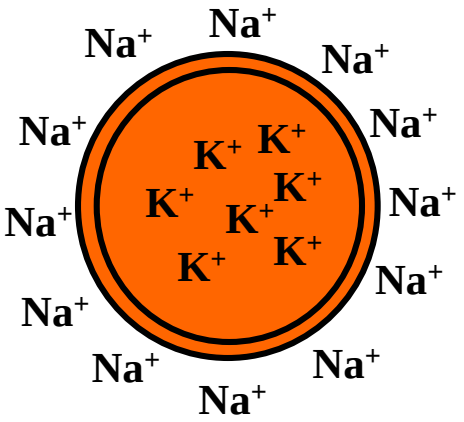
⇒ Li interferes with the metabolism in the human brain (hindrance of a enzymatic conversion whereby Mg^{2+} ions play a major role)

⇒ Diagonal relationship Li/Mg

Sodium/Potassium

- **Maintenance of membrane potentials (~ 60 mV) vie concentration gradients of Na^+ and K^+ across the cell membranes ⇒ signal line, renal function**
- **Transport of ions takes place through ion channels**

	Na^+ [mmol/l]	K^+ [mmol/l]
Red blood cells	11	92
Blood plasma	160	10



Rubidium, Caesium

No biological role known