

	1	
1	H	1,00797
2	Li	6,989
3	Na	22,9898
4	K	39,102
5	Rb	85,47
6	Cs	132,905
7	Fr	(223)

# The kings of reactivity

Chemistry of alkali metals  
- Metals from calcined ashes -

	1	
1	1	H
		1,00797
2	3	Li
		6,989
3	11	Na
		22,9898
4	19	K
		39,102
5	37	Rb
		85,47
6	55	Cs
		132,905
7	87	Fr
		(223)

# Occurrence

The Group 1 elements occur only in minerals (never in elemental state).

*Lithos* = stone, 18 ppm (in Earth Crust)



*Natrium* = soda, 22 700 ppm

*Kalium* = potash, 18 400 ppm

Sylvite (KCl)

*Rubidius* = ‘deepest red’, 78 ppm



*Caesium* = ‘dark blue’, 7 ppm

*Francium* = France, traces



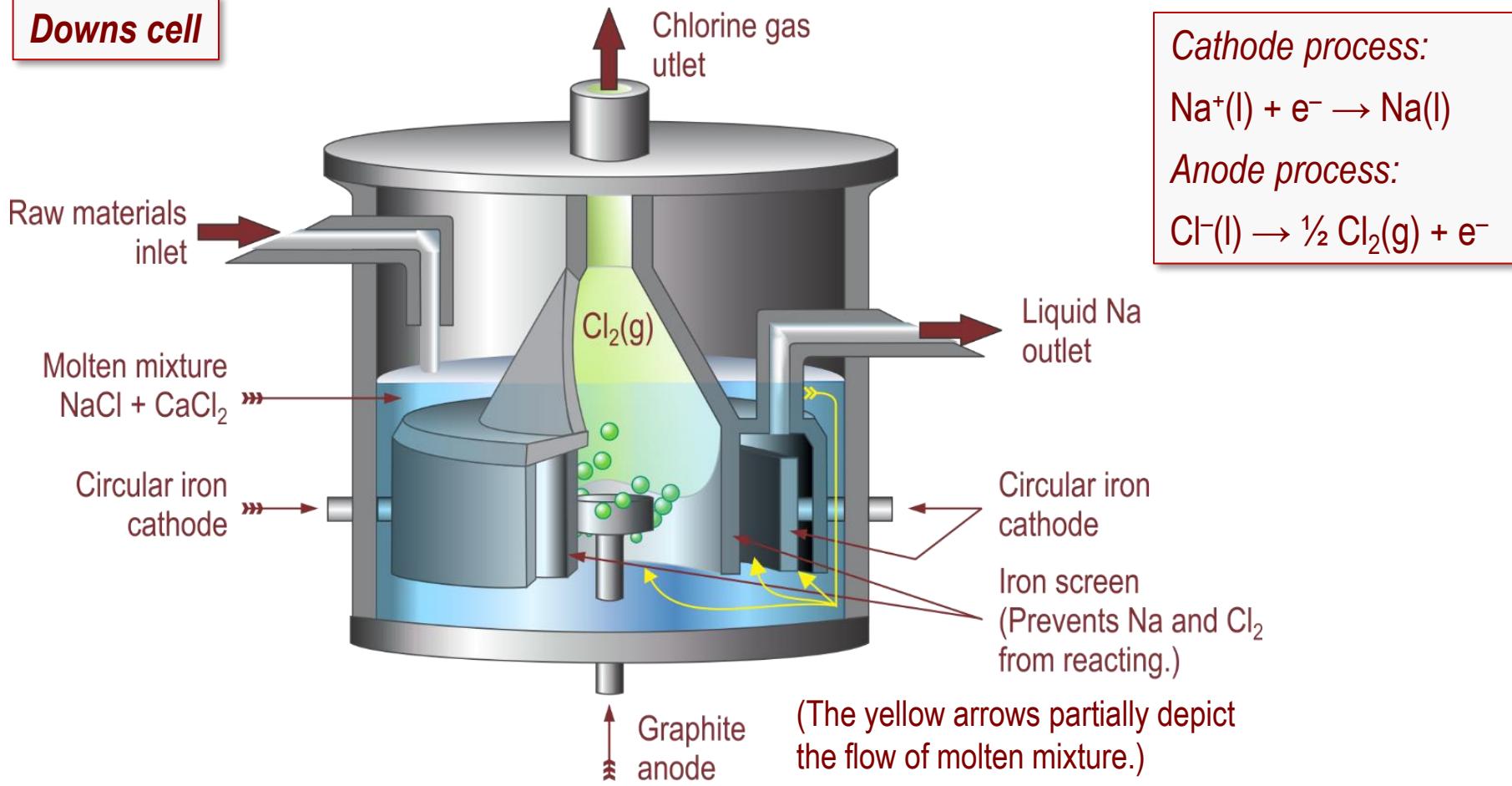
Petalite  
( $\text{LiAlSi}_4\text{O}_{10}$ )

Images: [www.webmineral.com](http://www.webmineral.com); data from J. Emsley ‘The Elements’ Oxford: Clarendon Press, 1989

# Isolation

- Isolation of elemental sodium: electrolysis of molten NaCl

**Downs cell**



- Isolation of elemental potassium: from KCl and Na



# Physical properties

- Physical properties of the Group 1 elements vary down the group as expected, except standard reduction potential

Property	Li	Na	K	Rb	Cs
Atomic number, Z	3	11	19	37	55
Ground state electronic config.	[He]2s <sup>1</sup>	[Ne]3s <sup>1</sup>	[Ar]4s <sup>1</sup>	[Kr]5s <sup>1</sup>	[Xe]6s <sup>1</sup>
Melting point (K)	453	371	336	312	301
Boiling point (K)	1615	1156	1032	959	942
$\Delta_{\text{sub}}H^\circ$ (kJ/mol)	161	108	90	82	78
$I_1$ (kJ/mol)	520.2	495.8	418.8	403.0	375.7
$I_2$ (kJ/mol)	7298	4562	3052	2633	2234
$\Delta_{\text{hyd}}H^\circ$ (kJ/mol)	-519	-404	-321	-296	-271
Metallic radius (pm)	152	186	227	248	265
Ionic radius (pm)	76	102	138	149	170
$E^\circ_{M+/M}$ (V)	-3.04	-2.71	-2.93	-2.98	-3.03

# Nuclear properties

- Li is predominantly created by *spallation* (fragmentation) of heavier nuclei in interstellar space or through fission of heavier nuclei.
  - Spallation is a break-up (fission) of heavy nuclides into lighter ones by cosmic rays (energetic and charged subatomic particles).
  - Li isotopes are important source of tritium ( ${}^3\text{H}$ ) and nuclear reactor coolants (first reaction):
$${}^6\text{Li} + n \rightarrow {}^4\text{He} + {}^3\text{H}$$
$${}^7\text{Li} + n \rightarrow {}^4\text{He} + {}^3\text{H} + n$$
- Potassium-40 is radioactive with  $t_{1/2} = 1.3 \times 10^9$  years:
$${}^{40}\text{K} \rightarrow {}^{40}\text{Ca} + e^-$$
$${}^{40}\text{K} \rightarrow {}^{40}\text{Ar} + e^+$$
  - These reactions are the major source of energy (heat) within Earth's interior and greatest source of radioactivity in living systems
  - The second reaction is important in geological dating as well
- ${}^{223}\text{Fr}$  ( $t_{1/2} = 21.8$  min) is the only naturally occurring isotope of this radioactive element.
  - It is formed during a rare alpha decay of  ${}^{227}\text{Ac}$

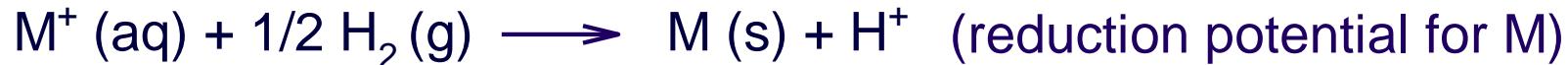
# Chemical properties

- Oxidation number +1
- Very reactive metals, strong reducing agents
- Handling precautions!
- Reactivity increases going down the group
- Combine directly with many elements of PSE giving binary compounds (hydrides, oxides, sulfides, carbides, nitrides, halides, etc.)
- React with water (Li slowly, Na vigorously, K ‘burns’ while Rb & Cs explosively) releasing  $H_2$  and giving hydroxides which are the strongest Brønsted bases.
- Many alkali metal compounds are important in every day life and both in industry and laboratory.

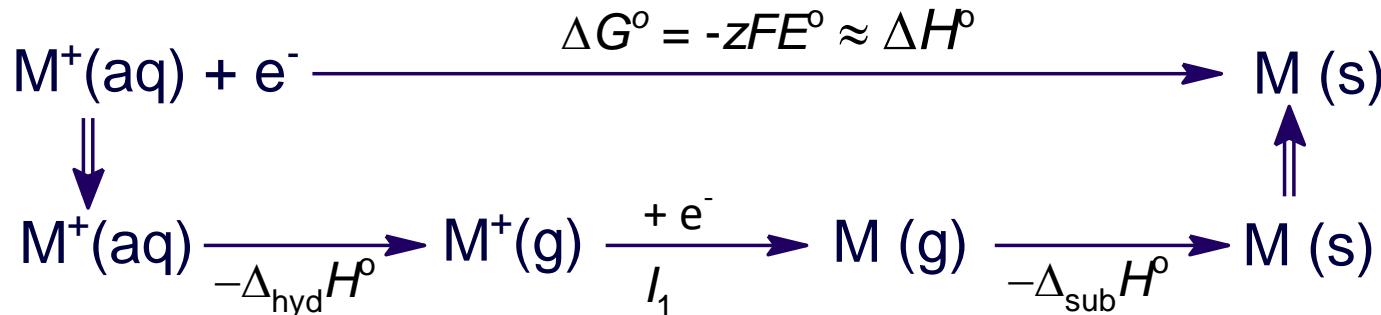
<http://www.youtube.com/watch?v=QSZ-3wScePM>

# Reduction potentials

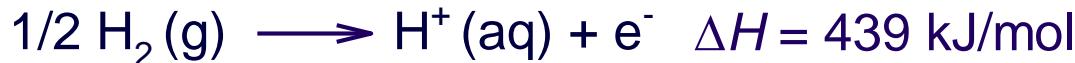
- Keep in mind:  $\Delta G^{\circ} = -zFE_{\text{cell}}^{\circ}$  &  $E_{\text{H+}/\text{H}}^{\circ} = 0 \text{ V}$



- Group 1 metal reduction potential broken into the Hess cycle:

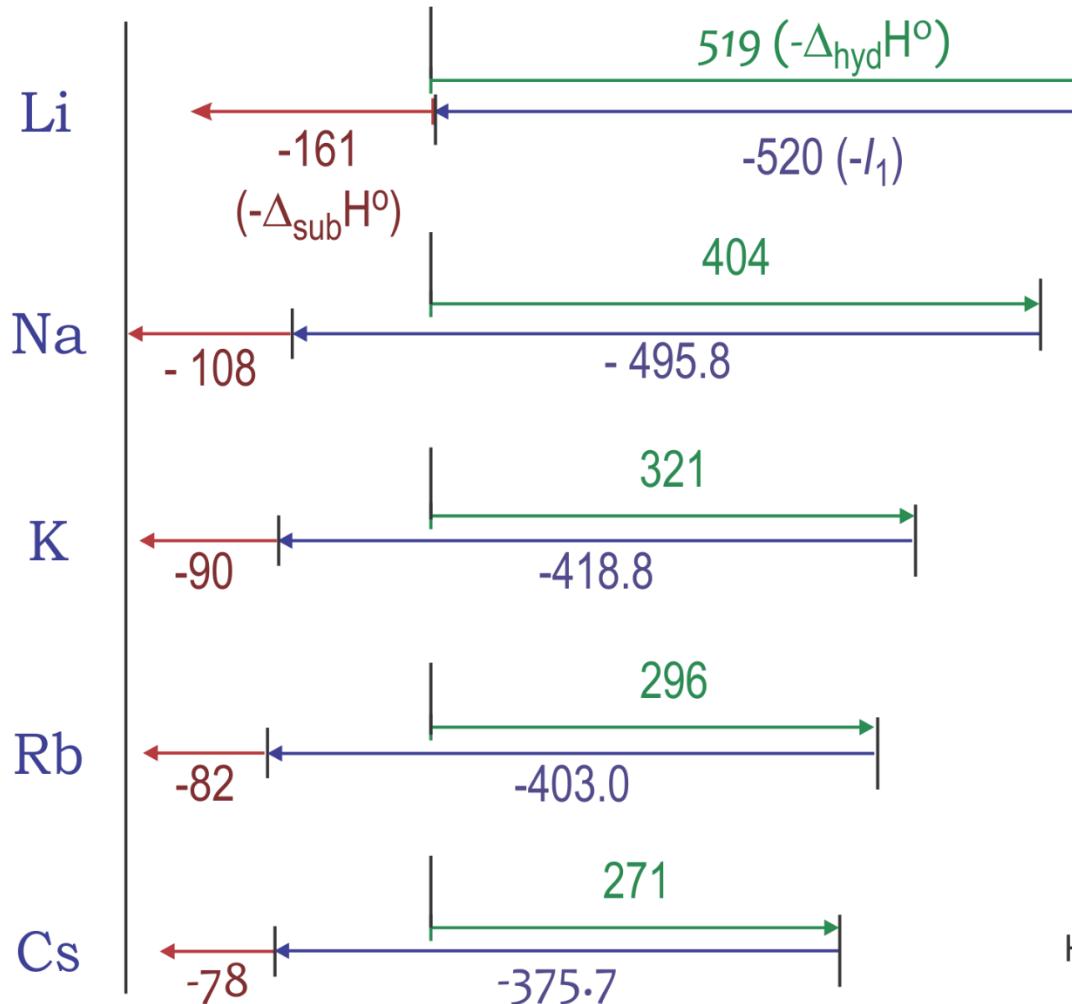
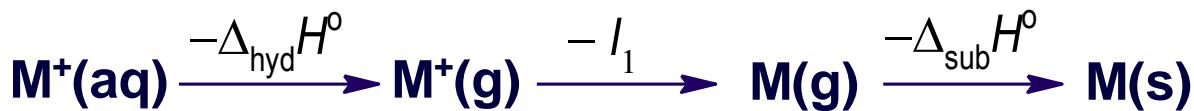


- 2<sup>nd</sup> half-reaction for reduction potential and its thermodynamics (always the same regardless of your M):



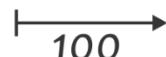
→  $\Delta H = 439 \text{ kJ/mol}$  is actually underestimated since it takes only the formation of  $\text{H}_3\text{O}^+$  in consideration!

# Reduction potentials (cont.)



Li<sup>+</sup> has a high hydration energy (due to very small cation size and high charge-to-radius ratio) which is sufficient to reverse the position of Li (the most positive instead of the least positive reduction potential)

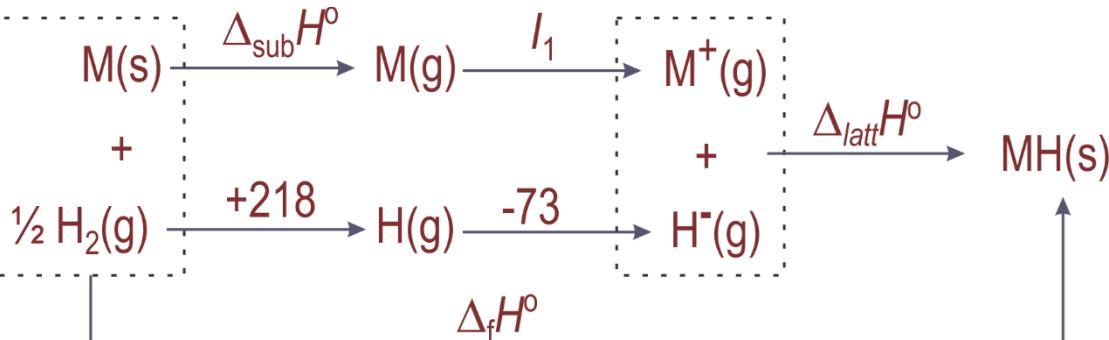
Scale:



All values in kJ/mol

# Hydrides (MH)

- Synthesis:* commonly direct reaction with H<sub>2</sub> at elevated temp.
- Structure:* All are saline (salt-like) with NaCl structure.
- Thermodynamics:*



Metal	$\Delta_{\text{sub}}H^\circ$ (kJ/mol)	$I_1$ (kJ/mol)	$\Delta_{\text{latt}}H^\circ$ (kJ/mol)	$\Delta_fH^\circ$ (kJ/mol)
Li	161	521	-920	-90.5
Na	108	492	-808	-56.3
K	90	415	-714	-57.7
Rb	82	405	-685	-52.3
Cs	78	376	-644	-54.2

As the radius of M<sup>+</sup> increases  $\Delta_{\text{latt}}H^\circ$  becomes more positive (because  $\Delta_{\text{latt}}H^\circ \propto 1/(r_+ + r_-)$ ) and as a result  $\Delta_fH^\circ$  becomes more positive (less exothermic reaction). Thus, although  $\Delta_{\text{sub}}H^\circ$  and  $I_1$  for Li are the highest,  $\Delta_{\text{latt}}H^\circ$  is sufficiently negative and compensates this ‘energy cost’ making LiH the most exothermic hydride of the Group 1.

- Properties:* All hydrides are strong bases and strong reducing reagents, react with water giving H<sub>2</sub> and MOH.

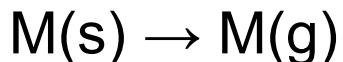
# Halides (MX)

- All halides are known and can be obtained by direct reaction  $M + \frac{1}{2} X_2$  (there are other ways...i.e.  $NaOH + HCl$  and alike)
- Thermodynamic data show trend in  $\Delta_f H^\circ$  but no clear trend in  $\Delta_f H$ :

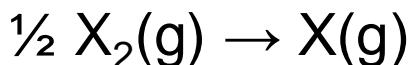
Metal cation	$\Delta_f H^\circ$ (kJ/mol)				$\Delta_{latt} H^\circ$ (kJ/mol)				Metal cation size increase ↓
	F <sup>-</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	I <sup>-</sup>	F <sup>-</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	I <sup>-</sup>	
Li <sup>+</sup>	-616	-409	-351	-270	-1030	-834	-788	-730	
Na <sup>+</sup>	-577	-411	-361	-288	-910	-769	-732	-682	
K <sup>+</sup>	-567	-436	-394	-328	-808	-701	-671	-632	
Rb <sup>+</sup>	-558	-435	-395	-334	-774	-680	-651	-617	
Cs <sup>+</sup>	-553	-443	-406	-347	-744	-657	-632	-600	
Halide anion size increase					Halide anion size increase				

# $\Delta H_{\text{latt}}$ and $\Delta H_f$ for the Group 1 Halides

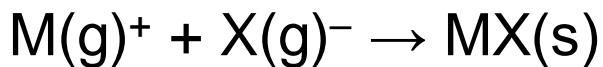
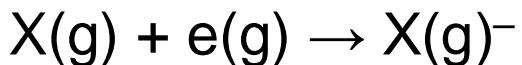
- $\Delta_{\text{latt}}H$  is only one component of  $\Delta_fH$ :  $\Delta_{\text{latt}}H$  can be judged based on radii but for  $\Delta_fH$  we have to know other values as well:



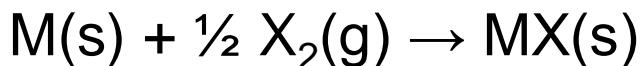
$\Delta_{\text{sub}}H(\text{M})$  Depend on the metal properties  
 $I_1(\text{M(g)})$



$\frac{1}{2} \text{BDE}(\text{X}_2)$  Depend on the halogen properties  
 $\text{EA}_1(\text{X(g)})$



$\Delta_{\text{lat}}H(\text{MX})$  Roughly depend on ionic sizes



$\Delta_fH(\text{MX})$

- The final  $\Delta_fH(\text{MX})$  thus depends on “how the numbers add-up”!

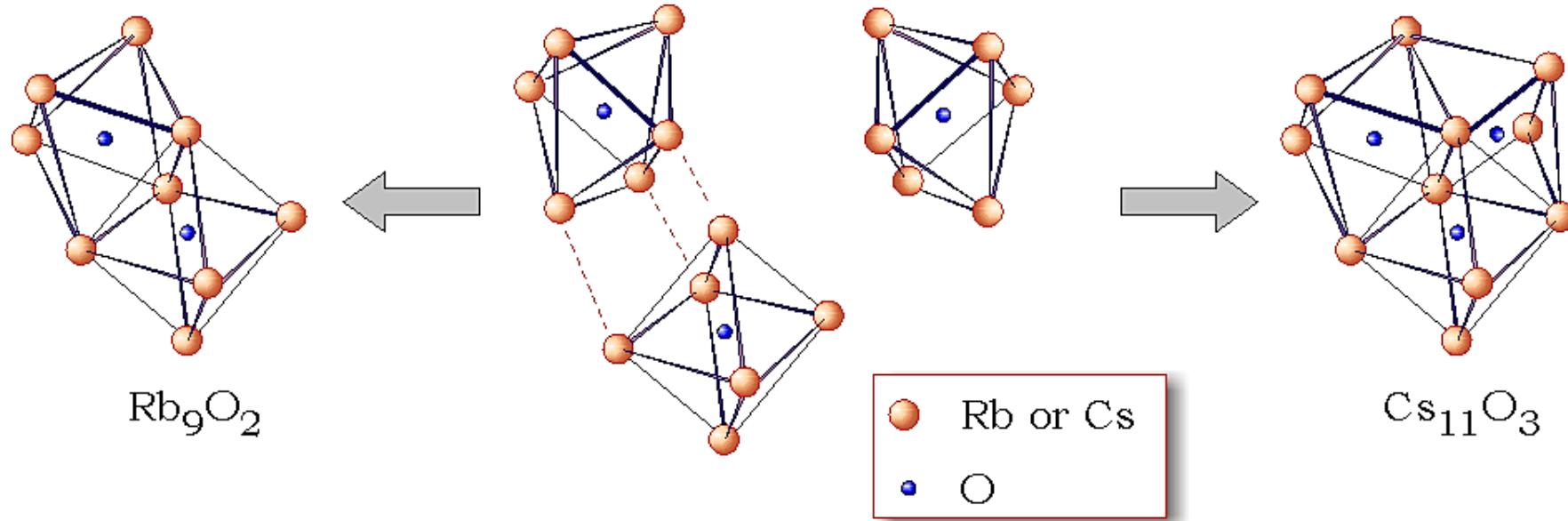
# Oxides ( $M_xO_y$ )

- A variety of oxides known particularly for heavier alkali metals
- When the amount of air is *not* controlled:
  - $4 \text{ Li} + \text{O}_2 \rightarrow 2 \text{ Li}_2\text{O}$  ('normal' oxide)
  - $2 \text{ Na} + \text{O}_2 \rightarrow \text{Na}_2\text{O}_2$  (peroxide,  $\text{O}_2^{2-}$ )
  - $\text{K} + \text{O}_2 \rightarrow \text{KO}_2$  (superoxide,  $\text{O}_2^-$ )
- Rb and Cs give mixtures predominantly containing superoxides
- Normal oxides ( $M_2\text{O}$ ) of Na, K, Rb and Cs can be obtained from  $\text{O}_2$  and M under controlled conditions or thermal decomposition of peroxides and superoxides (with liberation of  $\text{O}_2$ )
- Thermal decomposition of Group 1 nitrates can give normal oxides (commonly used for synthesis of  $\text{Na}_2\text{O}$ ) :



# Oxides (cont.)

- The stability of peroxides increases from  $\text{Li}_2\text{O}_2$  to  $\text{Cs}_2\text{O}_2$ 
  - This observation shows another important effect: large anions can be stabilized by large cations and vice versa.
- Partial oxidation of Rb and Cs gives several **suboxides** with interesting structures:



- Note that the oxidation number of Cs and Rb in these compounds is well below +1 expected for the Group 1 metals (i.e. ON for Cs in  $\text{Cs}_{11}\text{O}_3$  is  $+6/11$  or  $\approx +\frac{1}{2}$ ).

# Oxides (reaction with H<sub>2</sub>O) and hydroxides

- All oxides are basic oxides and react with acids and acid oxides to produce salts
  - Remember that the oxides of typical metals are basic!
- Reaction of all oxide types with water produces hydroxides (MOH) but other products vary depending on the oxide type:



- Hydroxides are also produced when aqueous solution of MCl are electrolyzed, from MH and H<sub>2</sub>O and from M and H<sub>2</sub>O.
- These are the strongest bases known with basicity increasing Li << Na < K < Rb < Cs (any idea why?)
- Reaction of peroxides with water is also used for production of H<sub>2</sub>O<sub>2</sub>

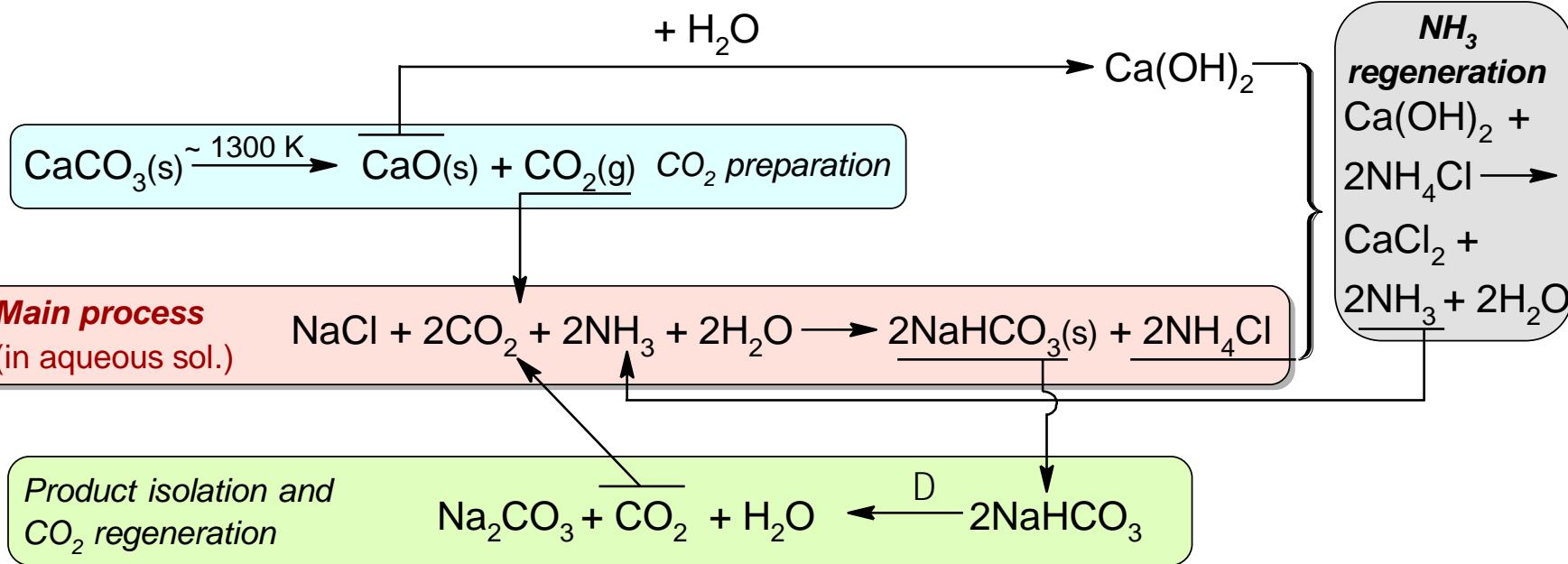
# Oxides - Overview

M	Suboxides	Oxides	Peroxides	Superoxides	Ozonides
Li	N/a	$\text{Li}_2\text{O}$ White	$\text{Li}_2\text{O}_2$ White	$\text{LiO}_2$ , stable at low temp	n/a
Na	N/a	$\text{Na}_2\text{O}$ White	$\text{Na}_2\text{O}_2$ (*) White to pale yellow	$\text{NaO}_2$ Orange, dec.	$\text{NaO}_3$ Dec. Red
K	N/a	$\text{K}_2\text{O}$ Yellowish-white	$\text{K}_2\text{O}_2$ (*) Yellow	$\text{KO}_2$ Orange	$\text{KO}_3$ Dec. Dark red
Rb	$\text{Rb}_6\text{O}$ bronze $\text{Rb}_9\text{O}_2$ red	$\text{Rb}_2\text{O}$ Yellow	$\text{Rb}_2\text{O}_2$ (*) Yellow	$\text{RbO}_2$ Orange	$\text{RbO}_3$ Dark red
Cs	$\text{Cs}_4\text{O}$ violet $\text{Cs}_7\text{O}$ bronze $\text{Cs}_3\text{O}$ blue $\text{Cs}_{11}\text{O}_3$ violet	$\text{Cs}_2\text{O}$ Orange	$\text{Cs}_2\text{O}_2$ (*) Yellow	$\text{CsO}_2$ Orange	$\text{CsO}_3$ Dark red

(\*) colour varies depending on the amount of  $\text{MO}_2$  or other oxides in the sample

# Oxosalts

- Many oxosalts (carbonates, sulfates, nitrates...)
- Solvay soda synthesis is a very important industrial process:



- $\text{NaHCO}_3$  formed in the main process is insoluble and easily removed; treatment of remaining solution with  $\text{CaO}$  (or  $\text{Ca(OH)}_2$ ) from  $\text{CO}_2$  preparation liberates  $\text{NH}_3$  which is reused, also  $\text{CO}_2$  formed from calcination of  $\text{NaHCO}_3$  is reused.
- Thus, this process produces almost no waste!

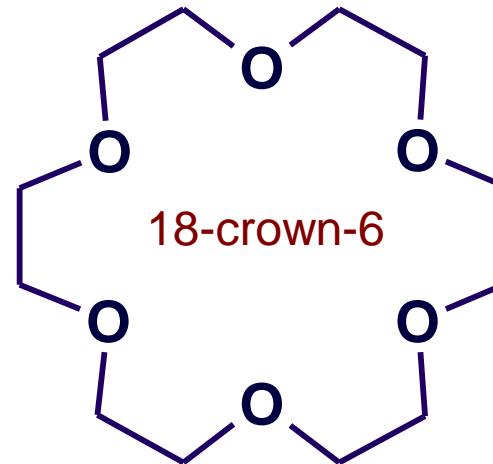
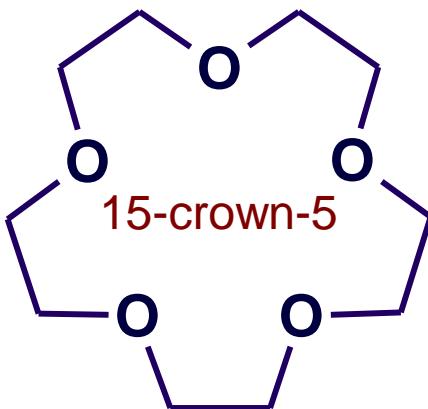
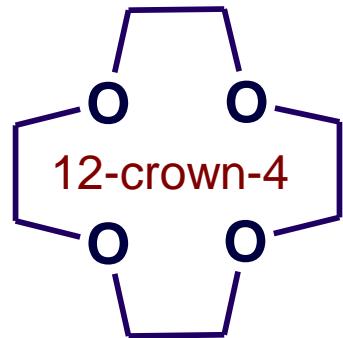
# Complexes – General remarks

- Several concepts important for chemistry of complexes or coordination compounds:
  - Complexes (coordination compounds) contain a central atom (or ion) coordinated by one or more molecules or ions (ligands)
  - Ligands donate an electron pair through a donor atom thus they behave as Lewis bases
  - Central atom or ion accepts this pair and is behaving like Lewis acid
  - This type of bond is usually referred to as coordinate bond
  - The true kings of coordination chemistry (or complex chemistry) are *d*- and *f*- block metals
  - Some examples of complexes you have seen before:  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ,  $\text{H}_3\text{B}\cdot\text{NMe}_3$ ,  $[\text{Co}(\text{NH}_3)_6]^{2+}$ ...

# Alkali metal complexes

- Limited mostly to the crown ethers and cryptand ligands

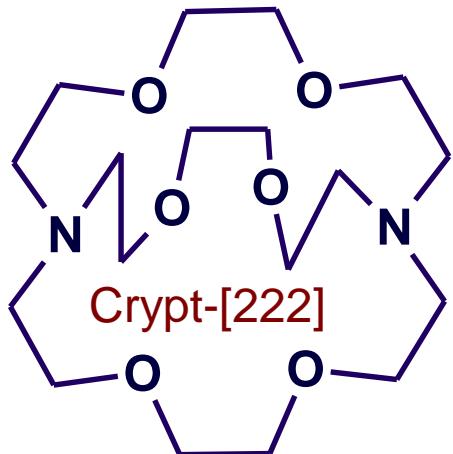
## Most common crown ethers



Crown ether names. 12-crown-4:

The first number (12) tells us how many atoms in total are in the crown (ring), the second number (4) tells us how many O atoms in the structure. Oxygen atoms are connected through  $-\text{CH}_2\text{CH}_2-$  bridges.

## A cryptand example

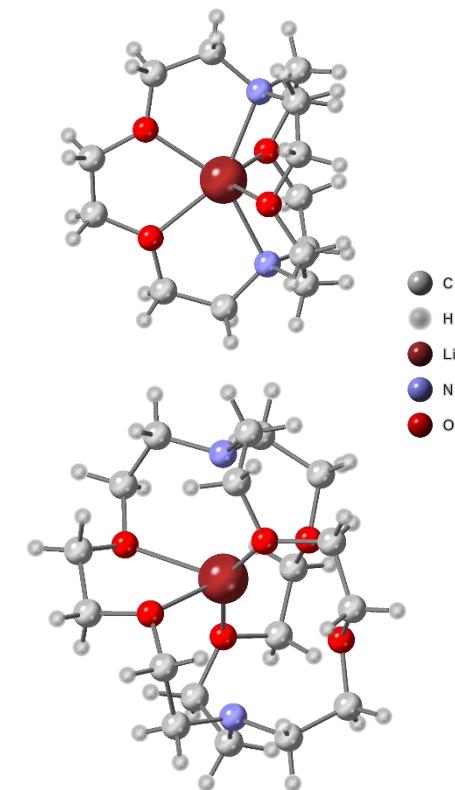
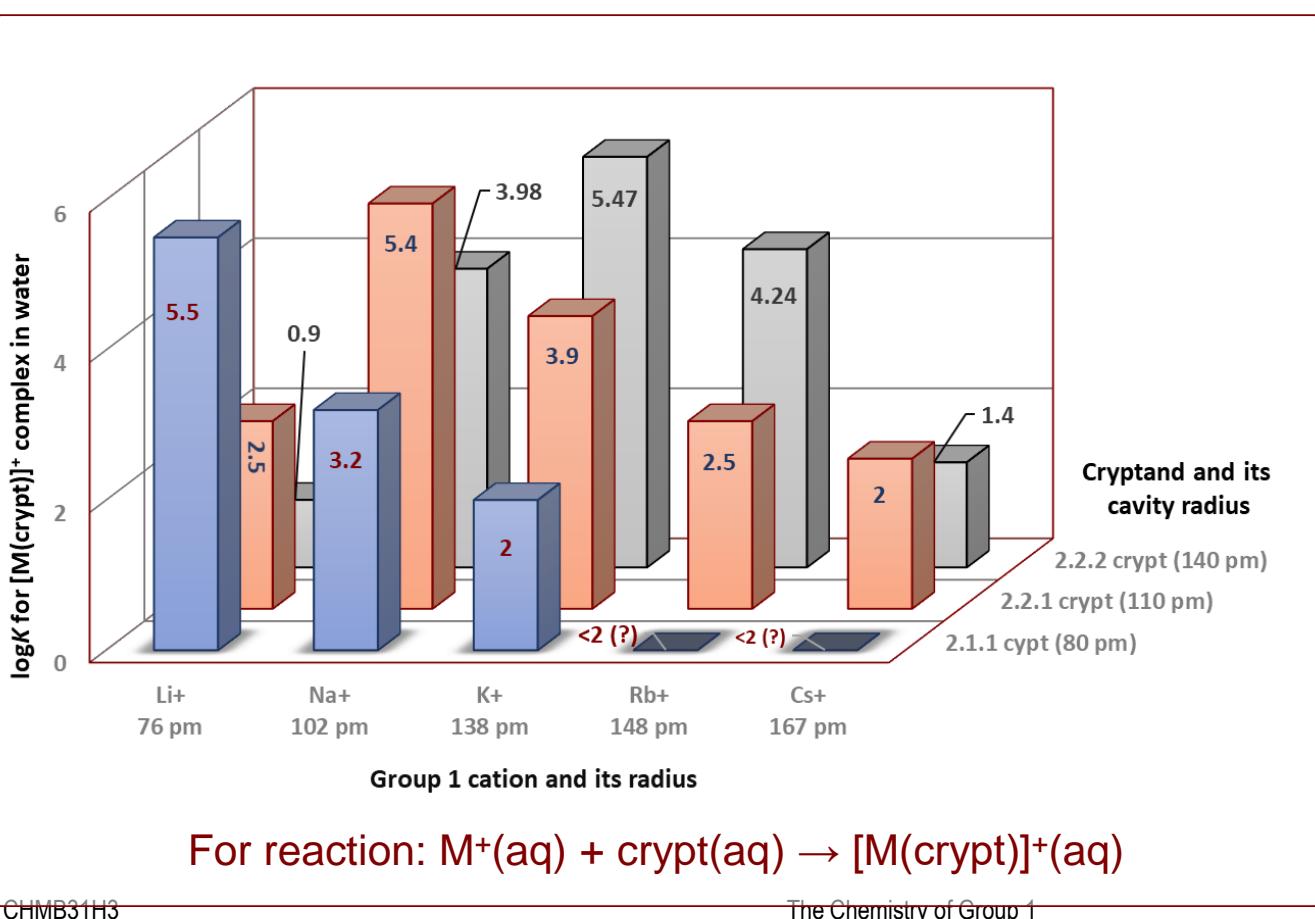


Cryptands are *polycyclic ligands that contain a cavity. Their complexes with metal ions are called cryptates (greek kryptos = hidden)*

Cryptand names. Crypt-[222] or 2,2,2-crypt:  
Three numbers (2, 2, 2) tell us how many oxygen atoms a cryptand has. All non-C atoms are connected via  $-\text{CH}_2\text{CH}_2-$  bridges.

# Formation & Stability of Macrocyclic Complexes

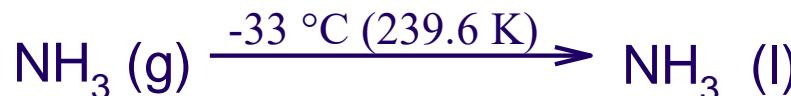
- A complex in aqueous solution is formed by substitution of coordinated water molecules (aquated cations) with other ligands.
- The stability of macro- and polycyclic complexes depend on how well the cation fits in the ligand ring:



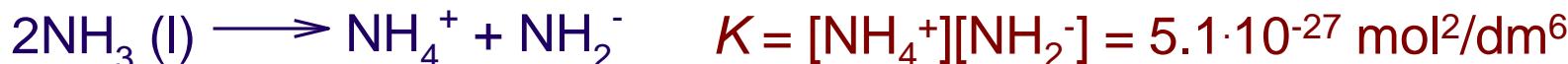
2.1.1crypt is a good fit for Li<sup>+</sup> (top) but 2.2.2 crypt is not (bottom)

# Liquid ammonia solutions

- Gaseous ammonia can be easily converted to liquid and used as a solvent



- Similarly to water, liquid ammonia is a polar solvent that undergoes autoprotolysis:



- Liquid NH<sub>3</sub> dissolves alkali metals producing deep blue solutions:



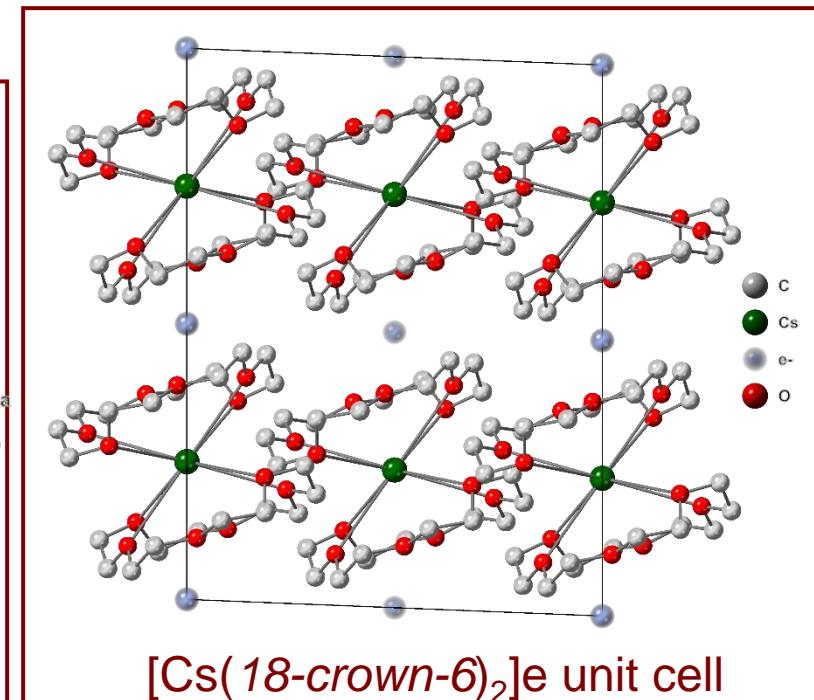
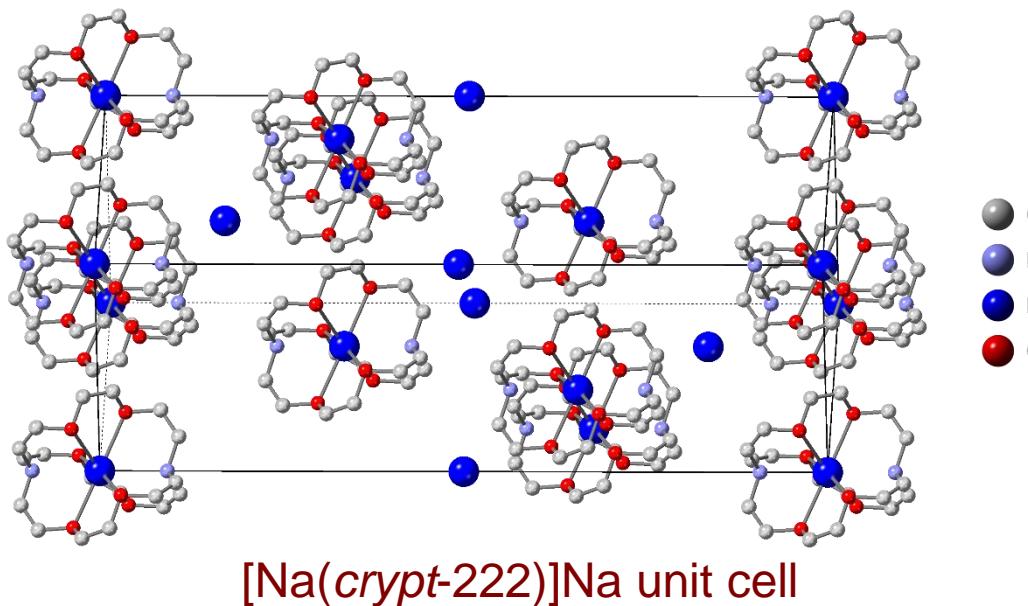
- These solutions are excellent reducing agents.
- The blue solutions decompose over time and lose colour (the free electrons reduce ammonia on standing):



*Under kinetic control give metal amides, MNH<sub>2</sub>, very useful strong bases.*

# Alkalides and Electrides

- Alkalides are alkali metal anions ( $M^-$ ) with an  $ns^2$  electronic configuration (known for all but Li)
- If 0.5 equivalents of crypt-222 is added to a Na solution in  $CH_3CH_2NH_2$  a golden yellow complex  $[Na(crypt-222)]Na$  containing  $Na^-$  anion, can be isolated.
- If 1 equivalent of crypt is used, or 2 equivalents of a crown ether electrides can be isolated – these contain a free electron in their structure, i.e.  $[M(crypt-222)]^+e^-$ .



# Overview

1	H	1,00797
2	Li	6,989
3	Na	22,9898
4	K	39,102
5	Rb	85,47
6	Cs	132,905
7	Fr	(223)

- Occurrence and isolation;
- Nuclear properties;
- Chemical and physical properties;
- Reactivity:
  - With water;
  - With  $H_2$  (stability of hydrides);
  - With  $X_2$  (with halogens; stability of halides);
  - With  $O_2$  (different oxides; reactivity of oxides with water);
- Solvay's soda synthesis;
- Alkali metal complexes;
- Solutions in liquid ammonia;
- Alkalides and electrides;

# Readings and problems

- Readings
  - **Both 6<sup>th</sup> and 7<sup>th</sup> editions:** Chapter 11: Group 1 – The alkali metals [you can skip the following sections: 10.9 ‘Sulfides, selenides & tellurides’, 11.12 ‘Nitrides and carbides’, 11.15 ‘Zintl phases’ and 11.17 ‘Organometallic Compounds’]
  - For basic concepts of coordination compounds see “The language of coordination chemistry” in Chapter 7 “An Introduction to Coordination Compounds” (pp. 199-202 6<sup>th</sup> ed./pp.216-218 7<sup>th</sup> ed.)
  - Pay attention to Box 11.2 and 11.3 (11.2 and 11.4 in the 7<sup>th</sup> ed.)
- Problems
  - From 6<sup>th</sup> edition:
    - Examples and self-tests: 11.1, 11.2, 11.3, and 11.4
    - Exercises: 11.1, 11.3, 11.4, 11.5, and 11.6
  - From 7<sup>th</sup> edition:
    - Examples and self-tests: 11.1, 11.2, 11.3, 11.4, 11.5, 11.6
    - Exercises: 11.1, 11.3, 11.4, 11.5, 11.7, 11.8, 11.13

# Readings and problems (cont.)

- A bit more practice
  - $^{223}\text{Fr}$  decays by alpha emission. Write a nuclear equation for this decay
  - How can we determine the differences in basicities of NaOH and KOH if both are considered strong bases in water?
  - Find  $\text{ReO}_3$  (rhenium trioxide, rhenium(VI) oxide) structure prototype. Starting from this structure, describe sodium nitride's ( $\text{Na}_3\text{N}$ ) *anti*- $\text{ReO}_3$ .
  - Would you expect Li salts to be more or less hygroscopic than Na salts? Explain.
  - $\text{KO}_2$  is used as a “ $\text{CO}_2$  scrubber” in submarines and space vehicles. Write a balanced chemical equation for the scrubbing process.
- If you want to explore more:
  - Lithium triangle
  - 7Up (yup, the drink)
  - Dating rocks on Mars
  - Humphry Davy
  - Leblanc process
  - Pollucite