Chemistry 1000 Lecture 11: Chemistry of the alkali metals

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The alkali metals

- Group 1, except H
- Soft metals
- Lowest ionization energies and electronegativities in periodic table, low melting and boiling points (for metals)

	Li	Na	K	Rb	Cs
$I_1/\mathrm{kJ\,mol^{-1}}$	520.2	495.6	418.8	403.0	375.7
χ	1.0	0.9	0.8	0.8	0.7
$T_f/^\circ\mathrm{C}$	181	98	63	39	28
$T_b/^\circ\mathrm{C}$	1342	883	759	688	671

Redox chemistry

- Alkali metal ions have among the most negative reduction potentials

  Reduction potential: Half-cell potential for gaining electrons

  In this case,

$$M^+_{(aq)} + e^- \rightarrow M_{(s)}$$

	Li^+	Na^+	K^+	Rb^+	Cs^+
E°/V	-3.040	-2.71	-2.931	-2.98	-3.026

$\Longrightarrow$ The alkali metals are very powerful reducing agents.

$\Longrightarrow$ In nature, these elements only ever appear as their $+1$ cations.

Some typical reactions

- Reaction with water:

$$M_{(s)} + H_2O_{(l)} \rightarrow M^+_{(aq)} + OH^-_{(aq)} + \frac{1}{2}H_{2(g)}$$

- Reaction with halogens (group 17: F_2, Cl_2, Br_2, I_2)

$$M_{(s)} + \frac{1}{2}X_2 \rightarrow MX_{(s)}$$

- Reaction of lithium with oxygen:

$$2Li_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow Li_2O_{(s)}$$

Note: the other alkali metals make oddball oxides.

$\Longrightarrow$ Alkali metal compounds are almost universally ionic.

Example: stoichiometry of the reaction with water

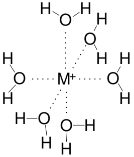
1.5 g of sodium is reacted with 150 mL of water, which represents a large excess.

1. What is the concentration of sodium hydroxide in the final solution?
2. What volume of hydrogen gas, measured at 25 °C and 1 atm pressure, is produced?
   Give your answer in units such that the numerical value is between 0.001 and 1000.

Answers: 0.43 mol L^{-1} NaOH and 0.80 L H_2

Hydration

- An ion in solution is surrounded by water molecules.



Hydration enthalpy ($\Delta_{\text{hydr}}H$): Enthalpy change for the transfer of an ion from the gas phase to solution

$$M^+_{(g)} \rightarrow M^+_{(aq)}$$

	Li^+	Na^+	K^+	Rb^+	Cs^+
$\Delta_{\text{hydr}}H/\text{kJ mol}^{-1}$	−515	−405	−321	−296	−263
r/pm	59	99	138	149	165

Solubility of alkali metal compounds

- Alkali metals have relatively large, negative enthalpies of hydration.
- Because they carry a single charge, the forces holding their crystals together, while significant, are less strong than those holding together crystals of more highly charged ions.
- As a consequence, almost all alkali metal compounds are extremely soluble in water (solubilities often reaching several hundred grams per litre).
- Exception: some lithium compounds with highly charged anions
  Lithium phosphate: $0.39\,\mathrm{g\,L^{-1}}$

Flame tests

- Metal ions are often identified by precipitation.
- Alkali metal compounds are extremely soluble, so that won't work.
- Instead, we use flame tests:
  - Putting a sample into a flame puts energy into it.
    This energy can put ions in excited electronic states.
  - When the ions return to their ground states (possibly in multiple hops), the emit light.
  - The emission spectrum depends on a number of factors (including the flame temperature), but is most strongly dependent on the energy levels of the emitter, leading to characteristic colors.
- A fancy (automated) version of a flame test is flame emission spectroscopy, often used in quality testing in the pharmaceutical industry.

Flame tests (continued)

Element	Li	Na	K	Rb	Cs
Flame color	crimson	yellow	lilac	purple	blue

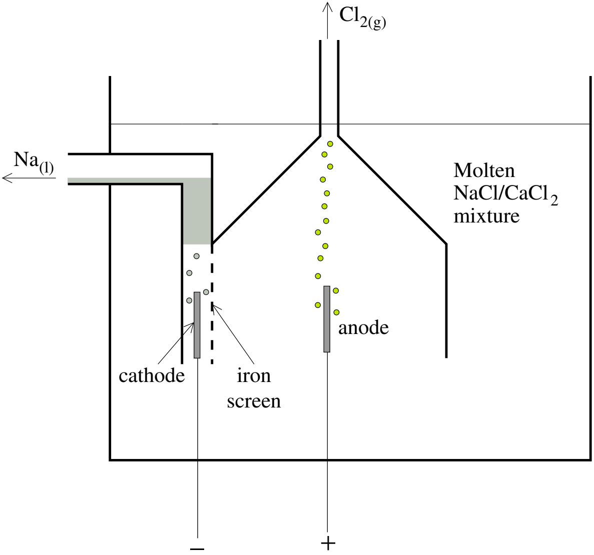
Production of sodium and lithium metals

- Lithium and sodium metal are produced by electrolysis of the molten chlorides.
  Overall reactions:

$$\mathrm{LiCl_{(l)}} \rightarrow \mathrm{Li_{(l)}} + \frac{1}{2}\mathrm{Cl_{2(g)}}$$

$$\mathrm{NaCl_{(l)}} \rightarrow \mathrm{Na_{(l)}} + \frac{1}{2}\mathrm{Cl_{2(g)}}$$

Downs cell



$Cl_{2(g)}$
$Na_{(l)}$
Molten
$NaCl/CaCl_2$
mixture
anode
cathode
iron
screen
−
+

- Melting point of NaCl: 804°C
  Melting point of 1:4 mixture of NaCl:$CaCl_2$: $\sim 600°C$
- Cathode reaction:

$$Na^+_{(l)} + e^- \rightarrow Na_{(l)} \qquad E^\circ = -2.713\,\mathrm{V}$$

- Anode reaction:

$$Cl^-_{(l)} \rightarrow \frac{1}{2}Cl_{2(g)} + e^- \qquad E^\circ = -1.358\,\mathrm{V}$$

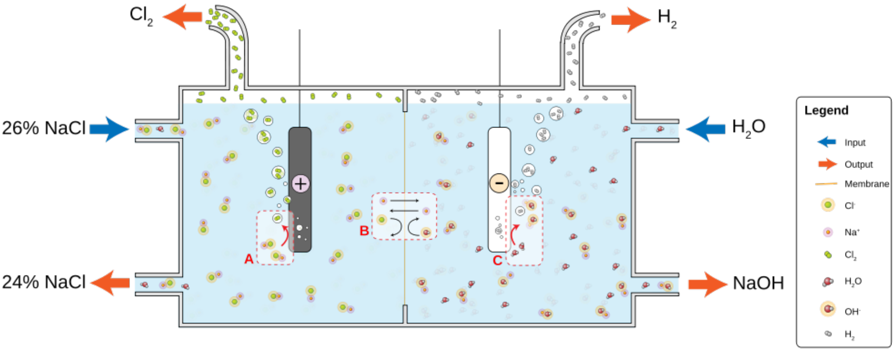
- Overall:

$$Na^+_{(l)} + Cl^-_{(l)} \rightarrow Na_{(l)} + \frac{1}{2}Cl_{2(g)} \qquad E^\circ = -4.071\,\mathrm{V}$$

- Calcium is not produced in appreciable quantities because calcium ions are harder to reduce than sodium ions: $E^\circ = -2.84\,\mathrm{V}$ for Ca^{2+}.

The chlor-alkali process

Electrolysis of aqueous NaCl



Source: Wikimedia Commons: `http://en.wikipedia.org/w/index.php?title=File:Chloralkali_membrane.svg&page=1`

The chlor-alkali process

Electrolysis of aqueous NaCl (continued)

- Electrolysis of an aqueous solution of NaCl involves the following half-reactions:

$$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^- \qquad E^\circ = -1.358\,V$$

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)} \qquad E^\circ = -0.828\,V$$

- Overall:

$$2Cl^-_{(aq)} + 2H_2O_{(l)} \rightarrow Cl_{2(g)} + H_{2(g)} + 2OH^-_{(aq)} \qquad E^\circ = -2.186\,V$$

- We are left with a solution of $NaOH_{(aq)}$.
- Industrially, this chlor-alkali process is the main source of both chlorine gas and sodium hydroxide.

Some questions and comments

- Why does electrolysis of molten NaCl produce sodium metal while electrolysis of aqueous NaCl produces NaOH?
- In the Downs cell, we need to make sure that the sodium and chlorine end up in different places. Why?
- We will see later why the chlorine and hydroxide which are products of the chlor-alkali process need to be kept apart.
  Briefly, they react together to make the hypochlorite ion (OCl^-).