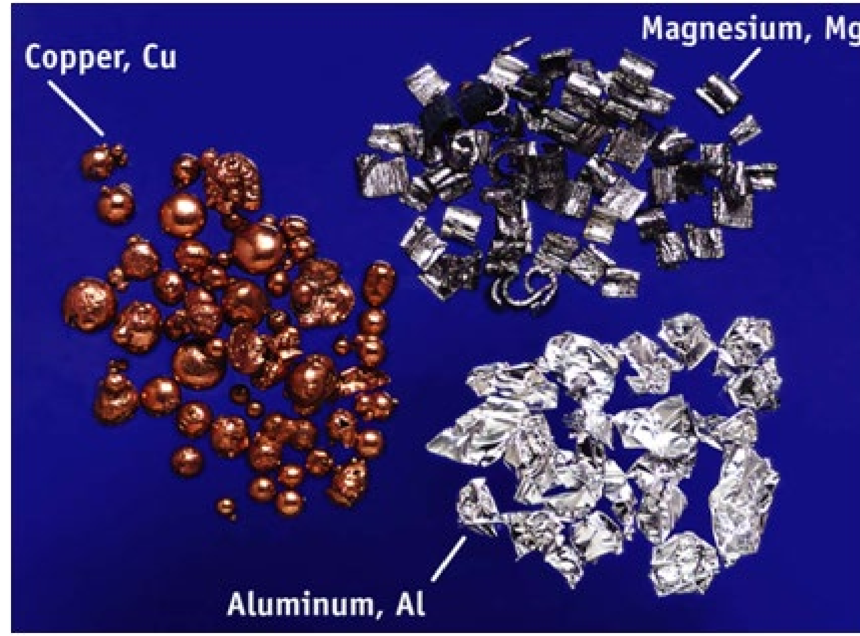
METALS



CHEMISTRY 1000

Topic #2: The Chemical Alphabet

Fall 2020

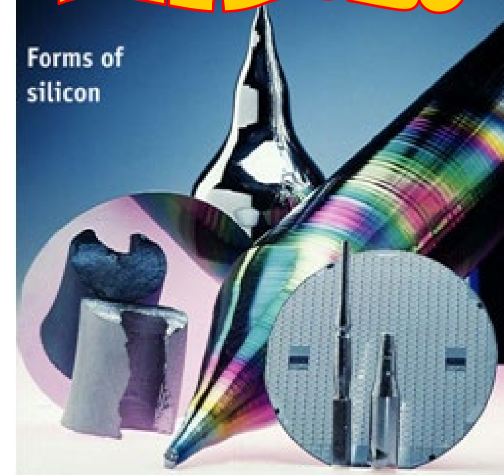
Dr. Susan Findlay

See Exercises 6.1 to 6.5 and 7.1

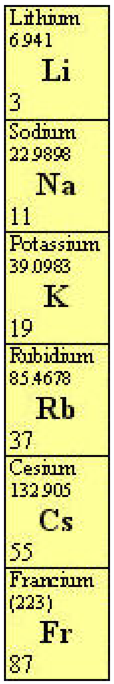
NONMETALS

Forms of Carbon

METALLOIDS



The Alkali Metals (Group 1 Except Hydrogen)

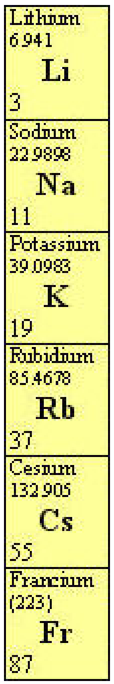


- What is an alkali metal?
  - Any element in Group 1 <u>*except*</u> hydrogen
  - A soft silvery metal that has a relatively low melting point, boiling point and density (for a metal):

	Melting Point	**Boiling Point**	**Density** (at 20 °C)
Lithium	180.54 °C	1347 °C	0.534 g/cm^3
Sodium	97.81 °C	883.0 °C	0.971 g/cm^3
Potassium	63.65 °C	773.9 °C	0.862 g/cm^3
Rubidium	39.05 °C	687.9 °C	1.532 g/cm^3
Cesium	28.4 °C	678.5 °C	1.873 g/cm^3

  - Typically stored under oil because it reacts with air (both oxygen and water vapour)

The Alkali Metals (Group 1 Except Hydrogen)



- What is an alkali metal?
  - Only forms one cation (+1) and no anions
  - Has only one valence electron (electron configuration $[N.G.]ns^1$) and a low first ionization energy
  - An excellent **reducing agent** (good at losing electrons so that <u>other</u> elements can be reduced)

	First Ionization Energy (kJ/mol)	**Standard Reduction Potential** (V = J/C)
Lithium	520.2	-3.040
Sodium	495.8	-2.713
Potassium	418.8	-2.924
Rubidium	403.0	-2.924
Cesium	375.7	-2.923

The Alkali Metals (Group 1 Except Hydrogen)

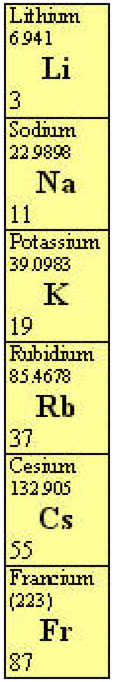
Lithium	6.941	Li	3
Sodium	22.9898	Na	11
Potassium	39.0983	K	19
Rubidium	85.4678	Rb	37
Cesium	132.905	Cs	55
Francium	(223)	Fr	87

- How can I distinguish between the alkali metals?
  - Flame test. All of the alkali metal cations give positive flame tests. Complete the table below after doing the Metals Lab.
  - Reactivity with water. All of the alkali metals react exothermically with water to give the corresponding hydroxide and hydrogen gas. For safety reasons, you will only test small amounts of sodium and potassium in the Metals Lab.

	Flame Colour	**Strength of Reaction with Water***
Lithium		
Sodium		
Potassium		
Rubidium	Bluish red	
Cesium	Blue	

*Video: http://www.youtube.com/watch?v=Ft4E1eCUItI&mode=related&search=

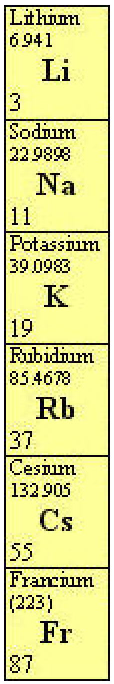
The Alkali Metals (Group 1 Except Hydrogen)



- That explains the “keep away from humidity” safety regulation. How does an alkali metal react with the oxygen in air?
  - That depends on the alkali metal.
    - Lithium reacts with excess oxygen to give lithium oxide:
    - The other alkali metals all react with excess oxygen to give more complex salts called peroxides and superoxides (reactions we won’t address in detail in CHEM 1000).
- Alkali metals also react vigorously with halogens:

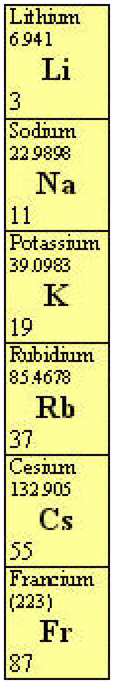
In each of these reactions of alkali metals, the alkali metal has formed an ionic compound. In fact, pure alkali metals are so reactive that they do not exist in nature. Alkali metals are only found naturally in ionic compounds (aka salts).

An Aside: Solving Stoichiometry Problems



- Best plan for solving any stoichiometry problem:
  1. Get to moles.
  2. Identify limiting reactant (where applicable), and use mole ratio to find moles of what you're being asked about.
  3. Answer question!

An Aside: Solving Stoichiometry Problems



- A 3 mm cube of sodium metal is added to 100 mL of distilled water in a beaker. When the reaction has completed, what is the concentration of the resulting sodium hydroxide solution? *Assume that no water evaporates.*

Another Aside: Naming Ionic Compounds

- You may have noticed that all of the ionic compounds we've seen so far were named similarly:

- All ionic compounds are named by listing the cation followed by the anion. All monoatomic anions end in **ide**, so the anion formed from chlor**ine** is chlor**ide**, sulf**ur** becomes sulf**ide**, etc. You are expected to know the anions listed on the "Master List for Nomenclature" posted on the class website.

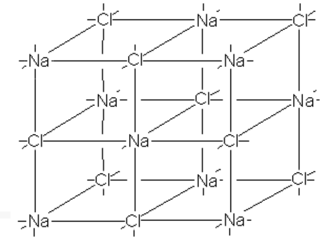
- Name the following:
  - KF
  - Li_3N
  - RbI

Another Aside: Naming Ionic Compounds

- When there is only one possible charge for the cation (e.g. an alkali metal is always +1), it is not listed in the name. If an element can form more than one cation (e.g. iron can be +2 or +3), it is necessary to list the charge as part of the name. This is normally necessary for transition metal cations.

- Name the following:
  - $TiCl_3$
  - CuO
  - Cu_2O
  - $CaBr_2$

Another(!) Aside: Ionic Lattices



- Opposites attract. When a **cation** meets an **anion**, the electrostatic force of attraction pulls them together to make an **ionic bond**.
  - The force each ion applies on the other can be calculated using **Coulomb's law**:

$$\boxed{F = \frac{1}{4\pi\varepsilon_0} \times \frac{(Z^+e)(Z^-e)}{d^2}}$$

    where ε_0 is permittivity ($1/4\pi\varepsilon_0 = 8.988 \times 10^9\ \mathrm{N{\cdot}m^2{\cdot}C^{-2}}$ in a vacuum), *Z* is the charge of the ion (±1, ±2, etc.), *e* is the charge of an electron (1.602×10^{-19} C), and *d* is the internuclear distance.

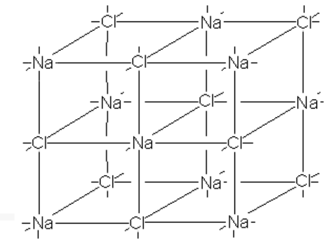
    Note that negative forces are attractive; positive forces are repulsive.

  - The energy of formation of an ionic bond can be calculated using a related formula:

$$\boxed{E = \frac{1}{4\pi\varepsilon_0} \times \frac{(Z^+e)(Z^-e)}{d}}$$

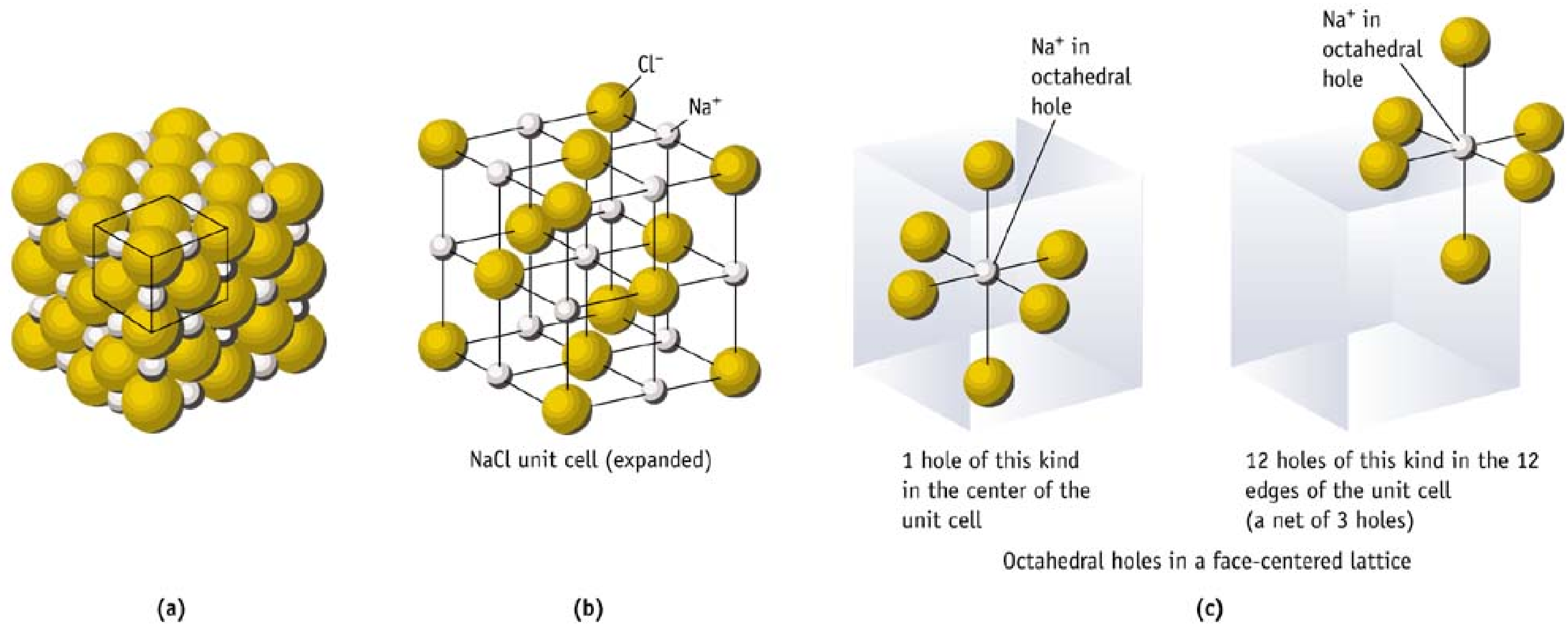
    This formula calculates the energy of bond formation for one gaseous molecule. *Note that a negative energy for bond formation corresponds to a <u>release</u> of energy when the bond is formed!*

Another(!) Aside: Ionic Lattices

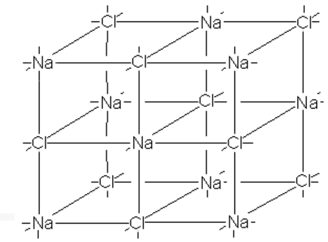


- Like most metals, ionic compounds exist as lattices under standard conditions. Since cations are usually smaller than anions, it is easier to think of the anions forming a lattice with the cations filling "holes".

- The lattice for solid NaCl is shown below:



Another(!) Aside: Ionic Lattices



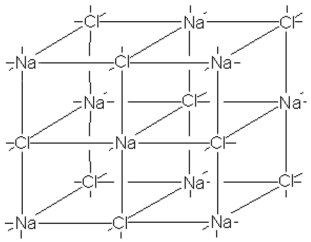
- The energy required to fully break an ionic lattice into gaseous ions is its **lattice energy**.
  - Lattice energy not only accounts for the energy of attraction between adjacent ions of opposite charge, it accounts for energies of attraction and repulsion between all ions in the lattice. *(Each cation is surrounded by anions which are surrounded by more cations which are surrounded by more anions, etc.)*

$$\boxed{E_{lattice} = -A \times \frac{N_A}{4\pi\varepsilon_0} \times \frac{(Z^+e)(Z^-e)}{d} \times \left(1 - \frac{1}{n}\right)}$$

where A is the Madelung constant (which depends on the geometry of the lattice), N_A is Avogadro's number and n is an integer dependent on (but not equal to) the highest energy shell of electrons in the ions.

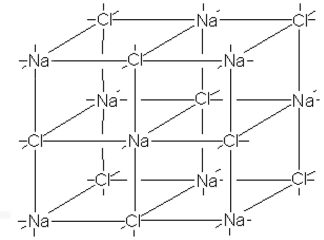
- Values for the Madelung constant (A) range from 1.6 to 4.0. For the NaCl lattice, A = 1.74756.
- Values for n range from 5 (if the nearest noble gas is He) to 12 (if the nearest noble gas is Xe)

Another(!) Aside: Ionic Lattices



- Based on these equations, what factors would you expect to lead to a large lattice energy for an ionic compound?

Another(!) Aside: Ionic Lattices



Compound	$E_{lattice}$ (kJ/mol)	Compound	$E_{lattice}$ (kJ/mol)	Compound	$E_{lattice}$ (kJ/mol)	Compound	$E_{lattice}$ (kJ/mol)
LiF	1049	MgF_2	2978	AlF_3	6252	Li_2O	2814
LiCl	864	$MgCl_2$	2540	$AlCl_3$	5513	Na_2O	2478
LiBr	820	$MgBr_2$	2451	$AlBr_3$	5360	K_2O	2232
LiI	764	MgI_2	2340	AlI_3	5227		
NaF	930	CaF_2	2651	GaF_3	6238	MgO	3791
NaCl	790	$CaCl_2$	2271	$GaCl_3$	5665	CaO	3401
NaBr	754	SrF_2	2513	$GaBr_3$	5569	SrO	3223
NaI	705	$SrCl_2$	2170	GaI_3	5496	BaO	3054
KF	829	BaF_2	2373				
KCl	720	$BaCl_2$	2069	TiF_4	9908	Al_2O_3	15916*
KBr	691			$TiBr_4$	9059		
KI	650			TiI_4	8918	ScN	7506

*This is a theoretical value. The rest were determined via Born Haber Cycle (values from CRC Handbook).

The Alkali Metals (Group 1 Except Hydrogen)

Name	Atomic mass	Symbol	Atomic number
Lithium	6.941	Li	3
Sodium	22.9898	Na	11
Potassium	39.0983	K	19
Rubidium	85.4678	Rb	37
Cesium	132.905	Cs	55
Francium	(223)	Fr	87

- What do we know about the ionic compounds of alkali metals?
  - **They are all soluble in water.** A solution of sodium chloride in water is often written as $NaCl_{(aq)}$, but that's a bit misleading. When table salt is dissolved in water, the following occurs:

    All the ionic Na-Cl bonds are broken, and the sodium cation is **solvated** by water molecules (as is the chloride anion):

    To indicate this solvation, we can write $Na(OH_2)_6{}^+{}_{(aq)}$ or $Na^+{}_{(aq)}$.
  - Alkali metals have large **hydration enthalpies**. *(The beaker gets <u>hot</u> when NaOH is dissolved in H_2O!)*

The Alkali Metals (Group 1 Except Hydrogen)

Lithium	6.941	Li	3
Sodium	22.9898	Na	11
Potassium	39.0983	K	19
Rubidium	85.4678	Rb	37
Cesium	132.905	Cs	55
Francium	(223)	Fr	87

- The lithium cation is particularly well stabilized by solvation with water. In other words, it has an unusually large enthalpy of hydration:

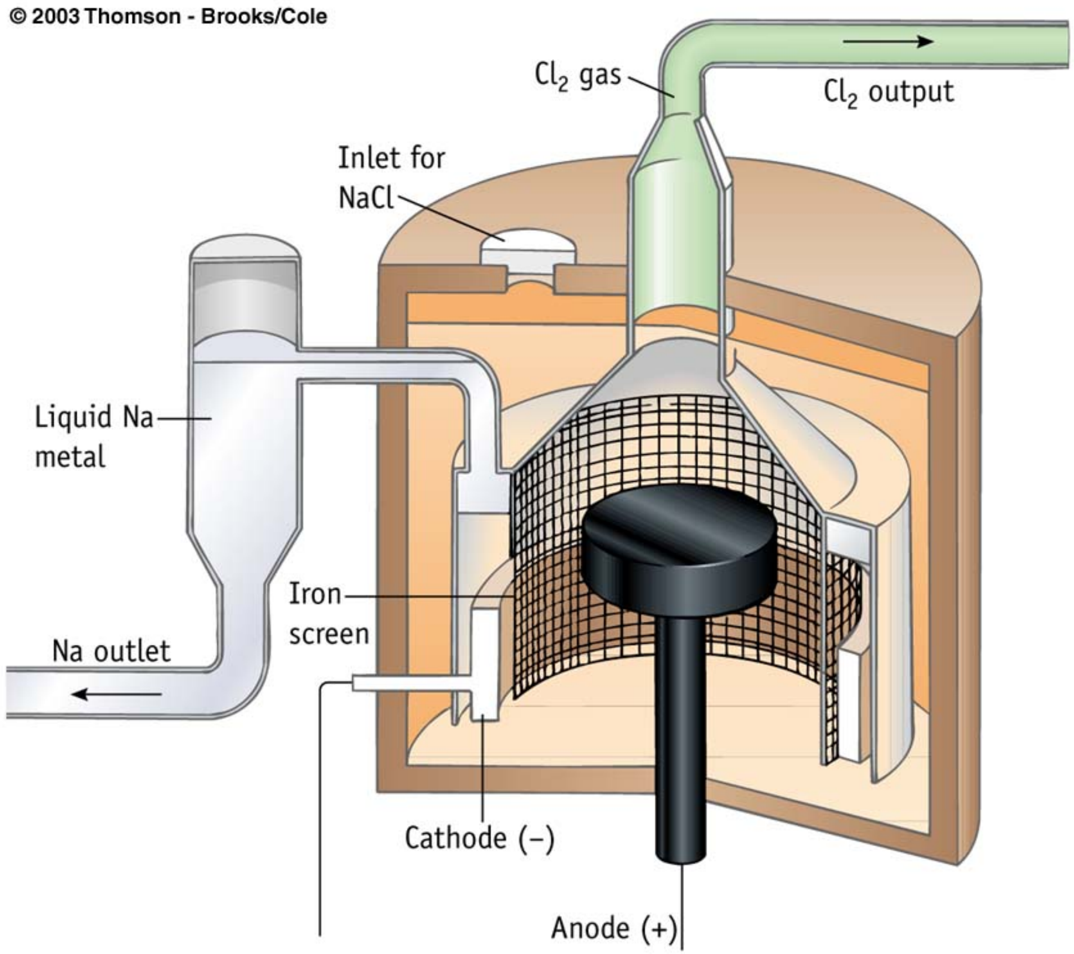
  The reason for this is the lithium cation's small size (only 59 pm – remember that the electron configuration of Li^+ is __________) which allows the oxygen atoms of the surrounding water molecules to approach more closely than they could for a larger cation:

- This unusually large enthalpy of hydration is the reason that lithium gives up its electron more easily in aqueous solution than any other alkali metal (hence the most negative standard reduction potential) despite having the highest first ionization energy.

The Alkali Metals (Group 1 Except Hydrogen)

- Pure alkali metals don't exist in nature, so how are they made?
  - Pure sodium is obtained by electrolysis of NaCl in a **Downs cell**.
    - Because sodium is so reactive, it is difficult to convert sodium salts to sodium metal. To do so requires a significant input of energy. Industrially, this is accomplished by electrolysis (application of a potential to "force" a reaction to go in the unfavourable direction).
    - Because H^+ is more easily reduced than Na^+, there can be no water present in the electrolysis. Instead, the sodium salt is melted. *(NaOH melts at 318 °C; NaCl melts at 808 °C; adding $BaCl_2$ or $CaCl_2$ lowers the melting point of NaCl to ~600 °C; Ba^{2+} and Ca^{2+} are more difficult to reduce than Na^+)*
    - *Pure sodium is insoluble in molten NaCl and less dense than it. As such, it can be removed from the cell. It must, of course, be kept separate from the other product of the Downs cell – chlorine gas!*
  - *Lithium is obtained in a similar fashion (electrolysis of LiCl).*

The Alkali Metals (Group 1 Except Hydrogen)



The Alkali Metals (Group 1 Except Hydrogen)

- If aqueous NaCl is electrolyzed (instead of molten NaCl), NaOH is obtained instead of sodium metal. This is the main way in which sodium hydroxide and chlorine gas are prepared industrially.
  - As in the Downs cell, the reaction at the anode is:
  - In an aqueous electrolysis of NaCl, the reaction at the cathode is:
  - Why does this result in NaOH?
  - It is important to keep the NaOH and chlorine gas separate. If they are allowed to react, they will make bleach (NaOCl):

The Alkali Metals (Group 1 Except Hydrogen)