

# INORGANIC CHEMISTRY

## Lesson 15

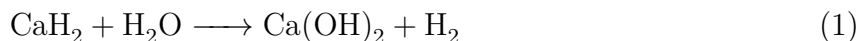
Pnictogens etc. Other classes of elements.

February 4, 2018

### 1 Hydrides of metals

In our classification of elements, we assume the elements belonging to the same group are supposed to form oxides<sup>1</sup> with the same general formula ( $X_2O_7$  for halogens,  $XO_3$  for halogens,  $X_2O_5$  for pnictogens), and these oxides should have similar chemical and physical properties. The second class of compounds we use for classification is hydrides: thus, all halogens form hydrides with a general formula  $HX$ , where  $X$  is a halogen, and these hydrides are acids, all halogens form hydrides  $H_2X$ , where  $X$  is a halogen, and they are weak acids (except water, which is amphoteric), all pnictogens form hydrides with a general formula  $H_3X$ , and they are not acidic at all. What about metals? Do they form hydrides?

Yes, all metals form hydrides, and these hydrides have interesting properties. Let's take calcium hydride as an example. Calcium is always divalent, and hydrogen is monovalent, so the formula of calcium hydride should be  $CaH_2$ . This compound is a hard solid, thereby resembling calcium chloride or fluoride. However, its chemical properties are different from those of calcium halogenides or other salts. If we drop a piece of calcium hydride into water, a violent reaction begins, some gas evolves, and the liquid becomes turbid. The gas that forms in this reaction is hydrogen, and another product of it is calcium hydroxide  $Ca(OH)_2$  (if we add few drops of phenolphthaleine to the solution, it turns pink).



The same reaction can be observed if we take sodium hydride or other metal hydrides. In general, most metals form hydrides, and these hydrides produce a metal hydroxide and hydrogen in a reaction with water<sup>2</sup>.

With this knowledge in mind, let's try to identify other groups of elements based on these two major traits:

1. The members of each group form hydrides with general formula  $H_nX$ , where  $n$  is specific to a certain group: it equals to 1 for halogens, 2 for chalcogens and 3 for pnictogens. Properties of hydrides formed by the elements belonging to the same group are similar.

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<sup>1</sup>For polyvalent elements, the oxides with highest possible valence are considered.

<sup>2</sup>The situation is more complex for heavy metals, however, we do not consider these exceptions now.

2. The members of each group form oxygen compounds, and the maximal valence of the elements in those compounds equals to  $8 - n$ . Thus, maximal valence of halogens is  $8 - 1 = 7$ , maximal valence of pnictogens is  $8 - 3 = 5$ .

Using this rule, one more group can be identified, the group of carbon. Thus, carbon and silicon are tetravalent both in their hydrides ( $\text{CH}_4$ ,  $\text{SiH}_4$ ), and oxides ( $\text{CO}_2$ ,  $\text{SiO}_2$ ).

## 2 Groups of metals

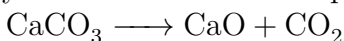
### 2.1 Alkaline metals

We already know that group metals are the most active and the most typical metals (of course, from the chemist's point of view). In addition to the metals we are already familiar with, three more metals, **Lithium (Li)**, **Rubidium (Rb)**, and **Cesium, or caesium (Cs)** belong to this group<sup>3</sup> These metals form oxides that oxides react with water violently to form hydroxides, which are strong alkali (hence the name *alkaline metals*: "Al kali" is the Arabian word that means "a caustic substance", "Al" is an article.) Another common feature of alkaline metals is high solubility of virtually all their salts<sup>4</sup>.

The important feature of alkaline metals is that **they are always monovalent**.

### 2.2 Alkaline earth metals

The typical representative of this group is calcium. Other members are magnesium, **Barium (Ba)**, **Strontium (Sr)**, and **Beryllium (Be)**. These metals also form highly alkaline hydroxides, but they are poorly soluble, hence the name "alkaline earth". In Medieval times the term "earth" was used to denote any insoluble non-metallic solid obtained after heating some material for a long time; when alchemists heated calcium carbonate or magnesium carbonate in an oven they observed their conversion into some other solid. The reaction they observed was a decomposition of carbonates:



The new solid was also an "earth" (poorly soluble solid), but we know it is a basic oxide (or an "alkaline earth", according to alchemical terminology). When other elements from this group (barium and strontium and berillium) were discovered their oxides also demonstrated the same behaviour, i.e. they were the "alkaline earthes", hence the common name.

Alkaline earth metals **are always divalent** in their compounds. This is one of important characteristic feature of that group.

We outlined six groups of elements based on their valence and on the chemical properties of their oxygen and hydrogen compounds. Now we are prepared for a wider generalization.

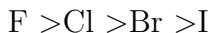
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<sup>3</sup>We are limit ourselves with non-radioactive elements only.

<sup>4</sup>Few lithium salts have low solubility. Other salts of lithium and all salts of other alkaline metals are soluble in water

### 3 Atomic mass and the properties of elements.

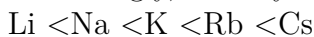
If we arrange halogens according to their nonmetallicity (which we provisionally define as the element's ability to act as an oxidizer) we will see that their nonmetallicity decreases in this order:



In other words, fluorine is the most active nonmetal, whereas iodine is the least active one. Interestingly, the masses of halogens increase in the same order:

Halogen	Atomic mass
F	19
Cl	35.5
Br	79
I	128

Accordingly, activity of alkaline metals (their *metallicity*) *increases* in that order:



That order corresponds to the increase of the element's mass

Alkaline metal	Atomic mass
Li	7
Na	23
K	39
Rb	85
Cs	133

In both cases, we observe some unambiguous dependence between the properties of elements and their masses.

One can conjecture such a dependence is universal, and it can be observed in other groups of elements: chalcogens, alkaline earth metals, and others. Later, we will check if that is the case, and, for a while, let's agree that the lightest element of the group can be used as a representative of the group as whole. In connection to that, let's take the lightest element from each group, and arrange all of them according to their chemical properties. Since the ability to oxidize other element, or the ability to be oxidized are hard to characterize quantitatively, let's choose some other, more quantitative criteria. Such criteria are the element's valence in their oxides and hydrides. Before we started, let's look at one more group of elements, the boron group.

### 4 Boron group

. This group is interesting because it is composed by both metals and nonmetals. The lightest element of this group, boron (chemical symbol B), is a nonmetal (sometimes it is called metalloid because of its metallic luster and hardness). Boron, as well as other representatives of this group (aluminium (Al), gallium (Ga), indium (In), and Thallium (Tl)) form oxides in reaction with oxygen, and their valence in the oxides is three:  $\text{B}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$ , etc. Interestingly, whereas boron is nonmetal, other elements of the boron group are metals, although majority of them are amphoteric.

The boron group elements, as well as other elements are capable of forming hydrides:  $\text{BH}_3$ ,  $\text{AlH}_3$ , etc, where they are also trivalent.

## 5 Periodic law.

Now we know seven groups of elements (halogens, chalcogens, pnictogens, carbon group, boron group, alkaline metals and alkaline earth metals), and we are ready to start to arrange all of them together. Let's take the lightest element from each group and arrange them according to their mass. In parallel, we will write the formula of the element's hydride and oxide.

Element	Li	Be	B	C	N	O	F
Hydride	LiH	BeH <sub>2</sub>	BH <sub>3</sub>	CH <sub>4</sub>	NH <sub>3</sub>	OH <sub>2</sub>	FH
Oxide	Li <sub>2</sub> O	BeO	B <sub>2</sub> O <sub>3</sub>	CO <sub>2</sub>	N <sub>2</sub> O <sub>5</sub>	-	-
Mass	7	9	10	12	14	16	19

We write the formula of water as OH<sub>2</sub> (not H<sub>2</sub>O), and the formula of hydrogen fluoride as FH, not HF. We do that for consistency only, that is not a correct style (although not a mistake either). In future, we will follow a standard style (H<sub>2</sub>O, HF).

From this table, it is clear that, when the mass of the listed elements increases the valence of the element in its hydride increases from one (in LiH) to four (in CH<sub>4</sub>), and then decreases back to one (in HF). In contrast, the valence of the elements in their oxides increases from one (in Li<sub>2</sub>O) to five (in N<sub>2</sub>O<sub>5</sub>), and never decreases back.<sup>5</sup> Interestingly, if we take the second element of each group, the valence of oxides will monotonously increase from left to right:

Element	Na	Mg	Al	Si	P	S	Cl
Hydride	NaH	MgH <sub>2</sub>	AlH <sub>3</sub>	SiH <sub>4</sub>	PH <sub>3</sub>	H <sub>2</sub> S	HCl
Oxide	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	(Cl <sub>2</sub> O <sub>7</sub> )
Mass	23	24	27	28	31	32	35.5

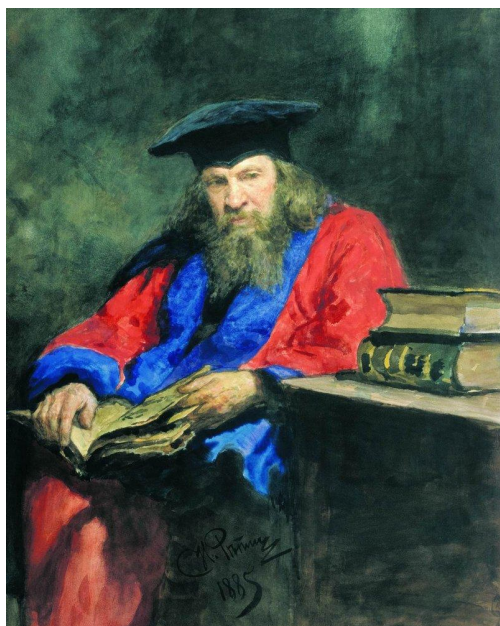
Chlorine (VII) oxide (Cl<sub>2</sub>O<sub>7</sub>) is shown in parentheses because this compound is not stable a pure form. However, its corresponding acid, perchloric (HClO<sub>4</sub>) is a stable and well characterized compound.

By combining the above rows into a single table, and by adding heavier elements from each group, we get the following table (we limit ourselves with four elements from each group, and we draw a generic formulas of hydrides and oxides):

**Table 1.**

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<sup>5</sup>Obviously, oxygen cannot form oxides. Fluorine is more active than oxygen, so it is incorrect to speak about fluorine oxides.



Dmitry Mendeleev (1834-1907), a discoverer of the Periodic Law.

Group	I	II	III	IV	V	VI	VII
Hydride	XH	XH <sub>2</sub>	XH <sub>3</sub>	XH <sub>4</sub>	XH <sub>3</sub>	XH <sub>2</sub>	XH
Oxide	X <sub>2</sub> O	XO	X <sub>2</sub> O <sub>3</sub>	XO <sub>2</sub>	X <sub>2</sub> O <sub>5</sub>	XO <sub>3</sub>	X <sub>2</sub> O <sub>7</sub>
I	Li 7	Be 9	B 10	C 12	N 14	O 16	F 19
II	Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35.5
III	K 39	Ca 40	Ga 70	Ge 72.5	As 75	Se 89	Br 80
IV	Rb 85	Sr 88	In 115	Sn 119	Sb 122	Te 128	I 127

As we can see, all seven groups fit nicely into this table, and one important thing can be derived from it: atomic masses of elements increase when we move from the top to the bottom, and from the left side to the right. That means the periodic dependence exists between the masses of elements and their chemical properties. Indeed, if we unwrap the above table, we get:

Li Be B C N O F Na Mg Al Si P S Cl .....

In this sequence, when we are going from left to right, the mass of the elements increase *monotonously*, but the properties change *periodically*: element's metallicity gradually decreases from lithium to fluorine, then we *jump* to sodium (an alkaline metal), and then the metallicity decreases again until we arrive to chlorine (a nonmetal). This periodicity was first formulated as a law by a Russian chemist Dmitry Mendeleev.

**Properties of elements are periodic functions of their atomic masses.**

Accordingly, each raw in the above table is called a *period*, and the table itself is called *Periodic Table*. Each table's column is called a *group*, and the number of each group is equal to the highest possible valence of the oxides of the elements from that group.



Sir Humphry Davy (1778-1829),  
a person who first used electrolysis for isolation of some elements.

## Homework

1. Watch the following YouTube videos<sup>6</sup>:

(a) <http://www.youtube.com/watch?v=D4pQz3TC0Jo>

(b) <http://www.youtube.com/watch?v=QoXaArRHfAw>

(c) <http://www.youtube.com/watch?v=vRKK6pliejs>

(d) <http://www.youtube.com/watch?v=vJslbQiYrYY>

Describe what do you see, and draw the equations of these reactions.

In which order can these metals be arranged based on their reactivity towards water?  
How does that order correlate with atomic properties of these metals?

2. Preparation of sodium and potassium metals was done for the first time by Sir Humphry Davy by decomposing sodium (or potassium) hydroxide using electrolysis. As we know from the previous lesson, it is impossible to prepare sodium by electrolysis in the presence of water. Davy solved that problem in a very elegant way: instead of dissolving the alkali in water he heated solid alkali until they melt, and performed electrolytic decomposition of liquid alkali. During those experiments he found that his standard corundum or quartz crucibles could not be used, because the alkali destroyed them easily. Please, draw the chemical equations of the reaction between the liquid alkali and the crucibles' material.

Which material, in your opinion, could Davy use for his experiments?

3. You decided to fill two balloons with hydrogen. To this end, you took 25 grams of zinc, placed it in the flask, added 200 g of 10% HCl, and attached a balloon to the neck of the flask. You also took another flask, and did the same using 20 grams of

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<sup>6</sup>If you open an electronic version of this document at our web site, you can click at the links directly

aluminium and 300 grams of 10% HI. When the reactions in both flasks have ceased, you disconnected the balloons and measured their lifting power. Which balloon will be capable of lifting the greater load?

4. What does the Periodic Law says?
5. How do metallic properties of element change when we move from the top of the Table 1 to the bottom?
6. Which element manifests stronger nonmetallic properties, arsenic or antimony?
7. Which sequence of elements is called period?
8. List the elements from the third period that form basic oxides.
9. Using the Table 1, can you predict which acid is stronger, sulfuric acid ( $\text{H}_2\text{SO}_4$ ) or perchloric acid ( $\text{HClO}_4$ )? Which hydroxide is more basic, magnesium hydroxide, or strontium hydroxide?

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