Inorganic Chemistry
Lesson 16
Periodic Law

February 11, 2018

1 How many groups?

As you can see, the Table 1 is incomplete: there is a gap between each halogen and the next alkaline metal. Indeed, whereas the mass of adjacent elements differ by 2 or 3 Daltons, the difference between the mass of fluorine (19) and sodium (23), or between bromine (80) and rubidium (85) is unusually high. By the moment Mendeleev made his discovery (in 1869), scientist knew no good candidates to fill this gap. Only in 1894, British physicist Lord Raleigh and chemist Sir William Ramsay separated a strange gas form air. This gas, called argon, was present in atmosphere in small amount (ca 1%). This gas was totally inert, it did not react with any known acid, base, or oxidizer. Later Ramsay discovered other gases with same properties: Neon (Ne), Krypton (Kr), Xenon (Xe), Neon (Ne). Due to their inertness they, as well as independently discovered helium (He) and radon (Ra) are called *inert*, or *noble* gases. Initially they were believed to have maximal possible valence of zero. Accordingly, they occupied the column number zero in the early periodic table (before alkaline metals). However, in second half of XX century chemists managed to oxidize xenon and krypton to tetroxides (XeO_4 and KrO_4, accordingly). These oxides are low boiling liquids that are very prone to explosion.

Are noble gas metals, non-metals, or they form a separate group? To answer this question, consider the properties of their oxides. When mixed with water, XeO_4 slowly reacts with it yielding perxenic acid:

$$XeO_4 + H_2O \longrightarrow H_4XeO_6$$

which is a very strong acid, instable is a free form. Its salts, perxenates, are stable compounds, although they easily decompose liberating oxygen. Besides perxenates, salts of xenic acid (xenates) were prepared where a xenon atom is hexavalent. Xenates, as well as perxenates are strong oxidizers, which is quite expectable, taking into account that oxygen conpounds formed by halogens, which are immediate neighbours of noble gases in the Periodic table, also are strong oxidizers.

All said above demonstates the noble gases are non-menatl, and it is correct to put them into the VIII group of the Periodic table.

Currently we know that the maximal possible valence of elements in their oxides is eight, and, accordingly, there are eight columns (groups) in the Periodic table.[1]

2 Iron and chromium, transition metals

Even if we add the noble gas group to the table 1, it still is incomplete. Indeed, there is no space there for such elements as iron, cobalt, zinc, platinum, etc. In addition, there are huge gaps between calcium (atomic weight 40 Da) and gallium (atomic weight 70), between strontium (atomic weight 88) and indium (atomic weight 115 Da). Obviously, the remaining elements are supposed to occupy those gaps, but how concretely should they be arranged? The idea to arrange them was arguably the most brilliant Mendeleev's idea. His considerations were as follows.

If we look at the properties of the metals with atomic weight from 40 to 70 Da (scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc) we will see a strange duality. From one hand, all those metals are capable of forming salts with common acids, and they are divalent in those salts. For example, iron or chromium react with hydrochloric acid to form ferrous or chromous chlorides, respectively.

$$\mathrm{Fe} + 2\mathrm{HCl} \longrightarrow \mathrm{FeCl_2} + \mathrm{H_2} \tag{1}$$

$$\mathrm{Cr} + 2\mathrm{HCl} \longrightarrow \mathrm{CrCl_2} + \mathrm{H_2} \tag{2}$$

Accordingly, chromium (II) hydroxide can be prepared, which can react with acids to produce other chromium (II) salts.

$$\mathrm{CrCl_2} + 2\mathrm{NaOH} \longrightarrow \mathrm{Cr(OH)_2} + 2\mathrm{NaCl} \tag{3}$$

$$\mathrm{Cr(OH)_2} + \mathrm{H_2SO_4} \longrightarrow \mathrm{CrSO_4} + \mathrm{H_2O} \tag{4}$$

In other words, the properties of chromium (II) hydroxide are similar to the properties of the hydroxides of other common divalent metals.

However, in addition to a divalent state, other valence state are possible for chromium. The maximal valence of chromium is six, and the typical example of Cr (VI) compounds is chromium trioxide (CrO_3). This oxide reacts with water to produce a compounds with the formula H_2CrO_4.

$$\mathrm{CrO_3} + \mathrm{H_2O} \longrightarrow \mathrm{H_2CrO_4} \tag{5}$$

This equation resembles the reaction we studied during previous lessons, namely the reaction between sulfur trioxide and water:

$$\mathrm{SO_3} + \mathrm{H_2O} \longrightarrow \mathrm{H_2SO_4} \tag{6}$$

[1] Actually, a new style Periodic table, which was obtained by a rearrangement of the old style table, has more groups. However, to understand the Periodic law better, it would be useful to start with the old style Periodic table.

This similarity is not just a coincidence. The compound with formula H_2CrO_4 has strong acidic properties, and, accordingly, is called *chromic acid.* For example, it reacts with sodium hydroxide to form sodium chromate:

$$H_2CrO_4 + 2NaOH \longrightarrow Na_2CrO_4 + H_2O \tag{7}$$

(Compare the reaction 7 with the reaction between sulfuric acid and sodium hydroxide:)

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + H_2O \tag{8}$$

The similarity between these two acids, sulfuric and chromic, is even deeper. Not only the acid properties of these two acids are similar, but the properties of the salts they form are pretty close. For example, whereas both sodium sulfate and chromate are soluble in water, barium chromate is as insoluble as barium sulfate.

$$BaCl_2 + Na_2SO_4 \longrightarrow BaSO_{4\,(solid)} + 2NaCl \tag{9}$$

$$BaCl_2 + Na_2CrO_4 \longrightarrow BaCrO_{4\,(solid)} + 2NaCl \tag{10}$$

Due to its dual nature, a special subgroups where allocated for this type elements.

3 Other transition metals

Chromium is not the only metal whose high valence oxides show acidic behaviour. Two other metals, molybdenum (Mo) and tungsten (W), also form trioxides (MoO_3 and WO_3) that are acidic, like CrO_3 and SO_3. When these three metals are hexavalent, they resemble chalcogens (sulfur or selenium) so closely that Mendeleev combined them together in one group.

To discriminate the three transition metals, their symbols were moved to the right (the symbols of “true” chalcogens are shifted to the left). As a result, we got one large group that consists of two subgroups. The first subgroup contain “true” chalcogens (oxygen, sulfur, selenium, and tellurium). It is a *major* subgroup. The second group contains transition metals that behave as chalcogens when they are hexavalent (chromium, molybdenum, tungsten). It is a *minor group.* Since the chalcogen group is the sixth group, these two groups are called **VIa** and **VIb**, accordingly.

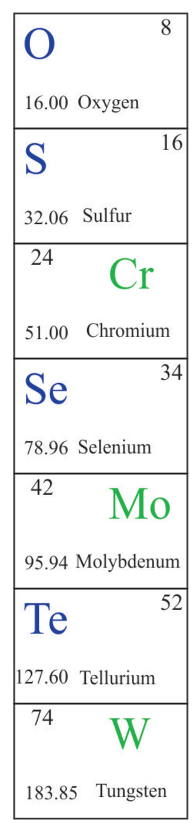

Figure 1

4 Combining everything together. Periodic table (short form)

Besides chromium, other transition metals also show similarity with the third period elements. Thus, scandium (Sc), which can be both di- and trivalent is an analog of aluminium (Al), titanium (Ti) is an analog of silicon (Si), vanadium (V) is an analog of phosphorus. Accordingly, by ordering these elements we get the following (2):

Li 3 6.94 Lithium	Be 4 9.01 Beryllium	B 5 10.81 Boron	C 6 12.01 Carbon	N 7 14.01 Nitrogen	O 8 16.00 Oxygen	F 9 19.00 Fluorine	Ne 10 20.18 Neon
Na 11 22.98 Sodium	Mg 12 24.31 Magnesium	Al 13 26.98 Aluminium	Si 14 28.09 Silicon	P 15 30.97 Phosphorus	S 16 32.06 Sulfur	Cl 17 35.45 Chlorine	Ar 18 39.95 Argon
K 19 39.10 Potassium	Ca 20 40.08 Calcium	21 Sc 44.96 Scandium	22 Ti 47.88 Titanium	23 V 50.94 Vanadium	24 Cr 51.00 Chromium	25 Mn 54.94 Manganese	26 Fe 55.85 Iron

Figure 2

If we continue to combine this puzzle, we eventually get the table you can see in the attachment. This table is the Periodic table in its original form (the one proposed by Mendeleev). It is called "a short form".

Homework

Read the CW materials.

1. Try to memorize first three periods of the Periodic table.[2]
2. Using scissors and glue, convert the attached Periodic table from the short form (classical) to the long (modern). Bring the long form you made to the school.
3. Using the short form Periodic table, try to predict the formulas of sodium titanate, potassium perbromate, lithium perrhenate.
4. Using the Periodic table, write formulas arsenic acid.
5. Can you write a formula of "strontic acid" (an acid formed by strontium (Sr))?

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[2]They contain most common elements we will be dealing with in future, so it would be useful to remember them.