Inorganic Chemistry

From the Periodic Law to the atomic structure.

February 24, 2018

1 Do atoms have an internal structure?

As we have seen from the Periodic table, properties of atoms of different type (elements) are very diverse, and there is some strict periodic interconnection between this diversity and the atomic mass. How can that be explained? Two different explanations are conceivable.

Firstly, one may argue the properties of different elements are different because their atoms have an intrinsically different nature. This concept, which is the original Democritus's concept, assumes atoms (we remember the word "atom" literally means "indivisible") are impossible to separate onto smaller parts, which means atoms have no internal structure. Therefore, atoms are intrinsically inconceivable, and nothing can be said about the reasons why the atoms of different elements have different properties. Obviously, such a concept would be hardly acceptable for modern scientists who believe there is no limits to knowledge. Interestingly, even John Dalton already anticipated the possibility that future generations of scientists would be capable of having a look inside atoms. Remember, when he wrote that atoms cannot be destroyed, he made an insightful reservation: cannot be destroyed ***by chemical means***. In other words, he admitted peoples would eventually be able to study atoms by some other, non-chemical means.

Accordingly, the second explanation of the difference in the atomic properties was that all atoms are composed of a limited set of some smaller particles, which are arranged differently in different atoms.

2 Discovery of atom's composition.

The composition of atoms was determined mostly in late XIX - early XX century by British and German physicists. This discoveriy became possible due to the progress in study of electric discharge in vacuum tubes (actually, the tubes filled with rarified gases, similar to modern luminiscent lamps) and the radioactivity phenomenon.

2.1 Discovery of electron.

Intense studies of an electric discharge in vacuum tubes (which would later lead to the discovery of X-rays by Rudolph Roentgen) revealed that such discharges generate so called *cathode rays*, which are a stream of some light negatively charged particles, *electrons*. In 1896, the British physicist J. J. Thomson, along with his colleagues John S. Townsend and H. A. Wilson, established that electrons that form cathode rays are the result of decomposition of the atoms of the gas which was present in their apparatus in trace amount. Thompson proposed that electrons, which are two thousand times lighter that the lightest atom, hydrogen, and which have smallest possible electric charge, are essential components of all atoms. Based on that assumption, he proposed the first model of atom, which we can call a "muffin model": according to him, an atom (which, as we know is electrically neutral) is a loose positively charged sphere, where small compact electrons are uniformly distributed like raisins in a muffin.

Figure 1: Sir Joseph John Thomson (1856-1940)
a discoverer of electron

The significance of this model was that it was the first rational model of atom. By no means that model could explain any chemical properties of the elements. However, it was a good starting point for further experiments, which were done by Thompson's student, Ernts Rutherford.

2.2 Rutherford's experiment.

By the moment Rutherford conceived his groundbreaking experiment, the *radioactivity* phenomenon had already been discovered. Scientist already knew that some radioactive materials irradiate some rays, which are composed of some very small particles with high energy. Rutherford's idea was to use those high energy particles (people called them "alpha"-particles, although they didn't know yet what they are) to probe the atomic structure. His rationale was as follows: "if atoms are loose spheres, an alpha particle will easy fly through atoms, and their trajectory will not change significantly. However, if an alpha-particle hits an electron, its trajectory will change more significantly. Therefore, by monitoring the average dispersion of an alpha particles passing through some material[1] it is possible to see how concretely the electrons are distributed within atoms."

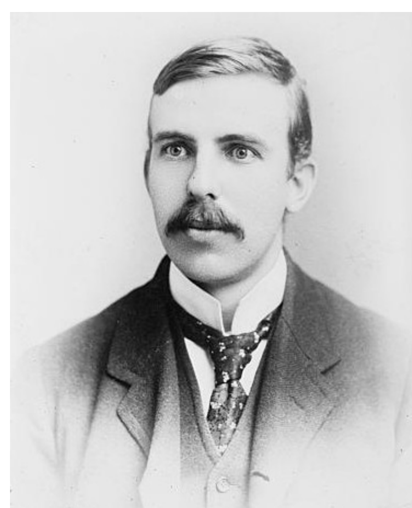

Figure 2: "We haven't money, so we've got to think"
Ernst Rutherford (1871-1937), a discoverer of atomic structure.

In other words, Rutherford expected that a narrow

[1]Rutherford used thin gold foil as a target.

alpha-particles beam passing through thin gold foil would undergo slight dispersion: according to Thomson's model, almost every alpha-particle would deviate slightly from its original trajectory, so instead of seeing a small bright spot in the screen Rutherford expected to see a larger and diffuse spot.

However, what he observed was totally unexpected. **During Rutherford's experiment, overwhelming majority of alpha-particles passed through the foil as if there was no foil at all. Only a tiny fraction of alpha-particles deviated from its original trajectory, however, this deviation was very significant: some of them even bounced back.** The only possible explanation for such observation was that Thompson's model is absolutely wrong. Rutherford concluded that some very compact object exists in atoms where virtually all atom's mass in concentrated. Based on the ratio between the number of alpha-particles that had not been deflected by the foil, and the number of particles that were strongly deflected, Rutherford was able to estimate the size of this small object (which he dubbed "a nucleus"). The size of a nucleus appeared to be astonishingly small: *atomic nucleus is one hundred thousand times smaller than the atom itself.*

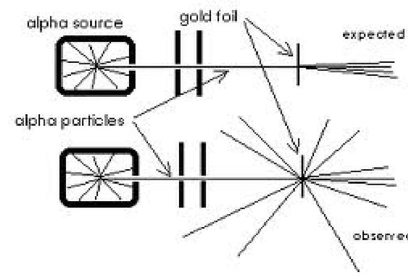

Figure 3: Rutherford's experiment

However, if all material atoms are composed of are concentrated in the tiny atom's nucleus, which force prevents electrons from falling on the nucleus? Rutherford proposed that force is a centrifugal force. According to him, atoms resemble our Sun system: light electrons, like planets, are rotating around a massive nucleus, which plays a role the Sun. Accordingly, this model was called a **planetary model of atom.**

3 Which material atomic nucleus is composed of?

Thomson's and Rutherford's studies allowed them to identify one type of particles (i.e. electrons) atoms are composed of, and to establish overall architecture of atoms. However, according to the planetary model, the lion's share of the material atoms are composed of was concentrated in the nucleus, a strange object situated in the center of each atom, whose size was unbelievably small (10^{-15} m, a hundred thousand times smaller than the size of the atom itself), and, accordingly, whose density was incredibly high. The first step to understanding of the composition of atomic nuclei was made by Rutherford in his experiments with *anode rays.*

3.1 Anode rays, and discovery of a proton.

During the previous class, we learned about cathode rays, i.e. accelerated electrons that form when the atoms of rarefied gas are being torn apart in a strong electric field. Obviously, when atoms break apart, their electrons fly from the cathode (which is negatively charged) towards the anode (which is charged positively), hence the name *cathode rays.* However, what happens to the nuclei of the atoms when the electrons fly away? Isn't it logical to suggest they will fly in the opposite direction, i.e. from the anode to the cathode? And if that is the case, is it possible to detect them?

Detection of nuclei (especially, the nuclei of the lightest element, hydrogen) was done in the apparatus named *anode tube*. This tube represents a modification of the cathode tube. The anode tube had a perforated anode, which made observation of positively charged particles possible. The holes in the anode allowed accelerated positive particles, which were falling onto the anode, to continue its flight further after they reached the anode. As a result, they were seen as a glowing beams behind the anode (Fig. 1, the right part of the tube.) Since they anode rays particles are charged, their were deflected in magnetic field. The deflection angle allowed Rutherford to calculate the mass of such particles.

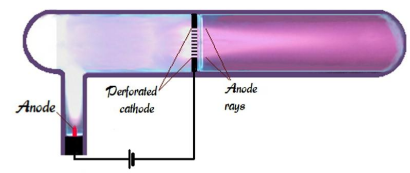

Figure 4: Anode tube. Anode rays are seen in the right part of the tube, behind the anode.

Rutherford found that, when the anode tube was filled with hydrogen, the mass of anode rays particles generated in such a tube was almost equal to the mass of a hydrogen atom. In a series of elegant experiments, Rutherford demonstrated this type particles are not possible to break apart further. He called this particle a **proton**, after the Greek word for "first", or "primary"[2]

3.2 Hydrogen atom

Based on his findings, Rutherford proposed the hydrogen atom is composed of two particles, a proton and an electron. A heavy proton, whose mass is almost exactly equal to 1 Da (the mass of the hydrogen atom) is situated in the center of the atom, whereas the electron is rotating around it in the same manner the Moon is rotating around our Earth. The p^+ and e^- are currently the standard symbols for protons and electrons, accordingly.

3.3 Other atoms. Moseley's law

Unfortunately, discovery of the proton did not fully clarified the composition of other atoms. Indeed, whereas the mass of hydrogen is 1 Da, the mass of the next element, helium, is 4 Da. Does it mean helium is composed of four protons and four electrons? If yes, why there are no elements between hydrogen and helium? To answer this question, it was absolutely necessary to measure the charge of nuclei of various elements. This had been done in early XX century by Henry Moseley, a brilliant British physicist. In a series of X-ray spectroscopy experiments

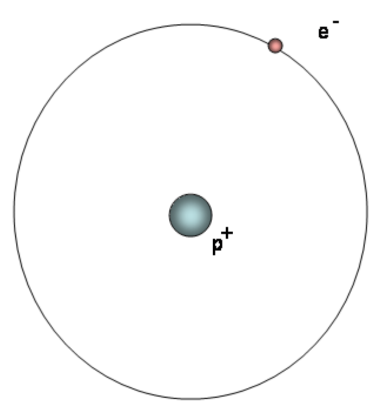

Figure 5: Rutherford's model of a hydrogen atom.

[2]Compare with "proteins" (a "first" or "primary" biological molecule), "prototype" (or a first representative of some class), etc.

(we cannot go into the details of those experiments yet)
Moseley demonstrated the profound linkage between the element's position number in the Periodic table and the charge of its nucleus. Concretely,

> **Moseley's law says: "The charge of the element's nucleus is equal to the proton charge times the element's number in the Periodic table."**

A discovery of this law by Moseley was a major breakthrough towards understanding of the structure of atoms bigger than a hydrogen atom. Interestingly, Moseley made this groundbreaking discovery on the eve of his scientific career. He could have become one of the greatest XX century physicists, however, outbreak of the First World War changed everything.

Figure 6: Henry Moseley (1887-1915), a British physicist who measured the charge of atomic nuclei.

> *When the World War I broke out in August 1914, Moseley enlisted in the Royal Engineers of the British Army and was killed in action 10 August 1915 during the Battle of Gallipoli in Turkey. Isaac Asimov once wrote, "In view of what he [Moseley] might still have accomplished ... his death might well have been the most costly single death of the War to mankind generally."*

Since the atomic number is equal to the charge of the nucleus, it is also equal to the number of electrons in each element (this is so because atoms are electrically neutral, so the positive charge of the nucleus must be fully compensated by electrons around it). In other words, there is one electron in a hydrogen atom, two electrons in a helium atom, three electron in a lithium atom, and so on.

However, the next conclusion one has to draw from the Moseley's law is the following: the nuclei of elements other than hydrogen are composed of protons and some other heavy and electrically neutral particles. Indeed, the electric charge of the nucleus of helium is 2 (two times bigger than the charge of hydrogen's nucleus) , but its mass is 4 (four times heavier than hydrogen's nucleus). What material is responsible for that mass difference?

3.4 "Beryllium rays" and discovery of a neutron.

This missing particle was discovered only in 1932 by James Chadwick, who studied so called "beryllium rays", strange rays that were observed earlier by German physicists Bothe and Becker during the bombardment of beryllium targets by alpha-particles (particles similar to those used by Rutherford). Chadwick demonstrated those "rays" consisted of uncharged particles of the mass roughly equal to the mass of proton. These particles were called neutrons, from the Latin root for "neutral" and the Greek ending -on (to preserve the same naming style as for electron and proton). Soon after that, it was demonstrated neutrons, along with protons are the only components of atomic nuclei. Based on this, the proton-neutron model of atomic nucleus had been proposed by Chadwick. The combined electron-proton-neutron concept of atom says:

Atoms are composed of a nucleus and electrons orbiting around it (see Fig. 5). A nucleus is composed of protons and neutrons. The number of protons is equal to the nucleic charge (i.e. the atomic number). The number of neutrons and protons is roughly equal to the atom's mass (in Daltons).

4 Atomic number and atomic mass. Isotopes.

Although the electron-proton-neutron model of atom is elegant and beautiful, there is something that it seems to fail to explain. Indeed, when you look at the Periodic table, you can see the masses of most elements are not multiple of the mass hydrogen. For example, mass of chlorine is 35.45, mass of magnesium is 24.31. How can that be possible if every atom is composed of the integer number of **nucleons** (i.e. protons and neutrons) and electrons? To explain that, scientists proposed the hypothesis that for each element, different types of atoms are possible. These atoms have the same number of protons and electrons, but the amount of neutrons can be different. For example, three different variants of hydrogen atom exist in nature. The most abundant type of hydrogen atom whose nucleus is composed of just one proton. Its atomic weight is almost equal to 1 Da. The second atom variant contains one proton and one neutron in its nucleus. Its weight is ca 2 Da. The third variant has two neutrons and one proton. Its mass is 3 Da. Since all of them have identical chemical properties and identical atomic charge, all of them occupy the same cell in the Periodic table. Accordingly, such variants of the same elements are called **"isotopes"**.

"Isotopes" (from Greek words "isos" (equal) and "topos" (place, position)) are the different variants of the certain element. Different isotopes of some elements have the same amount of protons and electrons, but different amount of neutrons (hence the difference in their masses).
Isotopes of the same elements are denoted by the same symbol. To discriminate between different isotopes, their mass is added left to the element symbol as a superscript number, e.g. ^{16}O, ^{23}Na, ^{2}H.

Different isotopes of the same element have identical (or almost identical) chemical properties, but their physical properties (boiling point, density, etc) may be slightly different. Due to the difference in physical properties, they can be separated from each other (although it is a very laborious process).

The existence of isotopes explains the non-integer masses of some elements. Thus, the observed mass of chlorine (35.45 Da) is due to the fact that natural chlorine exists in a form of two isotopes, ^{35}Cl (76%) and ^{37}Cl (24%).

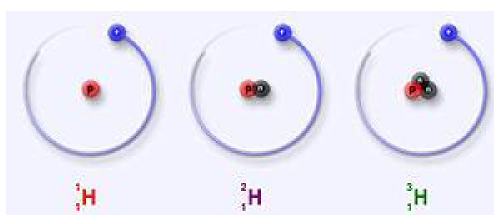

Figure 7: Three different isotopes of hydrogen. Protons are depicted as red balls, neutrons as blue balls.

In contrast, some elements, such as oxygen or carbon, exist in nature mostly in a form of one isotope (^{12}C and ^{16}O, accordingly.) Such elements are called **monoisotopic**.

Homework

Read the CW materials and answer the following question. Imagine Rutherford, during his experiment, observed that alpha-particles passed through the foil were distributed as follows: 95% of all particles were not deflected at all, and 5% of particles were deflected very strongly. The density of gold is 19.30 g /cm^3, foil thickness is 100 nm[3], the atomic weight of gold is 197, which means 197 grams of gold contain 6×10^{23} gold atoms. What can you say about the structure of the atoms that foil was composed of? Concretely, what is the ratio between the atom's size and the nucleus's size, according to those data?

As far as I know, most of you attend Physics in SchoolNova. During our next classes we will need to use physics for understanding atomic structure and the nature of chemical bond. Therefore, I would like you to refresh your physics knowledge, and to pay special attention to such concepts as Coulomb law, magnetism, energy, force. During the next class we will probably have a short quiz where I'll ask you some physics related questions. I need to know the state of your physics knowledge to decide how fast can we move further during this spring. Please, answer the following questions.

1. What does Coulomb law says?
2. How many fundamental forces (besides the electrostatic force) do you know?
3. How do you understand the term "energy"?
4. What is light?
5. Look at the Periodic table and name 20 elements that are essentially monoisotopic.
6. Find five elements that exist in nature as a mixture of roughly comparably abundant isotopes (in the same manner as chlorine). On the internet, find which isotopes they are.
7. As you know, the elements in the Periodic table are arranged lightest to heaviest. However, this order is broken for tellurium and iodine. Why did Mendeleev decide to swap tellurium and iodine? How can that be explained based on the electron-proton-neutron theory?

My e-mail is mark.lukin@gmail.com

[3] 1 nm = 10^{-9} m.