

**WOJCIECH  
SMUŁEK**

**Potential  
of  
electrochemistry**



**CHEMIA**  
W OŁÓWKU ....

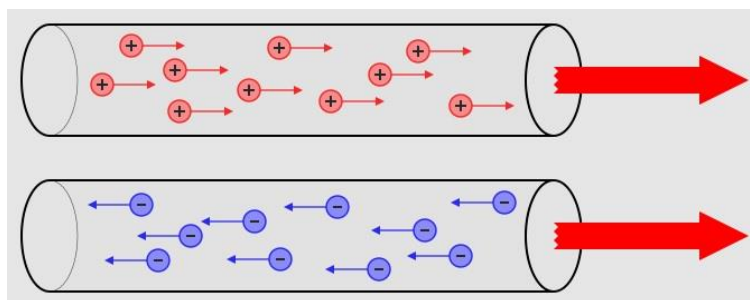
*I would like to thank my friends  
**Bartosz Gurzęda** and **Mariusz Rzeszotek**  
for their help and valuable comments  
during writing this book.*

## Potential of electrochemistry

Let's start with a little review of the concepts of electricity. First of all, let us answer the question: what is electric current? In simple terms, it is the orderly movement of charged particles, i.e. electrons in solids and usually ions in liquids and gases. We can call them “charge carriers”, as well. Electric current is characterized by its intensity and electrical voltage. The intensity (measured in amperes) seems fairly clear to understand - the more charge carriers moving per unit time the greater the intensity.

And what about electrical voltage? Here let us use the often quoted analogy between electric current and water flow. Assuming the same flow rate, which stream of water will have more energy - one flowing from a height of 3 metres or 3 centimetres? The answer is obvious, but let's translate it into questions of electricity. Voltage is a potential difference, something like the difference in water levels. The greater the difference, the greater the energy that can POTENTIALLY be given off by the charge carriers, i.e. electrons or ions.

Now for the final question. How do we compare which water/electricity stream has a higher useful power? You have to consider both amperage and voltage (potential difference). So power (of electric current) is the product of voltage and amperage (i.e. power in watts is obtained by multiplying voltage in volts and current intensity in amperes).



*An electric current exists when there is a regular movement of charge carriers (the red arrow shows the conventional direction of the current, which is in the direction of positive charge and the opposite direction of negative charge. [Source: User: ARTE, via Wikimedia Commons]*

From this brief excursion into the regions of physics, we are returning to electrochemistry. To understand it, the concept of the electrical potential of different materials is crucial. First of all, let us consider metals here. Well, each of them contains electrons, which are charge carriers, and also each metal atom can become an ion when it loses/gives up one or more electrons. And ions are already, as I wrote, a charge carrier in liquids, so in solutions as well.

It has also been observed that atoms of different elements<sup>1</sup> have different potential, that is, different "tendency" to give up electrons and become ions. It is like with people - one just sees an ice cream stall and, without looking at the price, buys five scoops at once, while another will hoard money and buy an ice cream scoop only when it is extremely cheap. In addition, the potential depends on the temperature and here our analogy with buying ice cream also becomes useful. Because we'd be more likely to buy ice cream in forty-degree heat than in frosty weather, wouldn't we?

Interestingly, the electric potential of atoms of a given element is not simply related to its mass, the size of its atomic nucleus, or other physical properties. It is a complex resultant of these properties and cannot be easily predicted or deduced. Therefore, one simply has to learn by heart what potential a given atom has. The so-called galvanic series (or electropotential series), i.e. a list of metals in order of their electric potential, helps in this task.

Electrode	$E^0$ [V]
Li/Li <sup>+</sup>	-3.04
K/K <sup>+</sup>	-2.93
Ca/Ca <sup>2+</sup>	-2.87
Na/Na <sup>+</sup>	-2.71
Mg/Mg <sup>2+</sup>	-2.37
Mn/Mn <sup>2+</sup>	-1.19
Cr/Cr <sup>2+</sup>	-0.91
Zn/Zn <sup>2+</sup>	-0.76
Cr/Cr <sup>3+</sup>	-0.74
Fe/Fe <sup>2+</sup>	-0.45
Ni/Ni <sup>2+</sup>	-0.26
Sn/Sn <sup>2+</sup>	-0.14
Pb/Pb <sup>2+</sup>	-0.13
H <sub>2</sub> /2H <sup>+</sup>	0
Cu/Cu <sup>2+</sup>	0.34
Ag/Ag <sup>+</sup>	0.8
Hg/Hg <sup>2+</sup>	0.85
Au/Au <sup>3+</sup>	1.5
Au/Au <sup>+</sup>	1.7

40

*The galvanic series (or electropotential series) of metals, is, in fact, a table of the standard potential of their electrodes.*

---

<sup>1</sup> element - a simple substance that cannot be reduced to smaller chemical parts, e.g. iron, hydrogen, mercury.

45 It is also important that the chemical electric potential of a given element is not an absolute value, i.e. it is determined in comparison with a certain standard, or reference point. After long battles, it was accepted many years ago that hydrogen and its tendency to donate electrons would be such a standard. It has been assumed that it has a potential of 0.0 V, but this does not mean that it does not donate electrons at all. On the contrary, it does so quite readily.

50 A voltage series is a powerful tool in the hands of the electrochemist, but how it can be used I will tell you in the next chapter.

### **Potential of electrochemistry - Questions**

1. What can carry an electric charge?
2. What describes the electrochemical potential?
3. What is a galvanic series?

## *A series of conclusions*

We ended the last chapter with a brief look at the galvanic series of metals. Now let's look at the conclusions and practical benefits that can be taken from it.

As I mentioned previously, the electrochemical potential is (in some simplified terms) a measure of the extent to which an element tends to donate/accept electrons and become an ion. If we immerse<sup>2</sup> a piece of metal in water then on its surface a dramatic fight for electrons starts (here I give a small remark, in chemistry if you don't know what the point is it is usually about electrons and energy). This process involves not only the atoms of the metal (forming a solid) but also the elements present in the water solution as ions.

Even in pure water (that is, which is only 100% water, i.e. chemically pure H<sub>2</sub>O), some of the water molecules are broken down into ions. Here we should discuss the whole issue of the pH of solutions, but for now let us stick to the fact that in a solution of perfectly pure water there are also ions, including hydrogen ions.



*Noble and semi-noble metals, i.e. those with a potential higher than hydrogen [Tomihahndorf, via Wikimedia Commons].*

As you will recall, hydrogen, although not a metal, has its place in the voltage series of metals, as a standard for which a potential of 0.0 V has been assumed. Returning to the battle for electrons, the question will probably arise as to who will win this competition. The hydrogen ions or the metal atoms? Well, the principle is simple. Whoever has a higher potential pulls

<sup>2</sup> to immerse - to put something or someone completely under the surface of a liquid

them more strongly to his side (if he has no electrons and is a cation) or holds them more strongly to himself (if he is an atom with a set of electrons).

This leads to a simple conclusion that metals with a negative potential will give up their electrons in water, which will result in the formation of molecular hydrogen and metal ions, which will no longer "stick" to the crystal structure of metals but will go into solution and happily float among water molecules.

How fast this process happens depends on several factors. Firstly, on the potential difference between the hydrogen and the metal (naturally, the greater the difference, the faster the process). Secondly, on the concentration of hydrogen ions (this is why, in acid solutions with a high concentration of hydrogen ions, the formation of hydrogen is so fast that we can see with the naked eye how its bubbles form on the metal surface).

But what if there is a metal with a potential higher than hydrogen in the water. Basically... nothing. It's just that its atoms hold their electrons so strongly that hydrogen ions can't take them away from them. So these metals don't react with water, and that's why long, long ago, when the causes were still unknown, they were called "noble" because they refused to react with common and ordinary water.

The situation becomes more complicated when there are other ions in the aqueous<sup>3</sup> solution, such as ions of another metal. However, the complication is only apparent since the rule remains the same. The one with the higher potential takes the electrons, and once the one with the highest potential has "satisfied" its needs, it can take electrons from the next metal in line. We are dealing with a peculiar chemical hierarchy and no revolution can overturn it. The laws of nature are inexorable<sup>4</sup>.

What does it look like in practice? Let us assume that we have a solution of iron ions into which we put a silver plate. What happens? Nothing happens. Silver has a higher potential than both iron and hydrogen ions (which are present in every aqueous solution all the time - let's not forget that). What if we put a lead plate in the solution? Let's look at the voltage series. Lead has a potential between hydrogen and iron, so iron "drops out" and there is a competition between lead and hydrogen ions. The hydrogen ions gradually win, forming molecular hydrogen, and lead ions appear in the solution.

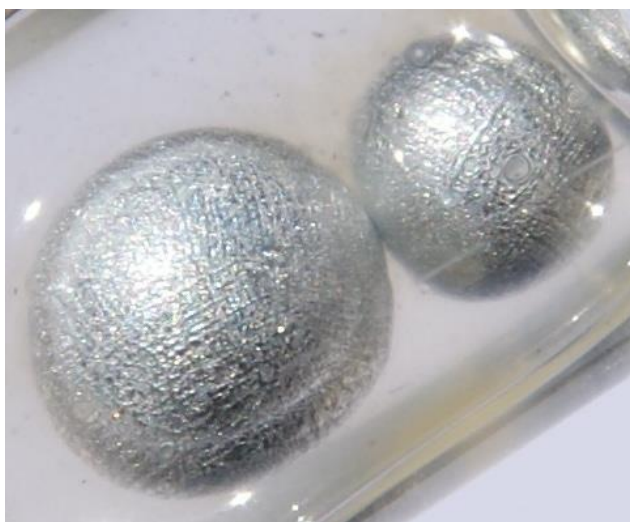
---

<sup>3</sup> aqueous – made with or containing water

<sup>4</sup> inexorable – continuing without any possibility of being stopped



50           The third option is when we put a magnesium plate into our solution. Here magnesium is on the losing end in comparison with both iron ions and hydrogen ions. As a consequence, hydrogen is produced, but what is more important for us is that the shiny magnesium plate is covered with a grey tarnish. This is a sign that iron atoms, which have stripped magnesium of their electrons, are deposited on its surface. Magnesium, unwillingly, has to give them back (ah,  
55 those inexorable laws of nature) and, as an ion, it goes into solution.



*Particles of potassium, one of the metals with the lowest electrochemical potential. Potassium displaces hydrogen from water, including steam, which is why it is stored in paraffin [via Wikimedia Commons].*

60           It is probably already dawning on some people that if we had ions of precious metal, such as silver, in solution, then if we put a less noble iron plate into the solution, a shiny layer of silver would form on its surface. This is true and any non-noble metal can be silver-plated or gilded<sup>5</sup> in this way and this method has been used for centuries.

65           However, we must remember that the layer created in this way is very thin. The process of its creation practically ends when the whole surface of the less noble metal is already covered with the nobler one. The ions remaining in the solution have no reason (because where would they get electrons from) to deposit on the surface formed by the same metal as they do. They would have to be motivated to do so somehow.

          However, to know how to do it, we have to enter the mysterious arcana of science area called “galvanotechnics”. But about this already in the next chapter.

---

<sup>5</sup> to gild - to cover a surface with a thin layer of gold or a substance that looks like gold

**A series of conclusions – Questions**

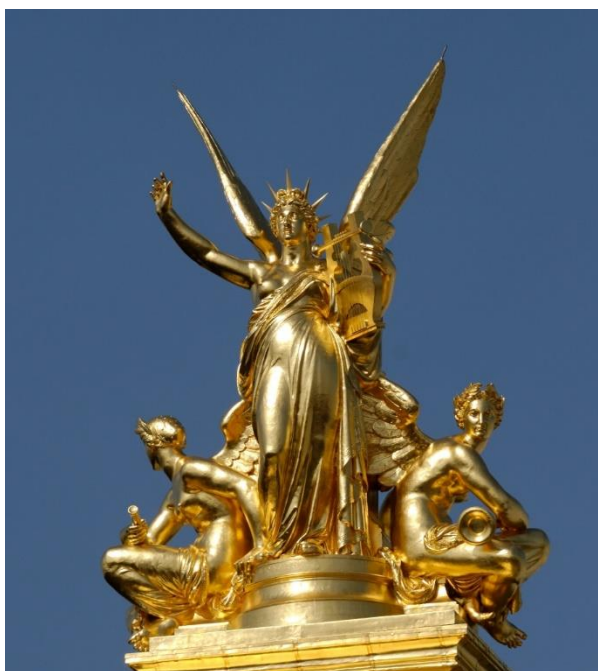
1. What is the electrochemical potential of hydrogen?
2. What determines the rate of formation of hydrogen gas, in a solution into which we introduce a metal?
3. What does the term "noble metals" mean?
4. What happens when an iron plate is immersed in a solution containing silver ions?

## *Serve and protect*

Regular visitors to the United States and viewers of Hollywood movies (of which the author is one) may have seen on the police cars there this motto. We are not, of course, going to write about the police now, but somehow this motto came to mind when I set about writing about protective coatings<sup>6</sup> for metals.

We already know from the last text that due to a potential difference (resulting from the differential strength with which metal atoms hold their electrons), a layer of more noble metal can be deposited on the surface of the less noble metal (with a lower potential). This process is driven as long as the less noble metal gives up its electrons to the other. But once the nobler metal is completely cut off from the solution (and a thin but tight layer of it is enough) the fun is over. Although not completely.

Let us think for a moment. The fuel of the process in our case is electrons. They are needed to make inert atoms from the ions of the noble metal. Then, the atoms can settle on the less noble metal surface. So where do we get the extra electrons from? Well, they are delivered by...electric current. Bingo! So, let's connect the wires and get to work.



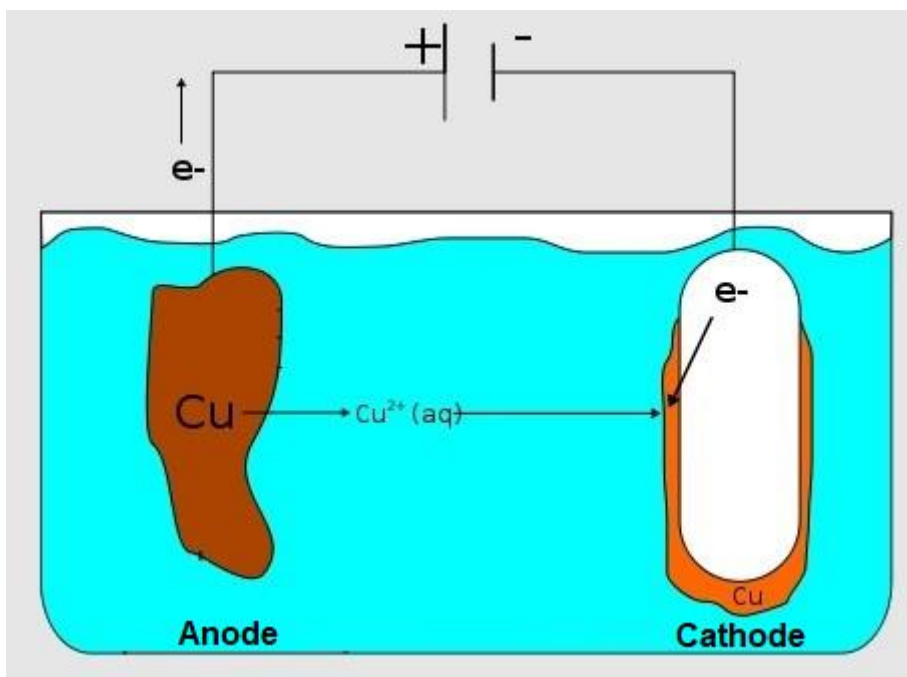
*The electrochemically gold-plated statue atop the Paris Opera building [Marie-Lan Nguyen, Public domain, via Wikimedia Commons].*

---

<sup>6</sup> coating - a layer of a particular substance that covers a surface

When we connect the metal plate with electricity we supply electrons to the system.  
 20 Let's not go into for a moment whether this current (that is, as you remember, a stream of electrons) is provided by a battery (chemical cell) or an electric generator<sup>7</sup>. But remember, the laws of nature are inexorable, and in the end, we have to get those electrons from somewhere. Whether a battery or an alternator does not actually “create” electrons in an electric circuit<sup>8</sup>, but directs their movement and gives them energy (creates a voltage in a sense). And how many  
 25 electrons a given current source can direct tells us what current that source can generate.

As I wrote, the transformation of ions into neutral atoms is no longer dependent in our system on the electrons donated by the less noble metal. However, if the transformation of positive ions (cations) into neutral atoms occurs in one place in an electrical circuit, then somewhere else must be the place where the neutral atoms give up electrons to become cations.  
 30 Chemists say that in the first case reduction occurs, and in the second oxidation (which is a term that generally has little to do with oxygen, but has historically remained so). The first occurs at a point in the circuit called the cathode, and the second process occurs at the so-called anode. The figure below will certainly explain a lot to you.



35 *The process of creating a copper coating [Based on Maxiantor, via Wikimedia Commons].*

<sup>7</sup> An electric generator is a device that converts motive power (mechanical energy) into electric power for use in an external circuit.

<sup>8</sup> An electrical circuit is an electrical network consisting of a closed loop, giving a return path for the current. An electrical network is an interconnection of electrical components (e.g., batteries, resistors, inductors, capacitors, switches, transistors) or a model of such an interconnection, consisting of electrical elements (e.g., voltage sources, current sources, resistances, inductances, capacitances).

In any case, the generation of the coating comes at the expense of the metal forming the anode, as its atoms become cations and move into solution. We can see the consequences of this because the anode literally "disappears" during this process.

40 Since the ions of the metal (of which we create the coatings) disappear from the solution (because they become atoms forming this solid layer), it is good for the anode to be made of the metal we are depositing. Then the ion balance is right, each deposited metal ion is replaced by the one formed on the anode. Hence, we don't have to worry about its electrochemical potential. The process will continue as long as we supply an electric current. During the process, we can also regulate the thickness of the layer that is deposited on the cathode. So we can  
45 control the whole process quite easily.

Let us focus for a moment on our coatings. So far we have considered the deposition of a more noble metal on a less noble one. This allows us, for example, to silver or gold plating objects made of iron or another metal with a lower potential. The advantages of such a process are quite obvious. First of all, there is the aesthetic aspect (nice shiny stainless coating) and the  
50 protective function (the noble metal does not allow the metal it covers to oxidise).

Unfortunately, this second function only makes sense when the coating is absolutely tight. A small crack is enough to start a dramatic process in which the less noble metal oxidises many times faster than it would without contact with the more noble metal. In the place of the scratch, an electrochemical micro-cell is formed.

55 I am not going to describe it now, as this requires a separate entry (it is the case that "the further you go into the forest the more trees you see"). In the meantime, I would like to ask you to accept that this is just the way it is. Those of you who have already learnt about it in the past, please try to refresh your knowledge of chemical cells in your free time.

Now I would like to tell you about one more consequence of this. Well, to avoid such a  
60 process, coatings made of less noble metals can be used, e.g. zinc on iron (e.g. steel). As the process is not spontaneous, it only takes place when an electric current is applied. The result is a coating, and if it is damaged (e.g. scratched), will oxidise (decompose) instead of the metal below the coating.



65 *Chrome-plated motorbike engine parts using electroplating [Atoma, CC BY 2.5 via Wikimedia Commons].*

Moreover, some less noble coatings are paradoxically more durable on their own than layers of more noble metals. This is because they can undergo the so-called passivation, i.e. they cover themselves in the air with an oxide layer, which is so tight that it does not allow  
70 further oxidation of the coating metal and the metal covered with it. But why this process occurs let me tell you another time.

### **Serve and protect - Questions**

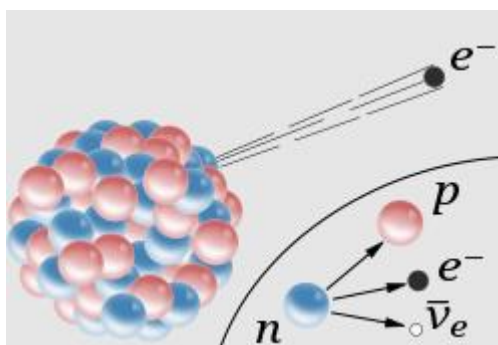
1. What is a 'protective coating'?
2. How to produce a noble metal layer on a metal surface with a lower electrochemical potential?
3. What is a cathode?
4. What is the most important disadvantage of coatings made of noble metals?

## *Nuclear families*

In various chemistry stories, the term "isotopes" often comes up. Although the subject is probably not entirely unfamiliar to most of you, let me devote a few sentences to it.

5 An atom of any element consists of an atomic nucleus and electrons which revolve around it. The atomic nucleus<sup>9</sup>, in turn, is made up of protons and neutrons. The chemical properties of an element, i.e. its reactivity, ability to form crystalline structures, etc., depend primarily on the number of protons and thus electrons since it is these that form chemical bonds<sup>10</sup>. Therefore, the atomic number, i.e. the number of protons in the nucleus, distinguishes a given element and allows to assign it a proper "place" in the periodic table.

10 Let us also add that if as a result of some physical processes the number of protons changes, e.g. one of them is "knocked out" or "attached" to the nucleus, then a transformation of one element into another takes place, e.g. of lithium into helium or of nitrogen into oxygen.



15 *A neutron (blue) can under certain conditions transform into a proton (red) electron and neutrino; this is called "beta" decay [Inductiveload, via Wikimedia Commons].*

20 And what about neutrons? They, in turn, are crucial to the stability of the atomic nucleus. Think about it, since protons have a positive electric charge and repulsive forces are acting on them then something must be holding them together in that nucleus. That something is atomic forces, resulting from all sorts of interactions between elementary particles, quarks, gluons, etc. Forgive me, but I will not go into this area. You understand, that it is an unwritten agreement between physicists and chemists. We do not enter the atoms, but they allow us to play with them and put them together into different molecules ;)

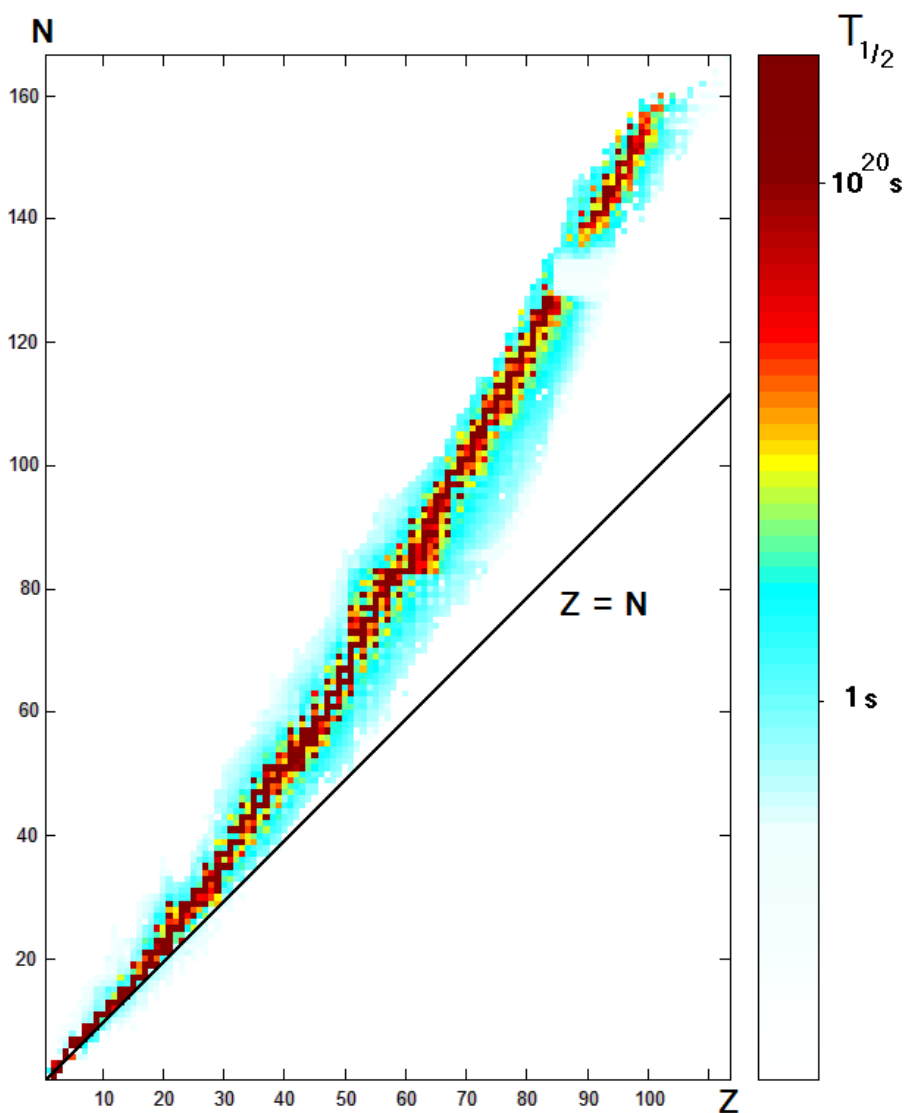
<sup>9</sup> nucleus - the central part of an atom, usually made up of protons and neutrons

<sup>10</sup> chemical bond - an electrical force that holds atoms together to form a molecule



25 More seriously, this would require a longer story. Now, the key point for us is that neutrons stabilise the atomic nucleus, but they practically do not change the chemical properties of the element.

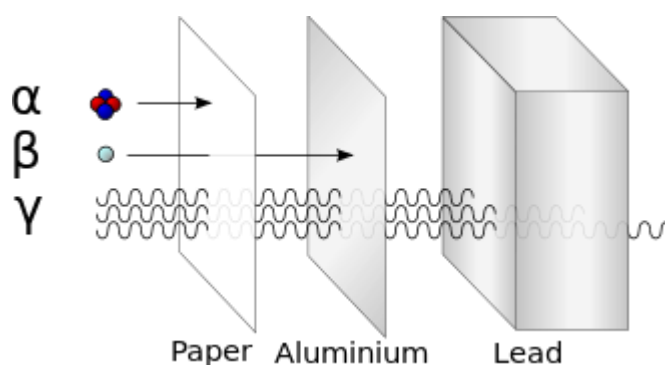
30 A consequence of this is that in the nucleus of a given element the number of neutrons is not strictly determined. To keep the nucleus together, there must be more or fewer neutrons than protons. This "more or less" is key here. There is a certain optimum number of neutrons to unite the nucleus, but with a slightly higher or lower number of neutrons, the atom will also survive, although the time of its existence will be limited.



35 *Diagram showing all existing isotopes (the colour indicates their half-life), the horizontal axis is the number of protons (Z) and the vertical one the number of neutrons (N); as you can see, the heavier the nucleus, the greater the excess of neutrons to form a stable nucleus [https://upload.wikimedia.org/wikipedia/commons/8/80/Isotopes\_and\_half-life.svg].*

And this is where the concept of an "isotope" comes in handy, i.e. an atom with a specific number of protons and neutrons. The first number is closely related to the name of the element, so we speak of isotopes of carbon, isotopes of uranium, etc. For precision, an additional number is given to indicate the total number of protons and neutrons in the nucleus of a given element,  
40 so we have, for example, phosphorus-19 or barium-138.

I mentioned a moment ago that some nuclei are stable, while others have a definite time of existence (sometimes they are called "lifetime"). The former are called stable (permanent) isotopes, the latter unstable (non-permanent) or radioactive or radioisotopes, because their decay is associated with the emission of ionising radiation, alpha, beta, or gamma.

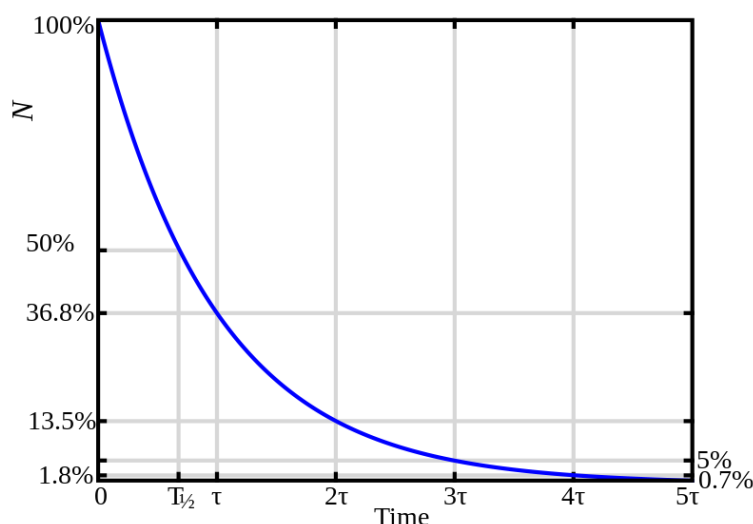


45 *The decay of unstable isotopes is accompanied by the emission of ionizing radiation; depending on the emitted particle we deal with "alpha" radiation (these are nuclei of helium-4 atoms), beta (electrons), gamma (high-energy electromagnetic wave); by the way, the figure illustrates the penetrability of these types of radiation [Alpha\_beta\_gamma\_radiation.svg: User:Stanneredderivative work: Ehamberg, via Wikimedia Commons]*

50 Isotopes are also divided into natural and artificial, i.e. obtained only under laboratory conditions. Although the former group includes both stable and unstable isotopes, artificial isotopes are exclusively radioactive isotopes.

55 Since we hear about isotopes mainly in the context of radioactive isotopes, it is necessary to say a little more about one of the most important parameters describing them, namely their duration. It is, as I mentioned, limited and, contrary to appearances, difficult to define unambiguously. However, if we approach the matter statistically, we can determine when on average half of the atoms present in a given sample will disintegrate. We are talking here about the so-called half-life. It does not mean, as students sometimes write, that the atoms  
60 will decay into halves, but that half of the atoms in a given group will decay. This time varies widely, from billions of years (e.g. uranium-238) to milliseconds (e.g. polonium-214).

About the half-life, we should add that if the decay time is, for example, 3 years, then after these three years half of the atoms will have decayed, and after another three years the other half and that's it. No, no, Dear Readers, the matter is somewhat more complex. After another three years, half of the remaining half, that is one quarter, will have disintegrated. After another three years, half of the remaining quarter will have collapsed, i.e. one-eighth, and so on.



Radioactive decay as a function of time. The vertical axis shows the number of particles (or the activity) as a percentage of the initial value; the half-life  $T_{1/2} = \ln(2) * \tau$ , where  $\tau$  is the average life time [Series\_RC\_resistor\_voltage.svg: User:Ktimsderivative work: Pieter Kuiper, Public domain, via Wikimedia Commons].

It is a bit like the size of the "front group" in long-distance running: just after the start almost everyone is running at the front, then in the first kilometres most of the competitors fall off, and then the rate of "falling off" decreases and the composition of the "front group" remains practically unchanged. The properties of isotopes are primarily of interest to physicists. For the chemist, they are generally irrelevant, although I will give two cases.

The first is the question of the atomic mass of an element. If each element had only one stable isotope then there would be no problem, but what about the case where, for example, chlorine, there is in nature 75% of the isotope with a mass of 35, and the remaining 25% is the isotope 37? Even if we operate on milligrams of a given substance, this still means that we are working with billions of billions of atoms. Hence, we have to resort to statistics and assume that in our sample the proportions between the isotopes are the same as in nature as a whole and for chemical calculations, we take the average mass (but taking into account the number of individual isotopes). For chlorine, this would be 35.5.

The second issue, although more subtle, is that heavier isotopes are slightly slower to enter into chemical reactions than their lighter cousins from the atomic isotope family. This is due to their greater mass because heavier atoms move slower (if they have the same energy as the lighter ones). This makes it take them longer, for example, to meet another element with which they can react.

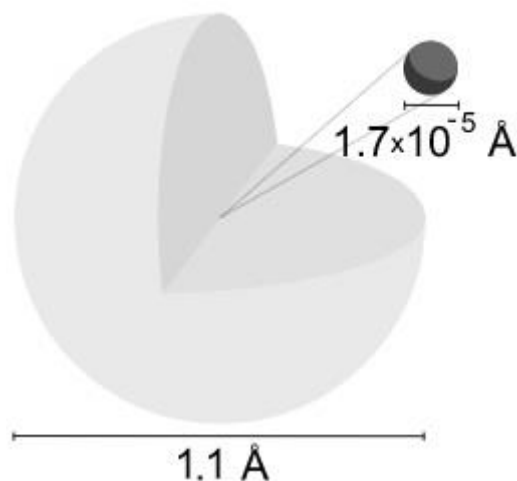
In practice, this does not matter so much. And so all the parameters of chemical reactions are usually determined experimentally, and so are themselves averages, like the atomic mass described above. Nevertheless, in the case of slow reactions and relatively large differences in masses between isotopes, differences in reaction rates may already be noticeable. This makes it possible to separate heavier isotopes from lighter ones. In this way, hydrogen-1 is quite often separated from hydrogen-2 (i.e. deuterium). But about the atomic family of isotopes of this lightest element I will tell you in the next chapter, and in the meantime thank you for your attention;)

### **Nuclear families - Questions**

1. What particles are in the atomic nucleus?
2. How do isotopes of the same element differ from each other?
3. What is the role of neutrons?
4. What is the half-life of an isotope?
5. Do different isotopes of the same element have the same chemical properties?

## Hydrogen triplets

Hydrogen is one of the most recognisable elements. I mean, that the statistical inhabitant of planet Earth, when asked to name several elements, is bound to name hydrogen among them (by the way, I wonder if there has ever been such a question on a quiz show).



5

*Comparison of the size of a proton (hydrogen nucleus) to the size of the whole atom (i.e. the region in which the electron circulates) [[https://upload.wikimedia.org/wikipedia/commons/4/4d/Hydrogen\\_atom.svg](https://upload.wikimedia.org/wikipedia/commons/4/4d/Hydrogen_atom.svg)].*

Hydrogen is indeed worth remembering because there are quite a few categories in which it is the "most": it is the most common element in the Universe, the one with the lowest density, the one with the lowest atomic mass, etc. Hydrogen is also known for being odourless, tasteless and colourless, but surely most of us associate it with being easily flammable.

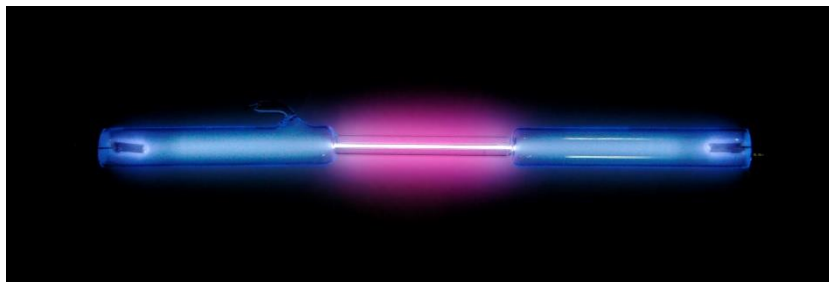
10

At this point, an anecdote comes to my mind about John Cavendish, the 18th-century discoverer of hydrogen, who wanted to see if it was assimilated by the human body. As you can guess, in his time, the methods for identifying hydrogen were quite primitive.... maybe I should say imperfect. So, to confirm that there was hydrogen in the exhaled air, the chemist simply blew on the flame of a candle after inhaling the gas into his lungs<sup>11</sup> (he knew that hydrogen was flammable, so he assumed that the rise of the flame would confirm its presence). Hmmm, you can probably guess what that ended up as: a small but spectacular explosion. However, Cavendish survived. As he recalled, "I thought all my teeth were going to fly out".

15

---

<sup>11</sup> a lung - either of the two organs in the chest with which people and some animals breathe.



20

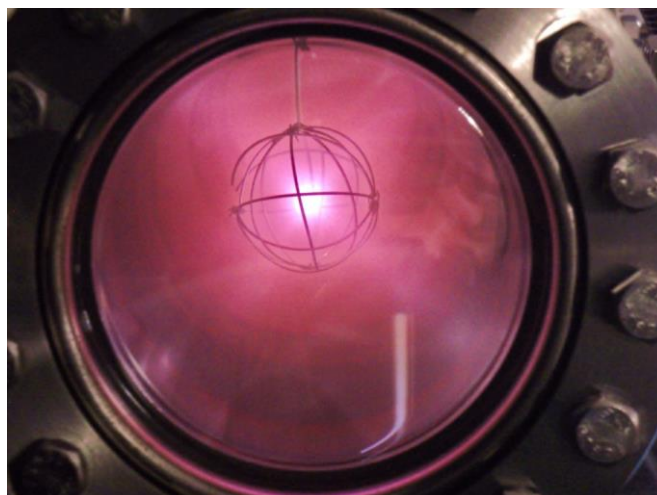
*Glass tube with purple glowing hydrogen excited by an electrical discharge [Alchemist-hp (talk) (www.pse-mendelejew.de), FAL, via Wikimedia Commons].*

One can write and write about hydrogen compounds. Practically with every other element, it can form a separate and permanent (more or less) compound. With metals, it forms hydrides, and with non-metals... well, there is no name for this group of compounds, but they include, for example, ammonia, methane, hydrogen chloride, hydrogen sulphide and, of course, water (called "hydrogen oxide" by some fanatics of chemical nomenclature). And the more complex compounds? Oh, that's a very broad topic and we will leave it for now.

But let us return to the previous chapter. We already know that in an atomic nucleus there are protons, which give it its charge (and thus "hold" electrons in orbits around it), and neutrons, which stabilise the nucleus. Hydrogen, however, has only one proton. So does it need neutrons to stabilise the nucleus? In principle, no. In fact, it does without them perfectly well, but if a neutron sticks around, then... it can stay. And then we are dealing with the second isotope of hydrogen, namely deuterium.

Deuterium is sometimes denoted by the letter "D", but this is only a common designation, not a chemical symbol, because such a symbol is given only to elements, and ordinary hydrogen (without a neutron in the nucleus) and deuterium are the same element. Deuterium is a stable isotope and its content in nature is about 0.015% of total hydrogen.

Due to their small diameter and low mass, deuterium atoms are excellent at slowing down free neutrons. So if you had a problem with low-flying neutrons, buy some deuterium. Seriously, heavy water (i.e. water molecules containing one or two deuterium atoms instead of "ordinary" hydrogen) is often used in nuclear reactors to moderate (slow down) the neutrons produced during radioactive decay. So (nuclear) physicists like deuterium, and like it a lot.



45 *Ionised deuterium used in a nuclear reactor gives a characteristic pink-red glow from interaction with neutrons [https://upload.wikimedia.org/wikipedia/en/a/a1/Deuterium\_Ionized.JPG].*

And what about chemists? As I mentioned a week ago the chemical properties of the isotopes are the same. So actually the existence of deuterium can be ignored by chemists, but... not really. Deuterated, chemical compounds, that is those containing deuterium (instead of "ordinary" hydrogen) have interesting applications. For example, they allow us to better understand the mechanisms of many chemical reactions, including biochemical ones, occurring in living organisms. Suppose we want to find out where the molecules of a drug administered to a patient migrate to? We give him a drug containing a deuterated compound and then take tissue samples to see where there is more deuterium than usual. Compounds labelled with other isotopes, such as phosphorus or carbon, can be (and are) used, but deuterated compounds are relatively cheap and, above all, safe.

Of the naturally occurring isotopes of hydrogen, tritium (T) is also known, containing two neutrons in the nucleus. It is an unstable isotope (with a half-life of a little over 12 years), which is produced as a result of some nuclear transformations (including the decay of naturally occurring radioisotopes) and also as a result of the action of cosmic radiation on hydrogen atoms.

Its practical significance is relatively small. In mining, tritiated water (superheavy water,  $T_2O$ ) is used to track the migration of groundwater. When such water is injected into a borehole, its spread in the mining deposit can then be tracked by radiation sensors (beta type). Sometimes radioluminescence of tritium is used, i.e. the emission of light radiation accompanying its radioactive decay.





*A watch (Swiss, of course) that uses tritium radioluminescence to illuminate the hands [I, Autopilot, CC BY-SA 3.0 via Wikimedia Commons].*

70            It is worth adding that tritium raises great hopes in the context of the possibility of carrying out controlled nuclear fusion and obtaining energy through the fusion of tritium nuclei into heavier elements, accompanied by the release of energy. However, everything is still at the experimental stage.

75            You may ask, are there heavier isotopes of hydrogen? I will answer enigmatically - yes and no. Yes, because physicists have managed to obtain such isotopes (with three, four, five or even six neutrons). No, because these isotopes existed in the laboratory for less than a zeptosecond, i.e. 0.000 000 000 000 000 001 s. Let us be honest - from our point of view, that is as much as nothing.

80            Finally, one more interesting fact. This "ordinary" isotope of hydrogen, with only one proton in the nucleus, is called "protium". So we already know the names of each of the hydrogen triplets of the title: Protium, Deuterium and Tritium. By the way, I heard about a chemist who named her three cats after them. You have to admit that she had a really nice idea.

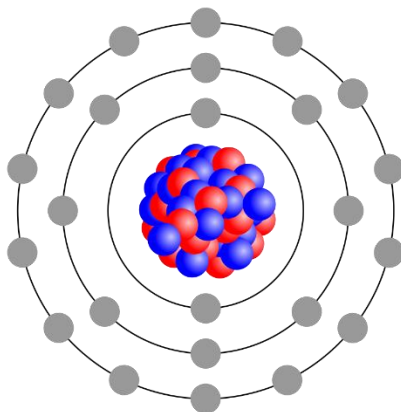
### Hydrogen triplets - Questions

1. What are the properties of hydrogen?
2. Name the three naturally occurring isotopes of hydrogen?
3. What is "heavy water"?
- 5 4. What are deuterium containing molecules used for instead of ordinary hydrogen?
5. Is tritium a stable isotope?

## *At a high level*

The flow of electric current is invariably associated with the movement of electric charge. In the case of liquids and gases, this is the movement of ions and in the case of solids the movement of electrons. The atoms that make up the structure of solids are made up of an atomic nucleus, containing protons and neutrons, and orbiting electrons held together by electrostatic attraction, as they have a negative charge and protons a positive charge. So where do electrons that can move come from in solids?

We should remember that electrons move in orbits at different distances from the atomic nucleus. We know from school textbooks the description of electron shells, which surround the nucleus like the shells of an onion, on which a few electrons circulate, the further away from the shell, the more electrons on the shell as a rule. This model, one could say "planetary", because it imposes associations with orbits of planets around the Sun, is somewhat simplified. Let us emphasize it clearly - not so much wrong as simplified. For we know that each electron shell (traditionally numbered 1, 2, 3... as it moves away from the nucleus) is divided into subshells (marked with small letters of the Latin alphabet a, b, c...). Moreover, the position of none of the shells/orbitals is unchangeable.

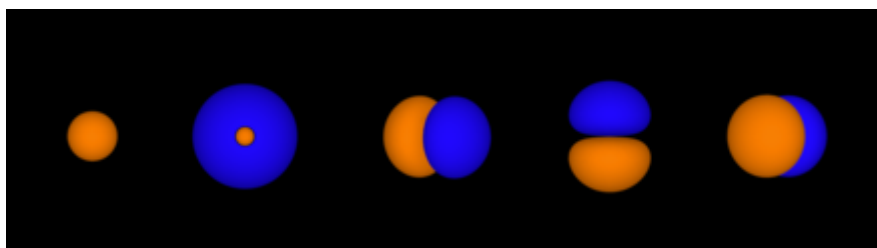


*Simplified model of the iron atom (grey dots are electrons, red dots are protons and blue dots are neutrons) [Eisenatom.svg: FornaxStylised\_Lithium\_Atom.png: Halfdanderivative work: Groogokk, CC BY-SA 3.0 Wikimedia Commons].*

When a given atom finds itself in the vicinity of another, the protons of the latter also begin to attract the electrons of the former and distort the trajectories of their orbitals. In the extreme case, the electrons of the first atom begin to circulate around the nucleus of the second atom and a chemical bond is formed. The second option is that the second atom takes over one or more electrons of the first one and both have a different number of electrons in comparison with the number of protons. Then, both atoms become ions. But let's not get into these topics

any more, because we are moving away from the main thread. I would also like to point out that in this model of electrons properties we omit the issue of quantum physics, which perceives electrons not as "balls" orbiting in orbits, but rather as waves, and treats an orbit as a fragment  
30 of space, where the electron most probably stays. But this is already a higher level of initiation.

Let us return to the issue of the variability of electron orbits. They may be deformed also when we supply them with energy from the outside. In other words, the electron can change its orbit to another one. But it cannot change its orbit at will, let us say, by any negligible distance away from the nucleus. No, no, no. At the level of elementary particles everything is  
35 quantised, i.e. divided into indivisible portions. It's a bit like we can't buy anything for a penny and a half, but we can for one penny or two. There are simply no intermediate "portions" of money. Analogically to the energy of electrons on orbits - they can only take certain values.



*The shapes of the first five atomic orbitals are: 1s, 2s, 2px, 2py, and 2pz; the two colours show the phase or sign of the wave function in each region [Rakudaniku, Public domain, via Wikimedia Commons].*  
40

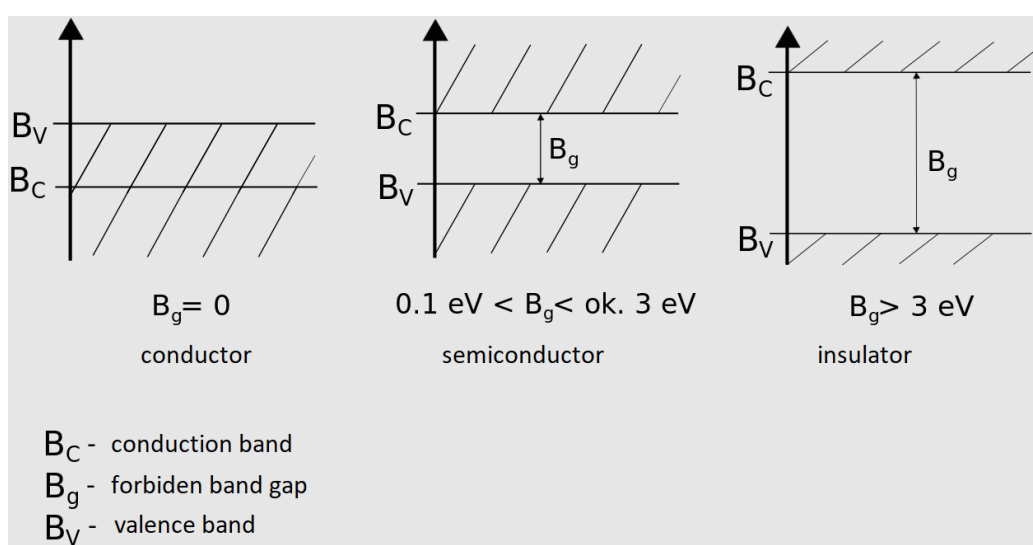
If enough energy is supplied to the electron (for example, the electron is "hit" by a photon of electromagnetic radiation of a certain wavelength), it changes its orbit to a different one - the electron is then said to enter the excited band from the base band. The term "band" is used, although one could speak of orbitals or shells. However, the term "band" is commonly  
45 and traditionally used in this context.

What energy an electron has is the same as determining what orbit and distance from the nucleus it can take. The orbits/bands that an electron can jump into are called the allowed bands and the ones that it cannot jump into are called the forbidden bands. I write "a given electron" because it depends on how protons from the atomic nucleus and other electrons  
50 around it interact with the electron. This means that the electrons of atoms in different elements and compounds will have different (allowed and exciting) levels.

If enough energy is supplied to the electrons, they can "jump" to a higher energy level (within the allowed bands, of course), so far away from the atomic nucleus that they practically lose "communication" with it. So, they can migrate, which allows us to define such an electron  
55 level as a conduction level. So, if we create such a situation that we apply a voltage to a material

made of atoms of the element/elements, whose electrons (only some of them) are in the conduction band or place it in the electric field, we will force the motion of these electrons which, like sailboats pushed by the wind on water, will "slide" on the conduction band (in this case accelerated by the electric field).

60 OK, this is how the so-called band theory of conduction roughly presents itself. You probably already know that since different elements and chemical compounds have electrons with different allowed and excited bands, they will also have different conductivity levels. That's right. This is the reason why we distinguish between conductors of electric current, insulators and semiconductors.



65 *Comparison of band model differences within the valence band forbidden gap. Overview diagrams for metals, semiconductors, dielectrics (insulators) [MonteChristof at Polish Wikipedia, CC BY-SA 3.0, via Wikimedia Commons].*

70 Conductors are materials with a structure in which the conduction band of electrons coincides with the base (or valence) band, i.e. already in the ground state, without supplying additional energy, some electrons can freely migrate in the material. Insulators, on the other hand, are materials in which the conduction band is so "high" that in order to transfer electrons to them it is necessary to supply so much energy that the material itself is sooner destroyed, for example by breaking the bonds of the crystal structure.

75 Intermediate materials are semiconductors, in which the entry of electrons to the conduction level is possible, but requires some additional support. But about this, let me write more in the next chapter...

**At a high level - Questions**

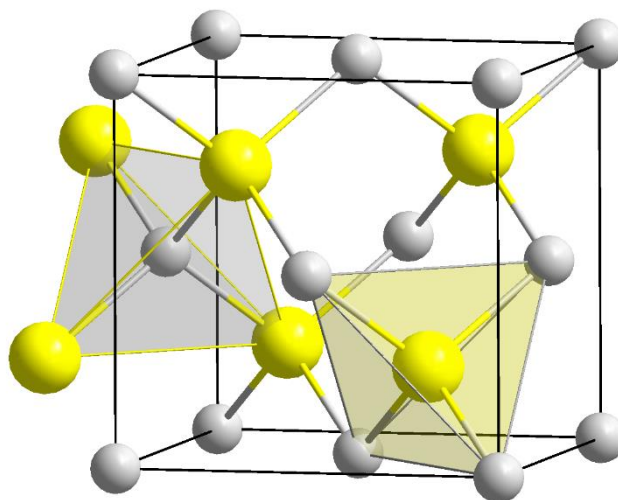
1. What are electron shells?
2. What happens to the orbit of an electron orbiting an atomic nucleus when we supply energy to it?
3. What is an insulator?
4. What are the characteristics of a semiconductor?

## *Holes you don't know*

In the last chapter, we talked about what distinguishes conductors from semiconductors and insulators. The key aspect here is the question of how much energy we need to supply for an electron to "jump" into a conduction band, in other words, such a distance from the atomic nucleus that it can move freely to carry an electric charge.

In the case of conductors, the electrons in the ground state are already essentially at the conduction level. In insulators, the so-called "forbidden band gap" is so large that the amount of energy needed for an electron to reach it far exceeds the strength of the material, which will sooner be destroyed than become a conductive material.

Semiconductors are, you guessed it, intermediate materials between conductors and insulators. In their basic state they do not conduct electricity, but if properly "motivated" they will do so. So let's look at these ways of "motivation" which, irrespective of their differences, all have the same goal - to provide energy to the valence electrons of the atoms that make up the material so that they become conductive.



*A model of the crystal structure of aluminium antimonide (AlSb), one of the semiconductor materials [Solid State, Public domain, via Wikimedia Commons].*

But before we go on to describe these methods of "motivating" electrons we must briefly mention something important in describing the behaviour of conductors and actually... does not physically exist. This something is a HOLE.

Admittedly, it is quite a prosaic concept of the sophisticated theory of conduction. However, the English language is no exception. In Polish it is *dziura*, and in German it is *Loch*, and both words mean precisely "hole". In these languages, as well as in English, the term

"electron hole" is usually added to clarify the term, but using the word "hole" in a scientific context I still have a feeling of dissonance;)

Well, let's finish these linguistic divagations. So what is this hole, if, as I wrote earlier, it does not actually exist? Well, the electron hole is the lack of an electron in its valence band in the orbit around the atomic nucleus. A hole is therefore a space left by a valence electron, but this "space" does not mean some kind of vacuum in the matter (like a hole in cheese), because, apart from elementary particles, all matter is empty. A hole is simply a term stating the absence of an electron. It is something as if we were sitting at the table as a family and at some point, Johnny got up from the table (taking a chair) and we would call this lack of his presence a "hole".

Note that an atom with such a hole is an ion, or more precisely a cation because it has an excess of protons (with a positive charge) concerning the number of electrons. If we were dealing with liquids or gases, such an ion could move, but in the case of solids, it is bound all the time in the crystal structure. So it cannot move, but a hole can move!

It sounds a bit absurd, but it is not about the movement of this particular "emptiness". Imagine atoms forming a crystal lattice one after another. If one of them has a hole (e.g. its electron has been "knocked out" from the valence orbit), then a valence electron from a neighbouring atom can "jump" to the atom with the hole, which then becomes a complete atom. But then its neighbour has a hole. This process can be quite chaotic, i.e., this electron will jump once from the atom situated in the crystal lattice above the atom with the hole, once from the atom below, either from the left or from the right. But when we apply an electric field this motion will be orderly, because electrons will "jump" according to this field (i.e., towards the "positive pole"). This means that the hole will "move" in the opposite direction. We are then dealing with what is called hole conduction, which does not require electrons to enter the conduction band.



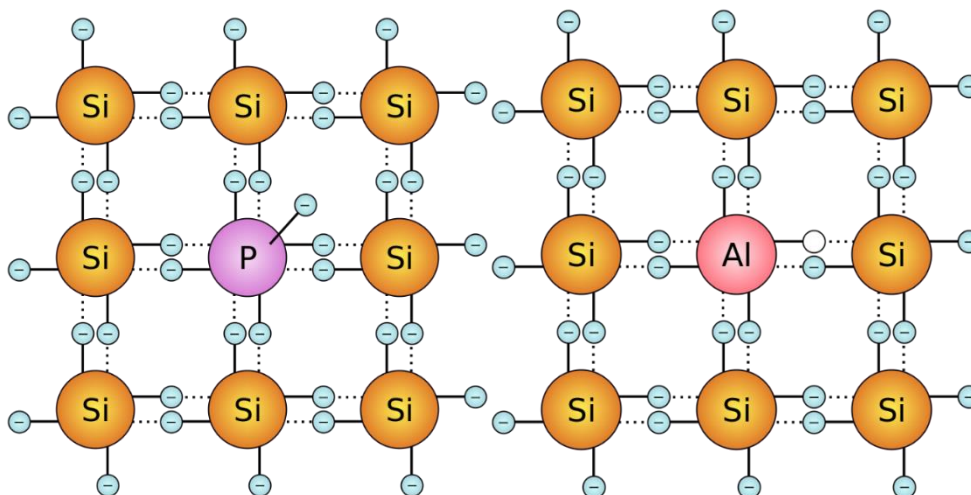


50 *A puzzle for children illustrating the mobility of holes in the atomic lattice. The tiles are analogous to electrons, while the missing tile (bottom right corner) is analogous to a hole. Just as a missing tile can be moved to different places by moving tiles, a hole in a crystal lattice can move to different places in the lattice by the motion of surrounding electrons [Micha L. Rieser, Attribution, via Wikimedia Commons].*

After this somewhat lengthy digression, let's return to describing the different types of  
55 semiconductors. Let's start with the materials called intrinsic semiconductors. These are crystalline substances (i.e. with a very regular internal structure) that have a certain number of hole-electron pairs in the conduction band, the more of them the higher the conductivity of the material. Intrinsic semiconductors, however, have few free charges (resulting in low electrical conductivity), so they are doped.

60 Doping is the introduction of atoms of elements into the crystal structure that are not part of the intrinsic semiconductor. It can be said that every atom of the crystal structure is exchanged for another one, and the dopant elements are chosen so that they have a higher or lower number of valence electrons than the atoms of the intrinsic conductor structure. This results in an excess or deficiency of electrons in the crystal. For example, silicon atoms (with  
65 4 valence electrons) are introduced into gallium arsenide, GaAs, where both Ga and As have 3 and 5 valence electrons each.

If the dopant is an element with more electrons than in the material atoms (e.g. phosphorus or germanium in silicon), then we have a semiconductor with an excess of electrons, i.e. negative charge carriers. This is called an n-type semiconductor. In the opposite  
70 case, when we doped an element with fewer electrons (e.g. boron in silicon), we have an excess of positive charges. In this case, we have a p-type semiconductor.



75 *Figure illustrating the essence of n-type (top) and p-type (bottom) semiconductor doping [Markus A. Hennig; SVG-Umsetzung: Cepheiden, GFDL <http://www.gnu.org/copyleft/fdl.html>, via Wikimedia Commons].*

Semiconductors are mainly all semimetals from group 14 of the periodic table with silicon at the top, or combinations of semimetals from groups 13 and 15, e.g. the mentioned gallium arsenide. The admixtures may be atoms of other semimetals, but also some metals, e.g. gold or platinum. The type of dopant, as you can guess, influences the properties of a semiconductor, e.g. its resistance and its change profile depending on the applied voltage or electric current flowing through the semiconductor.

80 Doping does not only increases the conductivity of semiconductors. Electromagnetic radiation may have a similar effect, e.g. visible light whose photons excite electrons allowing them to enter the conduction band. This, by the way, is one of the phenomena used in solar batteries (photovoltaic cells).

90 Another interesting feature of semiconductors is that as their temperature increases, their electrical conductivity increases, unlike ordinary conductors whose electrical resistance decreases dramatically when they are heated. This is because the vibrations of the crystal lattice and the oscillations of the particles within the material (caused by the higher thermal energy) impede the free flow of electrons in the conductor.

In a semiconductor, on the other hand, this extra heat energy results in higher oscillation of the particles inside the material and increases the chance of a statistical electron "jumping" into the conduction band. And the higher the temperature, the stronger the vibrations and therefore the higher the probability of becoming a conduction electron.



95

*A silicon monocrystal obtained by the Czochralski method [Stahlkocher via Wikimedia Commons].*

One last important note - semiconductors have a crystal structure that must be as perfect as possible, without the slightest defect, because any disruption of the crystal lattice is a barrier to an electrical charge. This is why the development of a method for the industrial production of single crystals was such a great achievement, which we owe to a brilliant inventor - Jan Czochralski (1885-1953) to whom many monuments should be erected, certainly in Silicon Valley in California.

Much has been written about the applications of semiconductors, especially in recent times, when their shortage on the markets has pushed up the prices of computer equipment, cars, etc. Semiconductors are the basis of electronic circuit design, including processors and diodes. And we have quite a lot of both around us, don't we...?

### **Holes you don't know - Questions**

1. What is an electron hole?
2. What is doping of a semiconductor?
3. How does temperature affect the conductivity of conductors and how does it affect that of semiconductors?
4. What did Jan Czochralski invent?