Serial: Electrochemistry 1 – introduction, reaction and electrolysis

Dear FYKOS solvers, welcome to the 38th year's serial. As every year, one episode of our serial will be released in every series. The serial should expand or add to your knowledge of the given topic and will contain the basic information to solve the last (serial) problem of the series. Do not be discouraged by the length and the content of the first episode, the following ones will be shorter and with a larger background in physics.

As this year's topic was chosen *electrochemistry*[1] Maybe you feel like this topic belongs to a different seminar; however, we will see that the opposite is true. Throughout the year, we will encounter many areas of physics, from thermodynamics through alternating currents to hydrodynamics. Perhaps you have imagined a serial dealing with quantum gravity or blackholes, theory of relativity or some similar topic, which comes to many people's minds when physics is mentioned. In the end, you know how it is. Chemistry is only (slightly) more complicated physics, biology is only (slightly) more complicated chemistry, etc.

Even though during physics education in highschools or fundamental elementary physics courses on universities this topic is rather on the margin of the lectures, the knowledge of electrochemistry is extremely important for the current and future society, as it plays a key role in many modern technologies and everyday applications.

Electrochemical principles and devices are omnipresent. Batteries in our mobile phones, wristwatches, earphones and other electronic devices are based on electrochemical processes. In industry, electrochemistry is used for electroplating, chemical substances production and many other different applications.

Another example of electrochemistry application is its keyrole in renewable energetics. Electrochemical processes are the basis for technologies using renewable sources of energy, such as fuel cells, solar panels, and batteries. These technologies enable sustainable energy production and storage, which is a necessity for the energetical security in the future. The development and improvement of batteries, such as lithium-ion batteries is essential for the developement of electromobiles, which pose an ecological alternative to the traditional automobiles with internal combustion.

Electrochemistry also plays an irreplaceable role in the area of environment and sustainability. Except for the mentioned sustainable energetics, electrochemical processes are used, for example, to remove pollutants from water, which is key to ensure clean drinking water and to protect the environment.

Electrochemistry also significantly contributes to the advancement of material sciences. Electrochemical methods enable the production and alternation of structures with unique properties, which then have a wide usage in industry and medicine. Another significant area is the protection of metallic materials from corrosion, which is immensely important to the con-

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[1]The author of the serial studies for his master's degree at the Department of physics of surface and plasma at MFF UK. In his master's thesis, he deals with this very topic, in particular with the development of water electrolysers with proton-conducting membrane.

struction, transportation, and energy industry. In this way, electrochemistry contributes to extending the lifetime of materials and lowering their maintenance cost.

Electrochemistry connects the findings from physics, chemistry, material sciences, and engineering, promoting an interdisciplinary approach to solving complex problems. In this way, electrochemistry promotes innovations and the development of new technologies. Therefore, it is not a surprise that, on the way, we will meet quite a few Nobel prize laureates.

In the rest of this episode, we will introduce important concepts and take a look at electrochemical reactions and electrolysis. In the next episode, we will describe the thermodynamics of electrochemical cells, in the third one, we will explore its dynamics. In the second half of the year, we will move on to more specific phenomena accompanying electrochemistry and take a look at some other research methods. We will interlace our path with important examples from praxis and other interesting information.

Phenomena exposition

So that we can get to unraveling the secrets of our topic, first of all, we need to explain or refresh some concepts, that we will use a lot onwards. Some of them will hopefully be intuitive, others may take some time to get used to their exact meaning.

Electrochemistry is a branch of physical chemistry, which deals with phenomena combining the transportation of electrical charge and the change of chemical composition. In the narrower meaning, electrochemistry describes processes where, by using electrical current or voltage, we can control chemical reactions, or the other way around, using chemical reactions, we can get electrical energy.

Electrochemical reaction is a chemical reaction, which includes the transport of electrons between *reactants* (the individual particles before the reaction) and *products* (stuff that is created during the reaction); however not directly as in the chemical reactions generally, but through a conductive circuit and the solution-electrode interface. It is through the external circuit that we can supply electrical energy to the system or we can draw it out the other way around. As with all other chemical reactions, even here the *law of conservation of mass* holds. The number of atoms of individual elements does not change, only the chemical bonds between them do.

If the reactant gains an electron during the electrochemical reaction, we call this reaction *reduction* and we say that the given substance gets reduced. The other way around, if the reactant loses an electron, we call such a reaction *oxidation* and we say that the given substance gets oxidized. These concepts are important, it is necessary to remember and get used to them a bit, which you will try in one of the serial problems. To save a bit of work, we will list here a mnemotechnical aid in English. The term *oil rig* means a platform for mining of oil in the sea. At the same time, it is also an abbreviation of the sentence *Oxidation Is Loss* (of the electrons), while *Reduction Is Gain* (of the electrons)[2] In the given electrochemical reaction, at least one reactant must always oxidize and at least one reactant must always reduce, so that the total charge before and after the reaction is conserved.

An electrolyte is a substance that enables the transport of charge by the transport of ions, not by electrons, however. *Ions* are atoms or molecules, that have an electrical charge, no matter

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[2]The word oxidation comes from the word oxide, which is a compound containing oxygen. This element has a high *electronegativity*, therefore it attracts very strongly electrons from other atoms in the molecule. These atoms lose electrons, e.g. they are oxidized. The term oxidation is, however, general, meaning the loss of electrons no matter if oxygen is present in the given substance.

if positive (one or more electrons are missing in their electron shell), or negative (electrons are in a surplus). Ions react to the presence of an electrical field and can move in the electrolyte in the direction of the *electrodes.* Electrodes are conductive (particularly metal) objects in contact with the electrolyte. Through a contact with the electrodes, the ions can gain or lose their charge by an exchange of an electron with the surface of the electrode. Electrodes are conductively connected to an external circuit. The basic idea of an electrolyte can be water, in which kitchen salt is dissolved (sodium chloride – NaCl). Here, dissolution means that the solid salt crystals split into individual ions – Na^+ and Cl^-. The individual atoms of sodium and chloride are charged and therefore react to an electrical field. The positive ions head to the negative electrode and vice versa. Electrolytes, however, do not just have to be liquid, solid electrolytes, in which ions can move, exist as well, as we will see later.

When ions with one charge head to one electrode and the ones with the opposite charge head to the other, a different change of charge on these ions happens on both electrodes. Electrode, on which the ions are oxidized (are losing electrons) is called *an anode*.[3] The other way around, the electrode on which the ions gain electrons (get reduced), is called *a cathode*. Therefore, electrons always head from the anode to the cathode and through the external circuit mentioned before. Again, we can mention an aid in English, this time with animals. *Red Cat* is an abbreviation for the words *reduction* and *cathode*. The other way around *an Ox* is an abbreviation for *anode* and *oxidation*.

Watch out, in electrochemistry, the name of an electrode is defined only by the process, which takes place on it, not by its charge! Anode can be both positively and negatively charged, cathode has a charge opposite to the one of the anode. The charge is determined by the type of the *electrochemical cell*, which is the name for the arrangement of the whole system – the external circuit, electrodes and the electrolyte.

We designate a cell as *electrolytical*, if we need to supply electrical energy from an external circuit for the electrochemical reaction to take place, for example from a socket. In such cells *electrolysis* (hence the name) can happen, where energy has to be supplied for the separation of the individual elements. We transform electrical energy into chemical energy. In these cells the anode is positively charged and the cathode is negatively charged.

Contrary to this, in a *galvanic* cell the reactions take place spontaneously after connecting the circuit, a voltage is generated between the electrodes, which can then power our electronic devices. Batteries in electronic devices are therefore galvanic cells, because they supply electrical energy. Chemical energy is transformed into electrical. Here, the anode is negatively charged and the cathode is positively charged.

(Electro)chemical reactions

As mentioned in the subsection before when introducing the concepts, electrochemical reactions include reduction and oxidation. We can also call these reactions reduction-oxidation or *redox* reactions for short. Retroactively, every such reaction can be split into two *half* reactions – oxidation and reduction, of course. During these reactions, the *oxidation numbers (states)* of the individual reactant and product atoms change.

No doubt, you have met the concepts of an oxidation number during chemistry classes, just to be sure, we will do a short reminder here. This number represents the charge on the given

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[3]This electrode gains electrons, therefore, we can say that it gets reduced, but let us keep these terms for the reactants in the chemical reactions for the following text.

atom in a hypothetical situation, where it would be bound to the other atoms purely by ionic bonds.[4] In many situations, the bonds between the atoms are of a different nature and the real value of a charge is different to the value of the oxidation number. Even then, the oxidation number is very useful and the chemical nomenclature is based on it.

For the oxidation number, some known rules hold. If the molecule is composed of the same atoms, the oxidation number is zero. The atoms are the same; therefore, none of them can attract the electrons from the others. For a negatively charged atom (more electrons) the oxidation number is negative, if an atom is missing electrons, then its oxidation number is positive. In a neutral molecule, the sum of all the oxidation numbers is zero, in a charged one it is nonzero. Some elements have their typical value of an oxidation number in compounds. The elements from the first column of the periodic table tend to have an oxidation number $+\mathrm{I}$, the elements from the second column $+\mathrm{II}$. The elements from the second to last column (halogens) tend to have an oxidation number $-\mathrm{I}$. Oxygen has, in most cases, number $-\mathrm{II}$.[5] We will not go into details, but these values are given by the structure of the electron shell of the individual elements, which derives from quantum mechanics. Here you can see the first connection to important areas of physics.

The oxidation number of individual atoms in the substance is written as an Arabic numeral preceded by the sign. There is a difference between free ions, where the sign of the charge is written after the numeral.

Balancing of chemical equations

When solving chemical equations, we usually have reactants on the left side and the products in the form of the given molecules on the right side. The law of conservation of mass holds, therefore the number of atoms of an arbitrary element on the left side has to be the same as its number on the right side. Similarly, the total charge before and after the reaction must be conserved. Before every reactant, we must therefore add a *stoichiometric coefficient*,[6] thus the number, which expresses how many molecules of the given substance must be supplied for the reaction. Usually, we choose such stoichiometric coefficients for the whole equation that they are the smallest possible indivisible whole numbers. On the other hand, we can also stumble upon a designation, where these coefficients are not whole numbers (for example in a reaction of the creation of water $\mathrm{H_2} + \frac{1}{2}\mathrm{O_2} \longrightarrow \mathrm{H_2O}$).

As an example of such an electrochemical reaction, let us list the transformation of zinc and manganese dioxide into zinc oxide and manganese(III) oxide. The following designation is still in the unbalanced form, the stoichiometric coefficients before the individual reactants and products are not correct. Thus, we only have the individual substances that take part in the reaction written down

$$\mathrm{Zn(s) + MnO_2(s) \longrightarrow ZnO(s) + Mn_2O_3(s)}\,.$$
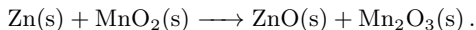
In these equations, to express complete information, we can also designate the state of matter of the given reactants and products. Here, the expression (s) stands for a solid substance,

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[4]One of the types of bonds between atoms, for example in NaCl. Simplified, an atom of chlorine gains one electron from the atom of sodium, so the sodium is positively charged and the chlorine is negatively charged, therefore a coulombic electrostatic attraction is created between these atoms, which keeps them close to each other.

[5]You can find more complex rules for example on Wikipedia, on the page about oxidation states.

[6]In particular, *a big* stoichiometric coefficient. *Small* coefficients are those that mark the number of atoms of the individual elements in the designation of the substances, for example, the two in $\mathrm{H_2O}$.

(l) would be for a liquid, (g) for gas, and (aq) for particles in a water solution (*aqeuous*). This reaction forms the basic principle of operation of the alkaline power cells, which we use, for example, in watches, alarm clocks, controllers, and other devices, while their voltage is approximately $1.5\,\mathrm{V}$.[7] As an electrolyte, potassium hydroxide dissolved in water is used.

We have to balance the equation, because, for example, with manganese we can see, that the amount on the right side is double that on the left side. Therefore, manganese oxide must have a stoichiometric coefficient 2 on the left side. Coefficients before zinc and zinc oxide have to be the same, let us try to keep them as 1. Then we can see, that the number of oxygen atoms on the left side is $2 \cdot 2$ and on the right side $1 + 3$, therefore it is equal. Thus, the balanced form of the equation is

$$\mathrm{Zn(s)} + 2\mathrm{MnO_2(s)} \longrightarrow \mathrm{ZnO(s)} + \mathrm{Mn_2O_3(s)}\,.$$
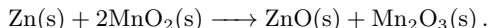
Now let us return to the oxidation numbers. If this reaction serves as a source of the electrical energy in batteries, it has to be an electrochemical reaction; therefore, the oxidation numbers should be changed in the process. To every atom, we will add its oxidation state. Zinc on the left side is not bound to any other element, thus its oxidation number is zero. We will add oxidation number $-\mathrm{II}$ to every oxygen atom. Because all the reactants and products are neutral, the sum of the oxidation numbers in all atoms (every atom counts, not only every element) is zero. In the equation, we will add oxidation numbers and skip the designation of the state of matter for clarity

$$\mathrm{Zn^0} + 2\mathrm{Mn^{+IV}O_2^{\,-II}} \longrightarrow \mathrm{Zn^{+II}O^{-II}} + \mathrm{Mn_2^{\,+III}O_3^{\,-II}}\,.$$
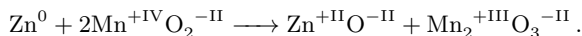
Has the oxidation numbers of the atoms changed during the transition from the reactants to the products? Yes! Zinc has transitioned from the oxidation state 0 to $+\mathrm{II}$, while manganese went from $+\mathrm{IV}$ to $+\mathrm{III}$. Oxidation number of zinc has increased; therefore, it has gained a positive charge, which means it has lost electrons. A loss of electrons means oxidation. Thus, zinc has been oxidized. The oxidation number of manganese has decreased; therefore, its positive charge has decreased and manganese has gained electrons. That means it was reduced. Thus we have fulfilled the condition, that in an electrochemic equation something always reduces and something always oxidizes.

Electrolyte as an environment for the movement of ions

Not always are all the products and reactants in solid state. For example, reactions, where one electrode dissolves into an aqueous solution, while the opposite process happens on the other one are of a great importance. Electrolyte starts to play a very significant role here. We can show this straight away on an example reaction

$$\mathrm{Zn(s)} + \mathrm{CuSO_4(aq)} \longrightarrow \mathrm{Cu(s)} + \mathrm{ZnSO_4(aq)}\,,$$
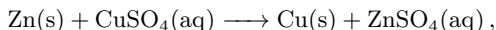
here, the zinc electrode dissolves into an aqueous solution of zinc sulfate $\mathrm{ZnSO_4}$, while the copper electrode gains copper from the solution of copper sulfate $\mathrm{CuSO_4}$. If we could build the whole cell from these two electrodes and electrolytes, it would be galvanic and it could supply us with electrical energy. Thus, this reaction is spontaneous and in suitable conditions happens on its own. But how can we build such a cell?

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[7]Do not worry, you will find out what creates a voltage on this type of cell in the following episode of the serial.

Let us consider a beaker with water, in which copper sulfate is dissolved and a copper electrode is submerged. In water, copper sulfate splits into Cu^{2+} and $(SO_4)^{2-}$ ions, an electrolyte, in which the ions can move is therefore created. Similarly, we can consider a different beaker, in which a zinc electrode is submerged in water, but zinc sulfate is dissolved in it for a change. If, for example, the zinc electrode started to dissolve, e.g. the zinc atoms would leave the electrode and became part of the electrolyte, they would change their oxidation number. In a solution they have an oxidation number Zn^{2+}, while in an electrode its zero (electrode is made out of a single element, therefore all the atoms have a zero oxidation number, as described above).

If we could observe individual atoms, we would have noticed, that some zinc atoms release into the solution from the electrode, while other zinc ions settle on the electrode surface. From a macroscopic perspective nothing happens – the number of atoms dissolved and settled is the same. The same thing happens on the copper electrode.

Let us connect both the electrodes with a conductive wire. What happens? Now, electrons can flow from one electrode to the other (and do so faster than the settlement of the ions happens), atoms of zinc can oxidize and lose electrons. These can pass through the wire to the other electrode; therefore, the beaker with copper is getting a negative charge and the one with zinc a positive one. Instead of a battery, we have built a capacitor. However, we can close the circuit with a so-called *salt bridge.* We connect both the beakers with a suitable electrolyte, in this case for example Na_2SO_4 dissolved in water, so that the ions can move between the beakers as well.

Now we can notice, that a current is passing through the wire. The zinc atoms leave the electrode in the form of Zn^{2+}, so for every one zinc atom two electrons pass through the external wire. These go to the copper electrode, where Cu^{2+} copper ions settle, while every copper atom needs exactly those two electrons to adsorb itself to the electrode. In the solution of $CuSO_4$ the concentration of copper decreases and a surplus of $(SO_4)^{2-}$ ions is created. Now we can see, why a suitable electrolyte in the salt bridge is important – it supplies positive Na^+ ions, which compensate the negative charge $(SO_4)^{2-}$. On the other hand, $(SO_4)^{2-}$ ions go through the salt bridge to the beaker with the zinc solution and compensate the charge of the Zn^{2+} ions.

In both the beakers, a neutral charge is therefore sustained. In principle, it would be enough to divide both the beakers by a material that enables the transport of $(SO_4)^{2-}$ from copper to zinc, but prevents mixing of Zn^{2+} and Cu^{2+} ions. In such a case, we could do without the salt bridge. Of course, once the concentration of Cu^{2+} or $(SO_4)^{2-}$ ions is depleted in the beaker with copper, the zinc electrode is completely dissolved or the salt bridge is worn out, the reaction does not have enough products to continue and is stopped. The processes described above, such as the settlement of zinc atoms on the surface of the zinc electrode or the dissolution of the copper electrode continue, these are however much less represented in comparison with the reaction discussed.

Such arrangement is good for a study of *half-reactions*, e.g. the oxidation and reduction alone. The individual beakers are then called *half-cells*. Here, these half-reactions are

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^- \,,$$
$$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)\,.$$
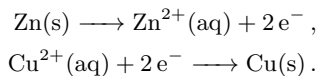
We can see that zinc oxidizes and copper reduces and that the zinc electrode is an anode and the copper one a cathode. During the oxidation, we write the electrons as a product, during a reduction we list them as reactants.

When we add the left sides and the right sides of both the half-reactions and remove two electrons from both sides, we get the total equation describing the reaction in a form

$$\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Cu(s)} + \text{Zn}^{2+}(\text{aq}),$$
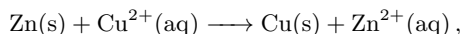
which is different from the original equation, which contained $(\text{SO}_4)^{2-}$ ions as well. These, however, do not change in this reaction, on top of that the copper and zinc ions in the solution are not bound to them. In principle, $(\text{SO}_4)^{2-}$ ion could be substituted by a different suitable substance. In this example, we have shown how important the arrangement of the electrochemical cell itself is. In the following serial episode we will show, how the voltage between such an arrangement of electrodes can be calculated.

Electrolyte as a reactant

We have seen, that the equation $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Cu(s)} + \text{Zn}^{2+}(\text{aq})$ is simple and describes the essence of the reaction – there is something which oxidizes and something that reduces. On the other hand much is skipped here - for example, we do not know which ions are contained in the electrolyte.

In this case, we at least have the correct number of atoms of the individual elements on both sides of the equation and the electrical charge is contained. But what to do with a reaction

$$(\text{MnO}_4)^-(\text{aq}) + \text{Fe}^{2+}(\text{aq}) \longrightarrow \text{Mn}^{2+}(\text{aq}) + \text{Fe}^{3+}(aq),$$
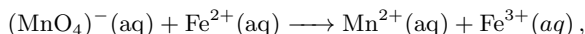
where the charge is not contained and there is even oxygen on one side, while there is none on the other. This designation does only really describe which substances change into which, but it is not yet clear, in what ratio and what else comes into play.

However, we can see, that all the reactants and products are in an aqueous solution. We have already discussed what happens with kitchen salt once we put it in water – it dissolves into Na^+ and Cl^-. A similar example would be CuSO_4 and ZnSO_4. What happens with, let us say, nitric acid? Analogically to the preceding cases, it dissociates into ions

$$\text{HNO}_3 \longrightarrow \text{H}^+ + (\text{NO}_3)^-,$$
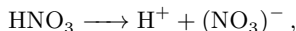
so $(\text{NO}_3)^-$ and H^+ ions are present in the water. They can bind to the water molecules and create hydronium $\text{H}^+ + \text{H}_2\text{O} \longrightarrow (\text{H}_3\text{O})^+$.

Analogically, if we dissolve sodium hydroxide in water, we get

$$\text{NaOH} \longrightarrow \text{Na}^+ + (\text{OH})^-.$$

Its exactly these H^+ and $(\text{OH})^-$ ions that will be important for our equations. A solution, in which more H^+ than $(\text{OH})^-$ is present is called acidic, in the other case its called basic. To describe the environment in dependence on the concentration of these ions, pH scale was introduced; we will talk about it more in the following episodes. Of course, these ions can interact between themselves and create a water molecule $\text{H}^+ + (\text{OH})^- \longrightarrow \text{H}_2\text{O}$.

Let us return to the currently analyzed electrochemical reaction. We will determine the oxidation numbers of all our atoms

$$\text{Mn}^{+\text{VII}}\text{O}_4{}^{-\text{II}}(\text{aq}) + \text{Fe}^{2+}(\text{aq}) \longrightarrow \text{Mn}^{2+}(\text{aq}) + \text{Fe}^{3+}(aq).$$
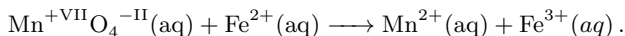
The oxidation number changes for the iron and manganese atoms. The half-reaction for iron is

$$\text{Fe}^{2+}(\text{aq}) \longrightarrow \text{Fe}^{3+}(\text{aq}) + \text{e}^- \,.$$
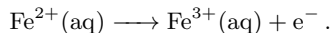
Iron has lost an electron, therefore it has been oxidized. Thus, this half-reaction is balanced both from the viewpoint of the charge and the number of atoms of the individual elements.

Therefore, manganese is reduced in a non-balanced reaction

$$\text{Mn}^{+\text{VII}}\text{O}_4{}^{-\text{II}}(\text{aq}) + 5\,\text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) \,,$$
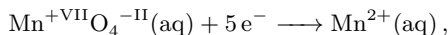
where we have calculated the oxidation number of manganese. Its initial oxidation number is $\text{Mn}^{+\text{VII}}$, as the whole charge of the ion is -1. Thus, the oxidation number has decreased from $+\,\text{VII}$ to $+\,\text{II}$; therefore, electrons were gained and reduction had happened.

As we have noticed already, there is oxygen on the left side of the equation, while there is none on the other side. This needs to be fixed. Let us consider a presence of an acidic environment, with a high concentration of H^+ (in a basic solution, this would proceed differently). The oxygen from the $(\text{MnO}_4)^-$ ion could bind with the H^+ cations and create water, which would become part of the solution. For every one $(\text{MnO}_4)^-$ ion, e.g. for every four atoms of oxygen $8\,\text{H}^+$ ions would have to be found in the solution, which is not a problem in an acidic environment. Thus, we get

$$8\,\text{H}^+(\text{aq}) + (\text{MnO}_4)^-(\text{aq}) \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4\,\text{H}_2\text{O}(\text{l}) \,.$$
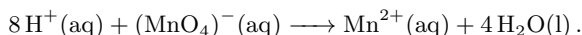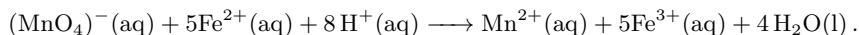
All the ions are dissolved in water, therefore we write (aq) after them. The water molecules created are the same as all the others around and are therefore in a liquid state, so we write (l) after water. In this equation the number of atoms of every element is balanced, the charge is not, however. We have determined, that the iron oxidizes; therefore, manganese must reduce.

Now the charge on the right side of the equation is $+\,\text{II}$, on the left side its $8\cdot(+1)+(-1) = = +7$. Because of that, we have to add five electrons to the left side to compensate for this charge. The total equation of this half-reaction (reduction) is therefore

$$(\text{MnO}_4)^-(\text{aq}) + 8\,\text{H}^+(\text{aq}) + 5\text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4\,\text{H}_2\text{O}(\text{l}) \,.$$
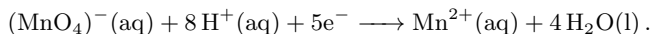
Now we are close to the finish line. The total balanced reaction is given by the sum of the reactants of both the half-reactions and their products. Again, to conserve the total charge, it is necessary to multiply the individual half-reactions by an appropriate coefficient. Five electrons are necessary for the reduction, only one electron is created in one oxidation of the iron. For one reduction, five oxidations must happen and the total reaction is therefore

$$(\text{MnO}_4)^-(\text{aq}) + 5\text{Fe}^{2+}(\text{aq}) + 8\,\text{H}^+(\text{aq}) \longrightarrow \text{Mn}^{2+}(\text{aq}) + 5\text{Fe}^{3+}(\text{aq}) + 4\,\text{H}_2\text{O}(\text{l}) \,.$$

How to balance electrochemical reactions then?

1. We write down the oxidation numbers above every element.

2. We determine, which particles reduce and which oxidize.

3. We write down the unbalanced half-reactions with the correct number of electrons.

4. If the mass is conserved, we can proceed to step number 8.

5. If we are in an acidic environment, we can add H^+ to the reactants. In a basic environment, we can add hand. In both cases, we try to create H_2O.

6. Sometimes, the products of one half-reaction can serve as reactants in the other, it is necessary to consider, whether our given equation is such a case.

7. We solve steps 5 and 6 until step 4 is fulfilled.

8. We multiply both the half-reactions, so that the number of electrons in both of them is the same, e.g. so that the same number of electrons is created on the anode as is consumed on the cathode.

9. We add the half-reactions. If the same substances are on both sides of the equation, we subtract them.

Electrolysis

One of the most important applications of the whole field of electrochemistry is a process called *electrolysis*, during which we use voltage to control reactions that would not have happened on their own. In a narrower sense, it is a process, during which we decompose compounds and get parts of them, for example, individual elements, which contain these substances. As was mentioned earlier, some periodic table elements were discovered using this method, while these substances are produced using electrolysis to this day. On the industrial scale elements such as, for example, aluminium, sodium, calcium, hydrogen, chlorine, potassium, and magnesium are separated in this manner; this process can be used to acquire even more complex molecules. Massive plants producing materials using electrolysis usually require an enormous amount of energy supplied, because of that the task of modern electrochemistry is to make the whole production process more efficient; even though, some of the production procedures have been known for decades.

Here we will not deal with the particular processes that take place during the separation of the atoms on the macroscopic scale, but we will mention the equations for the calculation of the macroscopic amount of substance that is created during the given electrochemical reaction. The quantitative laws of electrolysis were laid out by Michael Faraday already in the year 1834, with the current day knowledge of molecules, atoms, and the structure of substance in general, we can reformulate the interpretation of his time into a single intuitive equation.

Let us consider a circuit with an electrolyte, in which an electrochemical reaction takes place. In the external circuit, we have a flow of direct current, so the same current I must flow through the electrolyte as well. This current is not a flow of electrons, as in metallic conductors, but it is caused by the movement of the ions in the direction of the electrodes. Once the cation in the electrolyte (for example Ag^+) reaches the cathode, it gains an electron; an anion loses an electron at the anode. Now what happens depends on the particular element. Metal atoms can stay on the surface of the electrode after they reduce and a layer of the given element slowly starts to grow. After reaching the required volume, the pure substance can be just scraped from the electrode. Other elements, for example, hydrogen or oxygen form double-atom gas molecules and in the form of bubbles leave the electrolyte. A different gas is created on each electrode, which we can capture and use for the desired purposes. Some ions may require more than one electron to get neutralized (for example Cu^{2+}). In every case, it is obvious, that the amount of the *excreted* (captured, separated) material is *directly proportional to the passing*

current and the time. The greater the current, the more ions can reach the electrode and neutralize. The longer the process goes on, the more material is excreted.

We have got the first important proportionality $m \propto It$, where m is the mass of the material excreted and t is the time, during which the electrolysis is in progress with a constant current I. But what is the proportionality constant? Every atom or molecule we gain by the electrolysis has a weight. Because listing the weight of such small particles in kilograms is impractical, we can describe it using the *molar mass M*. From the definition, it is the weight of a single *mole* of particles, no matter whether molecules or atoms. The value of 1 mole is a unit of *amount of substance n*,[8] which denotes the number of particles, while from the definition of 1 mole $\doteq$ $\doteq 6.022 \cdot 10^{23}$ particles. The value $6.022 \cdot 10^{23}$ is then called the Avogadro constant N_A. To have an idea, molar mass of oxygen O_2 is $M_{O_2} = 32.0\,\mathrm{g \cdot mole^{-1}}$, therefore $6.022 \cdot 10^{23}$ molecules of oxygen weight only 32 grams.

From a current measurement and the knowledge of the given reaction, we know exactly what amount of substance was created. At a constant current of I, a charge of $Q = It$ has passed through the circuit after time t. This charge is carried by electrons, while every electron carries the elemental charge $e \doteq 1.602 \cdot 10^{-19}\,\mathrm{C}$. The number of electrons passed is then equal to Q/e, that is after recalculating to the amount of substance $n_e = Q/(N_A e)$. If the material created is comprised of atoms, whose charge was only ± 1 in the ion form (for example Ag^+), then the number of electrons passed is equal to the number of atoms of the given substance excreted. In the case of ions with a greater charge or multi-atom molecules, the excreted amount of substance n is equal to n_e/z, where z is the number of electrons, that are necessary to create one molecule of the excreted substance. For example, for a molecule of hydrogen H_2 is $z = 2$, because two electrons were necessary, one for every ion H^+.

Now the only thing remaining is to multiply the amount of substance and the molar mass to get the total weight of the substance separated. For simplicity of the designation, the *Faraday constant* $F = N_A e \doteq 96\,500\,\mathrm{C \cdot mol^{-1}} \doteq 10^5\,\mathrm{C \cdot mol^{-1}}$ is introduced to honor the discoverer of these laws. The final relation is therefore

$$m = nM = \frac{n_e}{z}M = \frac{Q}{N_A e}\frac{M}{z} = \frac{MIt}{N_A ez} = \frac{MIt}{zF} \,.$$

The relation listed holds true for a constant direct current I during the whole time t. However, in the following episodes of the serial, we will show this situation is not always easily reached. For example, it is obvious that if the reactants in the electrolyte start depleting, the current will decrease as there will not be enough charge carriers – ions. The value of the current I is also dependent on the voltage applied or the area of the electrode surface. For this moment, the presented information is enough, so that we have something to deal with in the following episodes as well.

Something on top − history of electrochemistry

The last paragraphs, just before the conclusion of each episode of our serial, will be dedicated to some interesting topic that has some connection to what we have been talking about in the given text. Because we have yet only explained the concepts and introduced basic nomenclature, it suits well to say here a bit about the history of this discipline.

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[8]Amount of substance is a base SI unit and it was thoroughly dealt with in the fourth serial episode of the 37th year https://static.fykos.cz/problems/fykos/37/media/serial4.en.pdf.

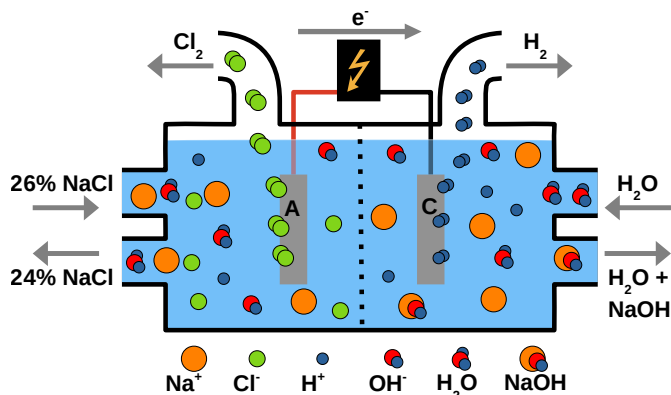[9]https://commons.wikimedia.org/wiki/File:Chloralkali_membrane_(multilang).svg

Figure 1: Scheme of electrolysis aqueous salt solution. Chlorine gas is released at the anode (pictured left), hydrogen gas at the cathode. NaOH is formed and it is necessary to supplement both the solution, then water. The electrodes are separated by a wall that allows only some of them to pass through ions.[9]

The basics of electrochemistry have been laid at the end of the 18th century in Italy. Luigi Galvanni in his famous experiment discovered that the movement of muscles in frogs legs is related to a connection to conductive objects. Galvanni surmised that he had discovered a new type of electricity, which causes a muscle mass reaction. Alessandro Volta was skeptical about this idea and found out that the movement was caused by applying voltage, which is created between two different metals. The whole experiment has led him to try different metal combinations. Using a series of connected zinc and copper electrodes in beakers with a solution he managed to create a *Volta colum* – the first battery, which allowed him to generate an electrical current for different physical experiments in 1799. Without this discovery, such an upswing in electromagnetism research in the 19th century, of which our society was witness, could not happen.

Already in the year 1800 William Nicholson and Johann Wilhelm Ritter were able to dissociate water into oxygen and hydrogen using electrical current and thus discovered the electrolysis principle. After that, Ritter stood by the foundation of the electroplating. Sir Humphry Davy was the first to use electrolysis to isolate elements potassium, sodium, calcium, magnesium, and more from their chemical compounds. One of his students, Michael Faraday, formulated the laws of electrolysis in the form in which they are used to this day and, therefore, laid the foundation for quantitative analysis of the electrochemical phenomena.

Gradually, the galvanic cells generating electrical energy were improved. Daniell cell (named after John Frederick Daniell), which uses the potential between copper and zinc, became an important part of telegraph systems development. Platinum and zinc were used in a cell, which was first constructed by William Robert Grove. The same person was also able to construct the first fuel cell, which could generate electricity using hydrogen and oxygen. Gaston Planté, on the other hand, was able to create the first lead accumulator, of which a modified version is still used to this day.

Electrochemistry has been developing for more than two centuries and to give an exhausting narration about all the revolutionary discoveries is over the scope of the length of this text. As a starting point, let us only introduce three Nobel prize laureates.[10] Wilhelm Ostwald got this appraisal in the year 1909 for research in the area of catalysis, chemical balance, and reaction speed[11], Arne Tiselius in the year 1948 for the research of electrophoresis and adsorption analysis, and at last, Czech physical chemist Jaroslav Heyrovský in the year 1959 for polarography. More will be certainly said about him in one of the following serial episodes.

A few words in conclusion

We have just finished one of six episodes of this year's serial. If you do not have a knack for chemistry, you can take a little rest as the number of chemical equations will decrease in the following episodes as we dive into the world of physics and mathematical equations, which describe the given phenomena as aptly as possible. So far we have gotten acquainted with the motivation, a short history of the topic, and the most significant terms, without which we could not proceed. Hopefully, you have gotten some understanding of electrochemical equations and their simplicity, but at the same time, complexity. We have also shown the first known application, e.g. electrolysis.

In the following episode, we will, for example, figure out what will the voltage given by the chemical reactions in our batteries be, or the other way around, why we have to apply voltage during electrolysis, while no molecules decompose on their own.

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[10]All of them got the prize for chemistry.
[11]We will mention these topics in the following episodes of the serial.