Serial: Electrochemistry 3 – kinetics and efficiency

In the third episode of our series, we are going to take a look at what affects the reaction rate and, therefore, what current and power we can obtain from our cells. In the previous part we learned about the voltage we can get from a cell depending on its specific configuration, such as the type of reacting substances, their concentrations and other conditions. This time more calculations and derivations await us, making it the most demanding episode of this year's series. However, we trust that the result will be worth the effort!

Arrhenius equation

In physical chemistry and in the studies of chemical reactions in general, the Arrhenius equation[1] is a very important building block for describing the reaction rate and it is expressed as

$$k = A \exp\left(-\frac{E_\mathrm{a}}{RT}\right) \ .$$

From the previous episodes, we already know R as gas the constant and T as the thermodynamic temperature. The *activation energy* E_a in the exponent indicates the energy required by the reactants for the reaction to proceed (in $\mathrm{J \cdot mol^{-1}}$). The constant A is the coefficient of proportionality, and k here represents the *rate constant*, which indicates the number of reactions per unit of time. The entire equation can be applied per unit of volume or area, depending on which defined space the reactions take place.

We will assume that neither A nor E_a are temperature-dependent in our approximation. With increasing temperature, the fraction in the exponent decreases. However, since the E_a is positive, the exponent becomes negative, therefore, the whole exponential increases. Consequently, with increasing temperature, the rate of constant also increases and so does the reaction rate. While the Arrhenius equation is mostly empirical, it effectively describes the behavior of some reactions, So, due to its simplicity, we will continue with it.

A straightforward explanation for the origin of this equation can be *Boltzmann distribution*. This term from thermodynamics and *statistical physics* determines the energy distribution of individual particles in the equilibrium system. You might have heard that e.g. in ideal gas at temperature T, not all particles are moving at the same speed. Some of them are almost at rest, and some of them are moving much faster, much faster than e.g. the root-mean-square speed of the gas molecules.[2] The Boltzmann distribution states that for a given particle, there

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[1]Svante August Arrhenius was a Swedish physicist and chemist, on of the founders of physical chemistry. He received a Nobel prize in 1903 for electrolytic theory of dissociation

[2]This kind of speed averages the speed of every particle and describes the kinetic energy of all the particles of given gas.

is a probability p that it will have the energy E, given as[3]

$$p = p_0 \exp\left(-\frac{E}{k_B T}\right) \,,$$

where p_0 is again constant of proportionality and k_B is Boltzmann constant. We see that the Boltzmann distribution and Arrhenius equation are practically identical, just the variables are different. Therefore, we can interpret the Arrhenius equation as the probability of the particle having enough activation energy E_a to react.

But what exactly does activation energy E_a represent? We came across non-spontaneous reactions, where the products have higher energy than the reactants. However, even spontaneous reactions require some energy to proceed. Let's consider reaction $A + B \rightarrow AB$. Particles A and B must first get close enough to each other to form the product AB. If their kinetic energy is too low, they cannot get close enough to form the product AB because of the mutual repulsion. When the energy is high enough, they can overcome the *energy barrier* and react. If the reaction is exothermic, the energy released during the reaction can be used by other reactants to react.
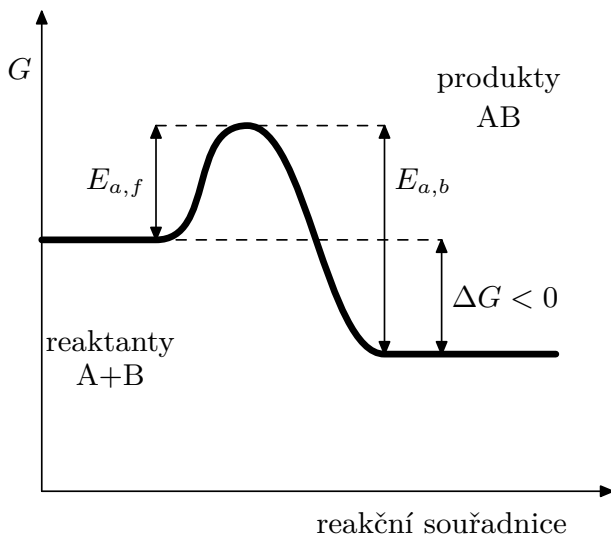

Figure 1: The dependence of free energy on reaction coordinate with designated activation barrier for both directions of the reaction

In figure 1, the course of the reaction as a function of *reaction coordinate*, which indicates how the products are formed from the reactants, is depicted. In our case, this coordinate can represent the distance between particles A and B. As this distance decreases, the reactants are forming the products, and the reaction coordinate progresses towards products. In the figure 1 we can also see that the reactants have higher Gibbs free energy G than products, so ΔG is

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[3]This relation applies to systems with discreet energy levels. With continuous spectrum e.g. for kinetic energies of ideal gas, we have to switch to probability density. However, this does not affect our description.

negative, meaning that the reaction can proceed spontaneously. However, there is an energy barrier E_a between the states of products and reactants, which has to be overcome by the particles. You can imagine it as if you are going from one valley to another. Even though the second valley can be lower in elevation overall, we have to overcome the hill, which is between our valleys, to get there. To get up the hill, we need energy. The smaller the hill, the faster you can get to the final destination. Similarly, for the reactions, the lower the energy barrier E_a, the higher the reaction rate.

Notice that, in our case, for the forward reaction, where the reactants are converted into products, the energy barrier $E_{a,f}$ is lower than for the reverse reaction, where the energy barrier is $E_{a,b}$. In the reverse reaction, the products must have not only the energy to overcome the activation energy but also enough energy to even out the change in ΔG.

Although this description of the reaction is highly simplified and does not address the quantum nature of interactions between particles, it provides an intuitive insight into reaction kinetics. In the following subsection, we will derive the dependence of reaction rate on potential from this understanding.

Butler-Volmer equation

Let's consider electrochemical half-reaction (that means oxidation or reduction) $R \pm ze^- \rightarrow P$, where R means reactant and P product of the reaction. This reaction can be a reduction of ions $Cu^{2+} + 2e^- \rightarrow Cu$ on a copper electrode, our well-known example from previous episodes. Let us denote the rate constant for this case k_f, where the letter f stands for *forward*, which tells us the direction of the reaction. However, as we have already indicated several times, on microscopic scales, the reaction always proceeds in both directions. It is a question of which one has the highest rate. For the reverse reaction, oxidation $P \rightarrow R$, we introduce the rate constant k_b (from the word *backward*).

The reaction will occur on one electrode, e.g. on the cathode. The number of particles R, which undergo the reaction (e.g. reduction), is proportional to the surface concentration of these particles alongside the electrode c_r^s (in units of $mol \cdot m^{-3}$). The superscript s indicates that is in fact *surface concetration* and subscript r refers to the reactants. Thus it represents the concentration of reactants right at the electrode surface.[4]. The reaction rate is then

$$v_f = k_f c_r^s \,.$$

Unit of this quantity is $mol \cdot s^{-1} \cdot m^{-2}$, implying that the unit of the rate constant as we derive is $m \cdot s^{-1}$.

For the opposite direction, the rate of oxidation is again proportionate to the surface concentration of the products c_p^s. Thus, the rate of the oxidation is

$$v_b = k_b c_p^s \,.$$

The net reaction rate, then is

$$v = v_f - v_b = k_f c_r^s - k_b c_p^s \,.$$

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[4]We will see later that the concentration close to the electrodes and in the volume of the solution can differ, that is why we must consider them separately.

If we multiply the reaction rates by the number of electrons transferred per reaction z and the Faraday constant, we obtain the *current density*

$$j = zFv = j_f - j_b = zF \left(k_f c_r^s - k_b c_p^s \right) .$$

The current density is simply the total current divided by the electrode surface area, assuming homogeneous surface concentrations.

For further derivations, let's consider the half-cell to be under standard conditions i.e. the concentrations of products and reactants are equal to 1 mol and the reaction potential is E_{reac}°.

We consider the progress of free energy G to be constant along the reaction coordinate for the reactants, and then it rises linearly until it starts to sharply decrease to the point when it creates an energy barrier. In the end, it is constant again for the products (see figure 2). The activation barrier for the forward reaction is, in our case, E_a, and for reverse reaction $E_a - \Delta G^\circ$ (for spontaneous reaction $\Delta G^\circ < 0$). Products and reactants correspond to the local minima of the G curve. We chose such progress of free energy to approximate in the easiest way possible the real dependence on the reaction coordinate. We can also draw important conclusions from it.
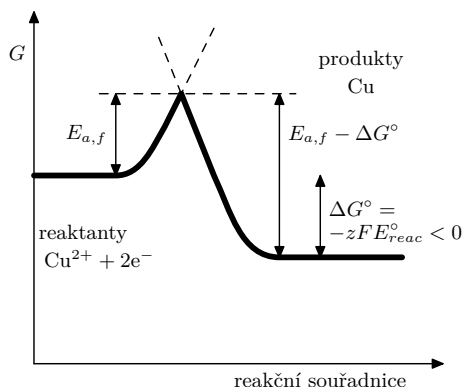

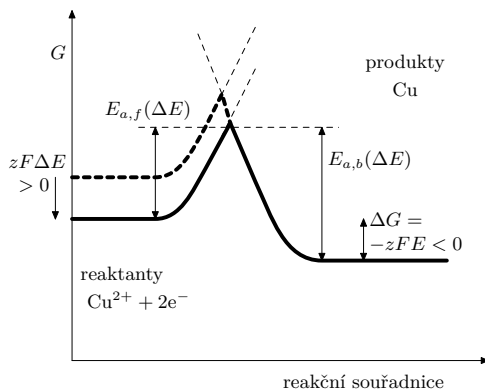Figure 2: Considered shape of activation barrier.

Figure 3: Shift in Gibbs free energy of the reactants and decrease in reaction potential. Full line represents the new shape of the barrier, dashed one the original barrier.

Let's now think about what will happen to rate constants if we lower the reaction potential to E by $\Delta E = E_{reac}^\circ - E$. The difference between the free energy of the reactants and the products will decrease by $zF\Delta E$. However, we are interested only in the difference in free energy, not its absolute values, so it does not matter whether we lower the reactants' energy or raise the products' energy by $zF\Delta E$. Let's consider that we lower the energy of the reactants, as shown in figure 3.

As a result, the entire energy curve of the reactants shifts downward in the graph. Now, what happens to the activation barrier for the forward reaction? At first glance, it might appear unchanged, but because the slopes of the energy barrier differ on both sides, it does change.

According to figure 4, the forward activation barrier increases by a fraction of the supplied energy difference. Let's denote this increase as $\alpha z F \Delta E$, where $0 < \alpha < 1$. The energy barrier is lowered for the reverse reaction. Moreover, the difference between the reverse and forward barriers must decrease by $z F \Delta E$, as it is also evident in 4.

This reasoning shows that the reverse reaction's energy barrier decreases by $(1 - \alpha) z F \Delta E$. One of the problems from the series might be useful for understanding this scheme better.
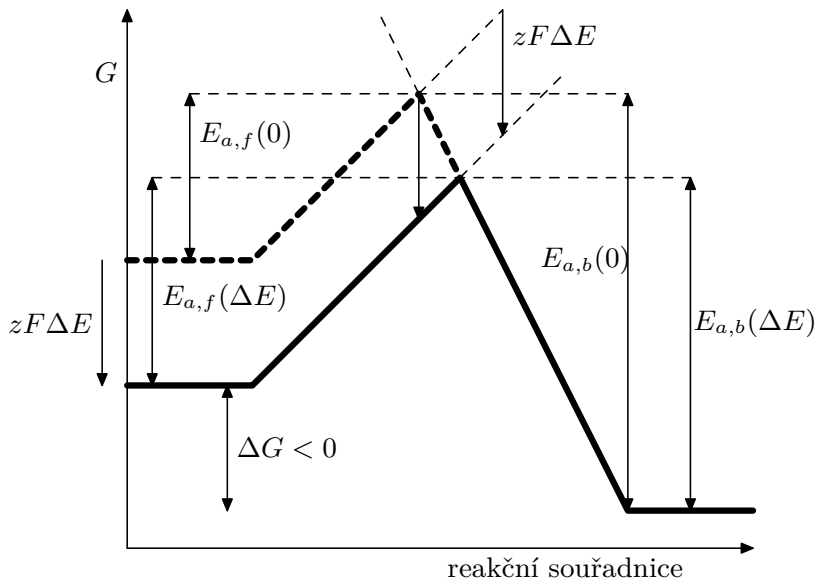

Figure 4: Schematic drawing of the change in activation energies, close up of the figure 3.

Let's still assume that we have lowered the energy of the reactants by $z F \Delta E$. The rate constants now become

$$k_\mathrm{f} = A_\mathrm{f} \exp\left(-\frac{E_\mathrm{a,f}(\Delta E)}{RT} \right), k_\mathrm{b} = A_\mathrm{b} \exp\left(-\frac{E_\mathrm{a,b}(\Delta E)}{RT} \right),$$

where the energy barrier $E_\mathrm{a,f/b}$ depends on the reaction type and the change in potential. In the paragraph above, we stated

$$E_\mathrm{a,f}(E) = E_\mathrm{a,f}(0) + \alpha z F \Delta E, E_\mathrm{a,b}(E) = E_\mathrm{a,b}(0) - (1 - \alpha) z F \Delta E,$$

where $E_\mathrm{a,f}(0)$ is the activation barrier without applied voltage, Similarly for the reverse reaction. Let us break down the energies in the exponents of rate constants

$$k_\mathrm{f} = A_\mathrm{f} \exp\left(-\frac{E_\mathrm{a,f}(0) + \alpha z F \Delta E}{RT} \right), k_\mathrm{b} = A_\mathrm{b} \exp\left(-\frac{E_\mathrm{a,b}(0) - (1 - \alpha) z F \Delta E}{RT} \right)$$

And introduce the rate constants for cases where we don't have any applied voltage

$$k_\mathrm{f0} = A_\mathrm{f} \exp\left(-\frac{E_\mathrm{a,f}(0)}{RT} \right), k_\mathrm{b0} = A_\mathrm{b} \exp\left(-\frac{E_\mathrm{a,b}(0)}{RT} \right).$$

Now we can get rid of activation energies in the notation, which will be hidden in these constants, and write

$$k_{\text{f}} = k_{\text{f0}} \exp\left(-\frac{\alpha z F}{RT}\Delta E\right), k_{\text{b}} = k_{\text{b0}} \exp\left(\frac{(1-\alpha)\, z F}{RT}\Delta E\right)\,.$$

For further simplification, let's consider for a while that $\Delta E = 0$. As we in the beginning considered the same concentrations of the reactants and products $c_{\text{r}}^s = c_{\text{p}}^s = 1\,\text{M} = c^s$, the current is

$$j = z F c^s \left(k_{\text{f0}} - k_{\text{b0}}\right)\,.$$

We found ourselves in a situation where the potential is given by the Nernst equation, the reaction is in thermodynamic equilibrium, and there is no net current. However, if the given $j = 0$, then the $k_{\text{f0}} = k_{\text{b0}} = k^\circ$ holds, where k° is rate constant at standard conditions.

Let's get back to the situation when $\Delta E \neq 0$ and remind ourselves of its definition

$$\Delta E = E_{\text{reac}}^\circ - E\,,$$

where E is the reaction potential and E_{reac}° is the reaction potential without outside influence and at standard conditions.

So far, we considered unit concentrations of the reactants and products. But as we mentioned above, the current of both forward and reverse reactions is proportional to concentrations. Let's put into the equation for current density, and we get *Butler-Volmer equation* in one of its forms

$$j = z F k^\circ \left(c_{\text{r}} \exp\left(-\frac{\alpha z F}{RT}\Delta E\right) - c_{\text{p}} \exp\left(\frac{(1-\alpha)\, z F}{RT}\Delta E\right)\right)\,,$$

where $\Delta E = E - E_{\text{reac}}^\circ$. We can see that when $\Delta E > 0$ a $c_{\text{p}} = c_{\text{r}}$ the net current is negative. That is because we considered the reduction to be the forward direction of the reaction. With increasing potential E, we prioritize oxidation, which is the opposite direction of the reaction for us, and therefore the total current is negative. Thus, it is a question of sign convention, and we can come across different formulations in the literature. The direction of the reaction, therefore, the sign of current (as we know from the previous episode), also depends on the concentrations c_{p} a c_{r}. When the concentration of reactants is high compared to the product, not even positive ΔE will be enough for a negative current.

Different forms of Butler-Volmer equation

If we do not have a unit concentration of the reactants and products, working with standard potential does not have to be ideal. Let's remind ourselves of the Nernst equation for one reaction, which describes this exact situation

$$E_{\text{reac}} = E_{\text{reac}}^\circ - \frac{RT}{zF} \ln Q\,,$$

Where Q is the reaction quotient defined in the previous episode.

Using this equation and the cell potential E, we can rewrite the definition of ΔE to

$$\Delta E = E_{\text{reac}}^\circ - E = E_{\text{reac}} - E + \frac{RT}{zF} \ln Q^b = \eta + \frac{RT}{zF} \ln Q^b\,,$$

where we introduce the quantity *overvoltage* $\eta = E - E_{\text{reac}}$ as a difference of potential on the cell and the potential determined by the Nernst equation.

The equation involves the reaction quotient Q^b, which is the ratio of the concentrations of products to reactants. It is important to note that these are the bulk solution concentrations far from the electrode surface (hence the subscript b). However, the reaction rates may differ depending on the concentrations near the electrodes. If the system is in thermodynamic equilibrium, no net current flows and the concentration is uniform throughout the solution. Thus, the reaction quotient at the electrodes is also Q^b.

By substituting the overvoltage into the Butler-Volmer equation, we obtain:

$$
\begin{aligned}
j &= zFk^\circ \left(c_r^s \exp\left(-\alpha \ln Q^b\right) \exp\left(-\frac{\alpha z F}{RT}\eta\right) - c_p^s \exp\left((1-\alpha)\ln Q^b\right) \exp\left(\frac{(1-\alpha)\,zF}{RT}\eta\right) \right) = \\
&= zFk^\circ \left(c_r^s \left(\frac{c_p^b}{c_r^b}\right)^\alpha \exp\left(-\frac{\alpha z F}{RT}\eta\right) - c_p^s \left(\frac{c_r^b}{c_p^b}\right)^{1-\alpha} \exp\left(\frac{(1-\alpha)\,zF}{RT}\eta\right) \right) = \\
&= zFk^\circ \left(c_p^b\right)^\alpha \left(c_r^b\right)^{1-\alpha} \left(\frac{c_r^s}{c_r^b} \exp\left(-\frac{\alpha z F}{RT}\eta\right) - \frac{c_p^s}{c_p^b} \exp\left(\frac{(1-\alpha)\,zF}{RT}\eta\right) \right) .
\end{aligned}
$$

By introducing *alternating current*

$$
j_0 = zFk^\circ \left(c_p^b\right)^\alpha \left(c_r^b\right)^{1-\alpha}
$$

we can rewrite the equation to a simplified form

$$
j = j_0 \left(\frac{c_r^s}{c_r^b} \exp\left(-\frac{\alpha z F}{RT}\eta\right) - \frac{c_p^s}{c_p^b} \exp\left(\frac{(1-\alpha)\,zF}{RT}\eta\right) \right) ,
$$

where the subscripts for concentrations denote *s* for the electrode surface and *b* for the bulk of electrolyte, far from the electrode. The constant j_0 depends on the bulk concentrations of the electrolyte, the activation barrier E_a, the temperature, and the coefficient α. This equation illustrates how the surface concentrations of reactants and products influence the current in the circuit. For example, if the formed products obstruct the access of new reactants, the surface concentration c_r^s decreases, and the reaction slows down. In extreme cases, there may be so few reactants at the surface that the reaction could proceed in the opposite direction despite the applied overvoltage η.

When $\eta = 0$, the cell potential is determined by the Nernst equation, $j = 0$, and the surface concentrations at the electrodes are equal to those in the bulk. This result is consistent with the assumptions made at the start of the derivation.

If the solution is well-stirred or the currents are small enough, the surface concentrations do not significantly differ from the bulk concentrations, and the equation simplifies to its most basic form

$$
j = j_0 \left(\exp\left(-\frac{\alpha z F}{RT}\eta\right) - \exp\left(\frac{(1-\alpha)\,zF}{RT}\eta\right) \right) .
$$

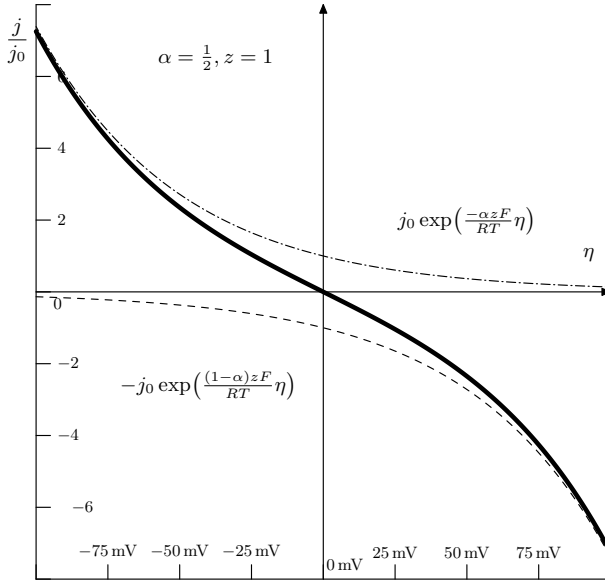The graph of the mentioned function is in the figure 5.

Figure 5: Dependence of the current on overvoltage according to the most basic form of the Butler-Volmer equation. In proximity of $\eta = 0$ we observe linear dependence

Special cases

If the overvoltage is sufficiently small that this equation is satisfied $\frac{\alpha z F}{RT}\eta \ll 1$, we get the relation between current and overvoltage

$$j = -j_0 \frac{zF}{RT}\eta \,,$$

This means that current and overvoltage in the proximity of $E = E_{\text{reac}}$ linearly decreases. Because of this, in analogy with Ohm's Law[5], we can express *odpor přenosu náboje* as

$$R_{\text{ct}} = -\frac{RT}{j_0 zF}\,.$$

On the other hand, if $\frac{\alpha z F}{RT}|\eta| \gg 1$, one of the exponentials will start to dominate the other one, which we can neglect. For example, if we have $\frac{\alpha z F}{RT}\eta \gg 1$, we get

$$j = -j_0 \exp\left(\frac{(1-\alpha)\,zF}{RT}\eta\right)\,,$$

Therefore, the current grows exponentially with the overvoltage. The negative sign corresponds to oxidation being preferred, not reduction, as we assumed at the beginning of the chapter. An

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[5]In this case, the current is negative, and this is caused by our sign convention, where we consider reduction to be the positive direction of the reaction.

equation of this form (exponential growth of current as a function of overvoltage) is called *Tafel's equation*.

On the contrary, if we want to increase the reduction current, i.e. at which copper is reduced, we must have η negative. This reduces the voltage on the given electrode. If, under standard conditions, the galvanic cell with copper and zinc from the previous parts of the series gave us a voltage of 1.10 V, then if we want to draw a higher current from it, this is only possible at a lower voltage!

On the galvanic cell, the voltage decreases with increasing current. If the power that the load in the external circuit can consume can be calculated as $P = UI$, then as long as we have a high voltage of around 1.10 V, we have a low current. On the contrary, we have a voltage going to zero for high currents. In both cases, the power is low. However, for some current and voltage values, there comes a point when the power of the galvanic cell reaches maximum!
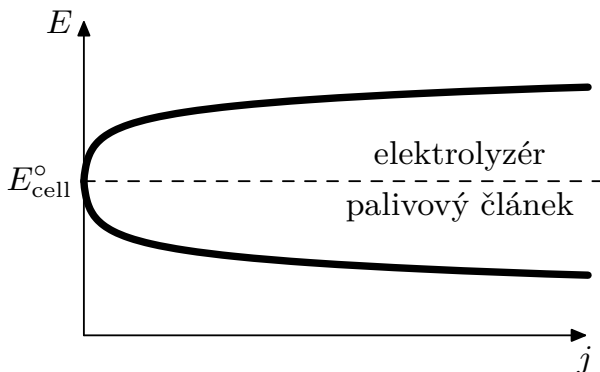

Figure 6: Relation between voltage and current for an electrochemical cell. Above E_{cell}° can work as an electrolytic cell, for example, as a water electrolyzer. On the contrary, below E_{cell}°, we get voltage on the galvanic cell (fuel cell). In this example, we assume that there are enough reactants for both reactions. At the same time, we always take the current density as the absolute value. At the point $j = 0, E = E_{\text{cell}}^{\circ}$ there is a sharp break between the two linear ends of the curves, as follows from Butler-Volmer's equation.

Efficiency

Let's imagine the conclusion of the previous part with a specific example. We have an electrolytic cell in which we want to decompose water by electrolysis. We have calculated that the voltage on the cell is $E_{\text{cell}}^{\circ} = -1.23\,\text{V}$ so the reaction does not proceed spontaneously. We gradually increase the voltage between the electrodes. When reaching 1.23 V, the barrier for the electrolysis of water and the reverse reaction is the same, so at the same concentrations, both reactions would proceed equally quickly. However, let's assume that we can quickly remove hydrogen gas and oxygen products and that no reverse reaction takes place. The current, therefore, grows exponentially with the applied overvoltage $\eta = E_{\text{WE}} - 1.23\,\text{V}$, where E_{WE}, is the voltage between the electrodes. The index WE indicates that the given quantity refers to the *water electrolyzer*.

The power consumption of our electrolyzer is $E_{WE}I$. Let us assume that with the same current I we can convert the chemical energy of hydrogen and oxygen back into electrical energy in the fuel cell in the reaction $2\,H_2 + O_2 \longrightarrow 2H_2O$.

However, we already know that the maximum voltage in this spontaneous reaction is $1.23\,V$. Even if we If an ideal fuel cell could always operate at a $1.23\,V$, its output would be only $I \cdot 1.23\,V$. The efficiency of one cycle, i.e. the production of hydrogen in the electrolyzer and its subsequent conversion in the fuel cell is

$$\eta_{WE} = \frac{1.23\,V \cdot I}{E_{WE}I} = \frac{1.23\,V}{E_{WE}}\,.$$

This is, however, only the efficiency of hydrogen production in the electrolyzer. In a fuel cell, the current increases with decreasing voltage. If the current from the device is I at the voltage E_{FC}, then the power of the fuel cell is IE_{FC} and its efficiency is

$$\eta_{FC} = \frac{E_{FC}I}{1.23\,V \cdot I} = \frac{E_{FC}}{1.23\,V}\,.$$

Therefore, the total efficiency is

$$\eta_{cycle} = \eta_{WE} \cdot \eta_{FC} = \frac{E_{FC}}{E_{WE}}\,.$$

This efficiency thus depends only on the voltages on the cell. It would be ideal to work at the smallest possible overvoltages and voltages around $1.23\,V$. Here, however, the current densities are extremely low, and a reverse reaction can also take place. However, if we increase the overvoltage, the current density starts to grow exponentially. Therefore, by sacrificing a small amount of efficiency, the current can increase significantly, which is important in many applications[6] Another option is to increase the size of the electrodes to get the necessary current and power. However, this solution can be technically impractical and financially demanding when using expensive catalysts. For a numerical idea, the efficiency of the hydrogen cycle is currently around $50\,\%$. Current densities in some types of electrolyzers reach $2\,A \cdot cm^{-2}$ at a voltage of $1.7\,V$.

Where did this energy go? When the charge passed between the reactants and products through the electrodes, it was converted into heat. Of course, that doesn't have to be a bad thing!

If you remember how we defined the Gibbs free energy G using enthalpy in the previous part, you know that ΔG is only a part of the energy of a given chemical reaction, namely the part that can do work. However, there is a term in the form of heat. Therefore, the mentioned $1.23\,V$ is not enough to produce hydrogen from water. They are only proportional to ΔG. Heat must also be supplied so that the products have ΔH more energy. This heat can be taken by the reactions from the energy losses during the movement of the charge.

We can, therefore, introduce a *thermoneutral voltage* E_{TN}, which is needed so that the necessary heat is supplied by electrical energy losses. For the electrolysis of hydrogen $E_{TN} \doteq$ $\doteq 1.48\,V$. At this voltage, no heat should be generated. If the electrolyzer operates at a higher voltage, excess heat is generated. If at a lower voltage, the reactions take heat from the surroundings.

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[6]However, it is not reasonable to increase the voltage and current to infinity. In addition to decreasing thermodynamic efficiency, losses caused by the limited conductivity of the solution increase. However, we will mention this in later parts.

In a fuel cell, however, this energy is unavailable to us, so we defined the efficiency using E_{cell}°. It is always released in the form of heat. However, for hydrogen, the ratio is

$$\frac{\Delta G}{\Delta H} = \frac{E_{\text{cell}}^{\circ}}{E_{\text{TN}}} = \frac{1.23\,\text{V}}{1.48\,\text{V}} \doteq 0.83\,.$$

So, once we have some hydrogen, we can get it from the energy of its chemical reaction with oxygen 83 % in the form of electricity. From this point of view, it is therefore considered efficient, but again, it is a different efficiency than in the previous sense.

Since heat is generated in the devices and they heat up, the reactions also proceed faster. In the Butler-Volmer equation, the exponent is dependent on $1/T$. The voltage on the cell also decreases due to the definition of Gibbs free energy

$$\Delta G = \Delta H - T\Delta S\ .$$

As temperature increases, ΔG decreases because ΔH and ΔS do not change that much. For example, at $80\,^{\circ}\text{C}$ the voltage for water decomposition decreases from $1.23\,\text{V}$ to $1.18\,\text{V}$.

We have illustrated this chapter with the example of hydrogen production by electrolysis. However, the ideas presented are generally valid across all electrochemical processes. Only the specific values depend on the reactions considered.

Something extra − back to activation energy

At the end of this series, let's go back to the very beginning, where we talked about the activation energy for a reaction and how its value affects the rate of a reaction. Let's illustrate the significance of this fact with an example of such importance that the number of people on our planet could quadruple in a hundred years. We will talk about the *Haber-Bosch process.*

In this process, the gases N_2 and H_2 react together in an exothermic reaction to form ammonia.

$$3\,H_2 + N_2 \longrightarrow 2\,NH_3\,.$$
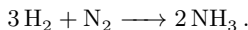
Ammonia is now used, among other things, to bind nitrogen for fertilizers in agriculture, so its artificial synthesis has increased the productivity of agricultural land fourfold. Approximately 80 % of nitrogen atoms undergo this process in the human body. Although the reaction of its formation is exothermic, energy is needed to produce hydrogen (obtained, for example, by burning natural gas), so that in the end, over 1 % of world energy production is consumed. From these last few pieces of information, it is clear that the Haber-Bosch process for producing ammonia is an indispensable and an unmissable milestone in the development of human civilization.

At the beginning of the 20th century, the demand for nitrates was increasing, precisely for the production of fertilizers but also for explosives and other industrial purposes. The basic raw material at that time was saltpeter, which was mined, but its reserves were not inexhaustible. The atmosphere contains about 80 % nitrogen. Still, it is made up of N_2 molecules with a very strong triple bond, so it is not easy to separate nitrogen atoms from each other and bind them into other compounds. In 1909, however, the German chemist Fritz Haber managed to start the above- mentioned reaction in laboratory conditions, and a year later, Carl Bosch reworked the entire process for industrial use. For their achievements, both were later awarded the Nobel Prize in Chemistry.

The key to success was not only finding the optimal temperature and pressure of the gaseous products but also suitable *catalysts*. Reactions between hydrogen and nitrogen do not occur when the reactants are in a gaseous state but when they are bound (*adsorbed*) on the surface of another solid. Choosing the right substance can significantly help break the strong triple bond between nitrogen atoms. The nitrogen bond with the surface significantly changes its electronic structure and weakens the triple bond, which reduces the activation energy for the separation into individual bonded atoms. The situation is similar for hydrogen molecules. The atoms then diffuse across the surface and react with each other in several steps until an ammonia molecule is formed, which leaves the surface in a gaseous state. The solid must, therefore, not bind the product too strongly so that it does not accumulate on the surface and take up space for further reactions. The explanation of this process also became the basis for awarding another German scientist, Gerhard Ertl, the Nobel Prize.

Over time and technological development, iron was used as a suitable catalyst for this reaction. However, in other applications, much more expensive catalysts must be used to accelerate the reactions. For example, in the production of hydrogen, we use the noble metals platinum and iridium as catalysts. However, the price and world reserves of these metals are a major obstacle to putting the hydrogen economy into economic practice, which is why people are devoting large financial and scientific resources to research into reducing the amount or completely replacing these metals with other alternatives while maintaining satisfactory reaction rates.

A few words in the conclusion

The summary of this part is simple – we found how the current density of electrochemical reactions depends on the voltage of the cell. We derived the Butler-Volmer equation, in several forms and approximations. In our procedure, we started with the Arrhenius relation, which describes the rate of reactions on a very wide scale. Finally, we thought a little about the energy efficiencies of electrochemical processes and realized that it is not so simple. In the first three parts, we introduced ourselves to electrochemistry and described the thermodynamics and kinetics of processes in a very general way. In the rest of the series, we will focus on more specific phenomena in electrochemistry, but we will still refer to what we have learned so far. In the fourth series, we will look at the double layer that forms around electrodes and get acquainted with an experimental method that uses alternating electric circuits.