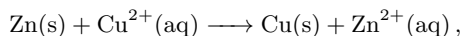


Serial: Electrochemistry – Potentials

In the first episode of this series, we introduced the basic electrochemical concepts, peeked into the world of chemical equations, and learned the basic law of electrolysis. We hope you have become familiar with these concepts because you will need them today and in future episodes. Now, let's dive into the tricky world of potentials in electrochemistry.

Cell Notation

Before we begin, let's briefly mention here the notation used to denote an electrochemical cell. For the reaction

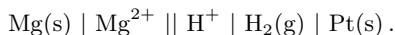


from the previous episode, which took place in solutions of CuSO_4 and ZnSO_4 with copper and zinc electrodes and a Na_2SO_4 salt bridge. Such a cell can be written using this notation as



Let's explain the different parts. The double vertical line in the middle separates the anode and cathode and represents the salt bridge. The anode is on the left and the cathode is on the right. The single vertical lines separate the phase boundaries, i.e. the solid electrode and the aqueous solution. On each side of a given electrochemical cell the reactants (Zn , Cu^{2+}) are on the left side while the products (Zn^{2+} , Cu) are on the right. The brackets indicate the state of the substance (electrodes are solids, ions are dissolved in a solution). For solutions, we specify its *concentration* in the unit M, which is the number of moles of the substance dissolved in one liter of water. Thus, in the notation above, the concentration of zinc ions is $1 \text{ M} \equiv 1 \text{ mol}\cdot\text{l}^{-1}$, while that of copper ions is $0.5 \text{ M} \equiv 0.5 \text{ mol}\cdot\text{l}^{-1}$.

The electrode material is sometimes not directly involved in the reaction. The products are formed from the particles in solution, while the electrode serves as a source or storage of electrons, or as a catalyst to accelerate the reaction. An example for this is a platinum electrode on which the dissolved H^+ ions are reduced as in the following reaction



The magnesium electrode is active because its atoms are directly involved in the electrochemical reaction. However, the platinum electrode is inert. It only serves as a source of electrons for the reaction, but platinum itself does not directly participate in the reaction.

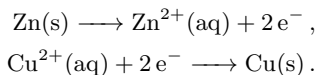
Cell Voltage

A typical alkaline battery produces voltage of 1.5 V. Car batteries provide 12.0 V. Yet it is not just 8 alkaline batteries connected in a series; there are actually completely different materials inside. So how do we determine the voltage generated in such a galvanic electrochemical cell?



Figure 1: A recall of Daniell cell, which was introduced in the first episode of the series.

Let's consider our favorite cell with zinc and copper, where one electrode is in one beaker, the other in a different beaker, and they are connected by a salt bridge. The two half-reactions that occur when we connect both electrodes with a conductive wire are



Instead of a conductive wire, we connect a voltmeter to the electrodes. Its display shows us a voltage of 1.10 V. If we replace the zinc part of the cell with an iron electrode and a solution of ferrous sulfate, the voltmeter displays a voltage of 0.78 V. Different combinations of materials lead to different voltages. To predict the total voltage of a cell, we use a table of *standard reduction potentials*¹

Each table lists the voltages at which a given *reduction* occurs. For the reduction of copper ions $\text{Cu}^{2+} + 2\text{e}^{-} \longrightarrow \text{Cu}$, it is $E_{\text{red}}(\text{Cu}^{2+} \longrightarrow \text{Cu}) = +0.34\text{ V}$. For the reduction of zinc $\text{Zn}^{2+} + 2\text{e}^{-} \longrightarrow \text{Zn}$, we would find the value is equal to $E_{\text{red}}(\text{Zn}^{2+} \longrightarrow \text{Zn}) = -0.76\text{ V}$. The total voltage of a cell is simply given as

$$E_{\text{cell}} = E_{\text{red}}(\text{cathode}) - E_{\text{red}}(\text{anode}).$$

We take the reduction potential of the reaction at the cathode (in our case, +0.34 V) and subtract the reduction potential at the anode (-0.76 V). The total voltage of our cell is then $+0.34\text{ V} - (-0.76\text{ V}) = 1.10\text{ V}$, as mentioned above. In the equation, we are using reduction

¹For all our calculations, we will refer to the tables at [https://en.wikipedia.org/wiki/Standard_electrode_potential_\(data_page\)](https://en.wikipedia.org/wiki/Standard_electrode_potential_(data_page)) and https://chem.libretexts.org/Ancillary_Materials/Reference/Reference_Tables/Electrochemistry_Tables, but it is certainly possible to find other more extensive tables.

potentials, even though oxidation is occurring at the anode with the reaction $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2\text{e}^-$. Nevertheless, we could also consider the *standard oxidation potential*, which for the oxidation of zinc is $+0.76\text{ V}$, where it simply has an opposite sign. In this case, we would calculate the cell voltage as the addition

$$E_{\text{cell}} = E_{\text{red}}(\text{cathode}) + E_{\text{ox}}(\text{anode}).$$

Of course, we get the same numerical result independently on a chosen method.

All this time we've talked about *standard potentials*. This is due to the fact that the measured values of potentials (e.g., $+0.34\text{ V}$ for the reduction of copper) vary depending on the conditions under which the measurement is performed. The tables therefore list the values measured under standard conditions, that is, a temperature of $25\text{ }^\circ\text{C} \doteq 298\text{ K}$, the pressure of all gases at $1\text{ atm} \doteq 10^5\text{ Pa}$, and the concentration of all dissolved substances at $1\text{ M} = 1\text{ mol}\cdot\text{l}^{-1}$. Additionally, we assume we are measuring with zero current, which means we need a voltmeter with high internal resistance. This is because the voltage changes with current, and the study of this dependence will be the topic of the next episode of this series.

In practice, however, it is not possible to measure the potential of a single half-reaction. Consider a beaker containing a solution and an electrode where a half-reaction is taking place, and we want to measure its potential. When we connect a voltmeter to the electrode and the solution, we will measure some voltage, but the value will not be correct. By inserting the voltmeter into the solution, we close the electrical circuit, allowing (a small) current to flow. The tip of the voltmeter in the solution acts as a second electrode, whether active or inert. Thus, a second electrochemical half-reaction occurs, and again we measure a total cell potential, not just the potential of the half-reaction. Therefore, a simple trick was introduced.

The measured electrode can be coupled with a reference electrode, whose potential is defined as zero. This way, we are still measuring the voltage of the entire cell, but since the reduction potential of the reference electrode is zero, the voltage of the cell is equal to the potential of the half-reaction. For the reference electrode, the *standard hydrogen electrode* (SHE) was chosen. The beaker with this electrode contains an aqueous solution of H^+ at a concentration 1 M and a platinum electrode. Above the surface level, there is hydrogen H_2 at a pressure of 1 atm .

If we connect our beaker with dissolved CuSO_4 and a copper electrode to this standard hydrogen electrode, copper will start to reduce ($\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cu}(\text{s})$) and hydrogen gas at the platinum electrode will start to oxidize ($\text{H}_2(\text{g}) \longrightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^-$). The copper electrode is the cathode and the SHE is the anode. We measure a voltage of $+0.34\text{ V}$ across the cell, and since the potential of the SHE is by definition zero, then

$$E_{\text{red}}(\text{Cu}^{2+} \longrightarrow \text{Cu}) = E_{\text{red}}(\text{cathode}) = E_{\text{cell}} + E_{\text{red}}(\text{anode}) = 0.34\text{ V} - 0\text{ V} = 0.34\text{ V}.$$

This value of the standard reduction potential for the reaction $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$ is therefore listed in the reference table.

However, if we connect a zinc electrode with ZnSO_4 to the SHE, zinc will begin to oxidize and hydrogen will reduce in the reaction $2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{H}_2(\text{g})$. The SHE is now the cathode and the zinc electrode is the anode. The voltmeter measures $+0.76\text{ V}$. Again, we can express the standard reduction potential of zinc as

$$E_{\text{red}}(\text{Zn}^{2+} \longrightarrow \text{Zn}) = E_{\text{red}}(\text{anode}) = E_{\text{red}}(\text{cathode}) - E_{\text{cell}} = 0\text{ V} - 0.76\text{ V} = -0.76\text{ V}.$$

We see that in both cases, we measured a positive value for the total voltage of the cell, even though the reduction potentials of copper and zinc have opposite signs. Nevertheless, this is not

a contradiction, because we also changed what is the cathode and the anode. When measuring standard reduction potentials, this is essential information.

We now also see why the electrochemical equations are presented in a shortened form, which does not satisfy the conservation of charge or mass. Each half-reaction has its own potential, which does not depend on the rest of the reaction. Hence, even from the shortened form, we can determine the total potential of the cell.

Up until now, we have always stated what happens in a given reaction. We said that copper is being reduced in the reaction with hydrogen, and zinc is being oxidized. But how do we know this for a different reaction? The answer again comes from the table of reduction potentials. The half-reaction with the higher reduction potential will occur as a reduction, and the other half-reaction will be the oxidation. The half-reaction $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$ has a higher reduction potential than both $2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$ and $\text{Zn}^{2+} + 2\text{e}^- \longrightarrow \text{Zn}$ ($+0.34\text{ V} > 0\text{ V} > -0.76\text{ V}$), so copper is reduced in these reactions. Hydrogen has a higher reduction potential than zinc, so it is reduced in the reaction with zinc, while it is oxidized in the reaction with copper.

Another piece of information that can be extracted from the table is the direction of the reaction. The simple rule is that if the calculated cell voltage is positive, then the reaction occurs spontaneously. For our favorite reaction $\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Cu} + \text{Zn}^{2+}$, the voltage is $+1.10\text{ V}$, meaning zinc dissolves into the solution and copper deposits on the electrode, everything happening on its own. In fact, this voltage can even be used as a power source for an external circuit. Such a cell is called a galvanic cell.

Now if we wanted to build a battery based on the reverse reaction $\text{Cu} + \text{Zn}^{2+} \longrightarrow \text{Zn} + \text{Cu}^{2+}$, we would get a cell voltage of -1.10 V . Such a reaction does not occur spontaneously. We would need to connect this cell to an external power source for the reaction to take place, and the voltage would need to be greater than 1.10 V . According to our terminology, this cell would no longer be galvanic but electrolytic.

Thus, the table of standard reduction potentials can be used to identify which of the products will oxidize and which will reduce in a spontaneous reaction. This allows us to determine the direction in which the reaction will proceed. On the other hand, if we have a reaction and want to know whether it will be spontaneous or not, the sign of the total cell voltage will be deciding. Furthermore, we even obtain precise values for the voltage that a given reaction produces, or alternatively, the voltage we must apply for a reaction to occur.

Potentials under non-standard conditions

So far, we have only dealt with cases where the electrochemical reactions occurred under standard conditions. However, in practice, this is often difficult to achieve. Sometimes, it is preferable to work at higher temperatures or pressures. Moreover, during the course of the reaction, the concentrations of the products and the reactants change, so their concentration in the solution will not remain exactly 1 M , even if it started that way. Therefore, it is necessary to introduce an advanced theory that can adequately describe deviations from the standard conditions.

But first, let us take a brief detour into thermodynamic potentials. Consider a galvanic cell that provides a voltage of E_{cell} (under certain conditions). One electron passing through the external circuit performs work of $-eE$, where $-e$ is the charge of an electron. For one reaction, let there be z electrons, as described in the previous episode is the section on electrolysis. Then, for one electrochemical reaction, the energy released in the form of electrical energy is $-zeE$. If we multiply this energy by the Avogadro constant N_A , we get the energy for one mole of

reactions. Further, we shall continue to work with one mole of reactions, as this is a usual practice in chemistry.

The work performed is then

$$W = -eN_A z E_{\text{cell}} = -zFE_{\text{cell}},$$

where the minus sign is used in situations where the work is done by the system, and $F = eN_A$ is the Faraday constant. The work is done at the expense of lowering the internal energy of the system.

Thermodynamic Potentials

Not all potentials are the same. For instance, in classical mechanics we use the potential energy in the gravitational field, which can also perform work, for example to accelerate a falling object. In electrostatics we have the electric potential which can in turn accelerate charged particles. In thermodynamics we have a multitude of quantities which are referred to as *thermodynamic potentials*. While these quantities have a lot of interesting properties, we will mainly be using them to describe the amount of energy conserved in the system.

You may be most familiar with the *internal energy* U of the system, which appears in the *1st law of thermodynamics*

$$\Delta U = Q + W,$$

where the change of internal energy of a system ΔU is given as a sum of the heat Q received and the work W performed on the system. This law is an intuitive formulation of the energy conservation law.

We encounter internal energy, for example, in the description of an ideal gas, where the internal energy is equal to the sum of the kinetic energies of all its particles. By supplying heat, we increase the velocity of the molecules, similarly as when the gas is rapidly compressed and work needs to be performed to reduce the volume of the gas.

However, as mentioned previously, internal energy is not the only thermodynamic potential. Another one is *enthalpy* H , which is defined as

$$H = U + pV,$$

where p is the pressure and V is the system volume. We can interpret this quantity simply as the energy needed to completely create a system of volume V in an environment of constant pressure p . To create a thermodynamic system we need to deliver its internal energy U and compress the surrounding environment with pressure p by the volume V , which explains the final element of the equation.²

Enthalpy is an important quantity in chemical calculations. Given the pressure remains constant, then the difference between the enthalpy of the reactants and that of the products is equal to the heat released (or absorbed) during the reaction

$$Q = \Delta H = H(\text{products}) - H(\text{reactants}).$$

If the value of Q is negative, then the reaction is *exothermic* and heat is released. Otherwise, heat must be supplied to the reaction and the reaction is *endothermic*. The value of enthalpy is

²This interpretation of enthalpy could be seen in problem 5, series 3, year 37 <https://fykos.org/problems/37/3>.

dependent both on the pressure and temperature of a thermodynamic system. Releasing heat proves to be useful for instance when heating up the stove or when converting part of the heat into mechanical energy, which happens in steam or internal combustion engines.

Nonetheless, not all energy is released as heat in electrochemistry. We saw that in a galvanic cell, voltage, which can be used to perform electrical work, is generated. To describe this, we introduce another thermodynamic quantity, the Gibbs free energy G .

It is defined as

$$G = H - TS = U + PV - TS,$$

where T is the thermodynamic temperature of the system and S is its *entropy*. Since the thermodynamic temperature and entropy of the system are always positive quantities, the Gibbs free energy is always less than enthalpy.

The Gibbs free energy has a very important property. The change G is the maximum chemical work (that is, not the work done by pressure and volume change) that the system can perform at constant pressure and temperature

$$W = \Delta G = G(\text{products}) - G(\text{reactants}).$$

Whether reactants or products are present in the system was chosen as the free parameter of the system (pressure and temperature are constant). However, this relation generally applies to any system, not just for an electrochemical cell. The difference between ΔH and ΔG is that ΔH describes the heat change, whereas ΔG describes the performance of the chemical work. For driving analog clocks with a conventional battery, the work done by electrochemical reactions is clearly more important than the heat released, so we see that the Gibbs free energy is a very important quantity in electrochemistry.

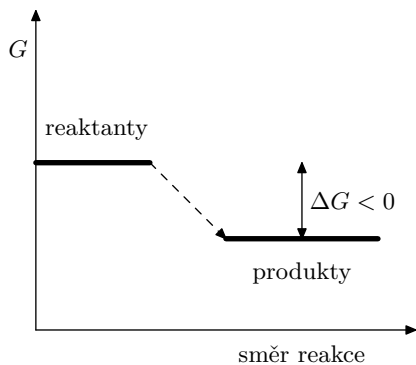


Figure 2: Change of the Gibbs free energy for a spontaneous reaction. This situation corresponds to a galvanic cell.

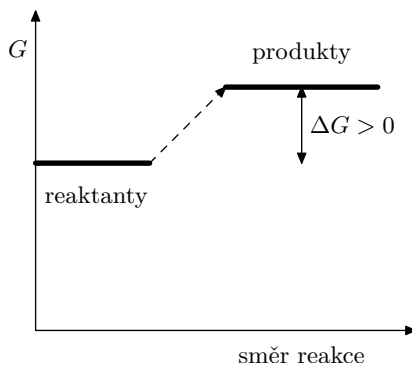


Figure 3: Change of the Gibbs free energy for a reaction that does not occur spontaneously, that is, in an electrolytic cell.

Let us recall that all the mentioned thermodynamic potentials have the unit joule – J. Yet, we can always relate their values to a system that has exactly 1 mol of particles. In such a case, the unit of the potentials is $\text{J}\cdot\text{mol}^{-1}$. For most systems, it is very challenging to determine the absolute values of potentials (especially for the internal energy). For this reason, we work

with their differences. We will briefly encounter entropy in the next episode of this series, but a deeper understanding significantly exceeds the scope of this text, so we will not delve into it further.

Nernst Equation

Let's return to the equation $W = -zFE_{\text{cell}}$, which describes the electric work performed by one mole of reactions. It is the maximum work the system can perform, so we can equate it with the difference in Gibbs free energy of the system

$$\Delta G = G(\text{products}) - G(\text{reactants}) = -zFE_{\text{cell}}.$$

We already mentioned that if the cell voltage is positive, the reaction occurs spontaneously. Thus, this equation implies that in such a case, ΔG is negative, and the free energy of the products is lower than that of the reactants. This makes sense, since systems tend to transition to states of lower energy. Just as a ball spontaneously rolls down a hill and lowers its potential energy, a spontaneous reaction occurs and lowers the Gibbs free energy of the substances in the cell. Conversely, if the reaction is not spontaneous, we need to add energy to the system, thereby increasing its free energy. The cell voltage is then negative.

Now, we finally get to the Nernst equation, which describes cell voltage under non-standard conditions, usually in relation to concentration. Thermodynamics allows us to derive³ that during the reaction, the change ΔG depends on the conditions as follows

$$\Delta G = \Delta G^\circ + RT \ln Q,$$

where ΔG° is the variation of G under standard conditions. From this point on, all quantities considered under standard conditions will be marked with the symbol $^\circ$ to distinguish them from the others. Until now, we did not use this notation for simplicity. The value ΔG° can be found in reference tables or measured for each reaction under standard conditions.

But what does Q mean? This quantity is called the *reaction quotient*. It is dimensionless and gives the relative ratio of reactants and products. For our purposes, we introduce it through the relation

$$Q = \frac{[\text{products}]}{[\text{reactants}]}.$$

Maybe, you are now wondering again, what is the meaning of the brackets in the equation above. In many areas of physics that are related to chemistry, the molar concentration of a substance A is denoted using (square) brackets $[A]$. For example, the concentration of ions H^+ , which is 0.75 M, can be written as $[\text{H}^+] = 0.75 \text{ M}$. It is simply a way to avoid complicated subscript notations.

If we have a more complex reaction, e.g., in the form

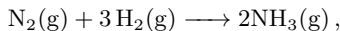


then the reaction quotient takes the form

$$Q = \frac{[C]^\gamma \cdot [D]^\delta}{[A]^\alpha \cdot [B]^\beta}.$$

³A hint on the derivation of the formula can be found on Wikipedia https://en.wikipedia.org/wiki/Nernst_equation, but for our purposes, that part is not essential.

The concentration of each product is raised to its stoichiometric coefficient, multiplied together, and divided by the concentrations of reactants. As an example, let us use the equation for ammonia production



where $Q = \frac{[\text{NH}_3]^2}{[\text{N}_2]^1 \cdot [\text{H}_2]^3}$. All three substances are in the gaseous phase. How do we determine the concentration? We define it the same way, i.e. as the number of moles per liter. Moreover, if we divide the ideal gas law equation $pV = nRT$ by the volume V , we obtain pressure on the left side and particle concentration on the right! For gases, we can therefore plug the partial pressures of individual substances into Q . If the reaction involves a solid or a pure liquid, then we substitute the numerical value 1 for its concentration (in Pa or M). Thus, these substances do not play any role numerically in the reaction quotient.

To present the Nernst equation, one last simple step remains – converting the equation $\Delta G = \Delta G^\circ - RT \ln Q$ into the language of the electric potential. We do this by dividing the entire equation by zF , thus obtaining the *Nernst equation* in the following form

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{zF} \ln Q.$$

This equation gives the cell voltage as a function of temperature, concentration of the individual reactants and products, and the voltage under standard conditions. The constants for a given reaction are $R \doteq 8.31 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, $F \doteq 96\,500 \text{ C}\cdot\text{mol}^{-1}$, and the number of electrons z . Again, note that this equation is a result of thermodynamic calculations and does not consider current in the circuit. When a non-zero current is present, the voltage deviates from the one predicted here.

If the concentration of all reactants and products equals to 1 M, then $Q = 1$, the entire logarithm is zero, and the cell voltage equals to the voltage under standard conditions. Thus the Nernst equation is internally consistent.

Consider now a galvanic cell (e.g. a regular battery) under standard conditions, for which $E_{\text{cell}} = E_{\text{cell}}^\circ > 0$. We let the reaction proceed, but we will not remove the products nor supply new reactants (just as in a battery). The concentration of products increases as new products form from the reactants in the reaction, while the concentration of reactants decreases. The reaction quotient Q increases, which means that the cell voltage decreases, $E_{\text{cell}} < E_{\text{cell}}^\circ$. However, as long as it remains positive, the reaction continues, Q increases, and so on. Eventually, Q will become so high that the cell voltage drops to zero $E_{\text{cell}} = 0$.

At this point, no further reaction seems to occur. In fact, at a microscopic level, the reaction still occurs, but the reverse reaction occurs simultaneously and at the same rate. The reaction coefficient Q hence stabilizes at a value we call the *equilibrium constant* K .

The equilibrium constant is not a quantity specific only to electrochemistry, but is generally used in chemical equations. It describes the state in which the forward and reverse reactions occur at the same rate, so the concentrations of the individual substances do not change in this state. In electrochemistry, we can express K as

$$E_{\text{cell}} = 0 \quad \Rightarrow \quad E_{\text{cell}}^\circ = \frac{RT}{zF} \ln K \quad \Rightarrow \quad K = \exp\left(\frac{zF E_{\text{cell}}^\circ}{RT}\right).$$

Then, for any (not only electrochemical) reaction

$$K = \exp\left(\frac{-\Delta G^\circ}{RT}\right).$$

Once the concentrations of the products and reactants change enough, that $Q = K$, equilibrium establishes between the reactants and products, the cell voltage of the galvanic cell drops to zero, and our battery discharges. In practice, of course, the battery effectively discharges much sooner, as our devices need a certain threshold voltage to operate. On the other hand, if we had an electrolytic cell, we could increase the cell voltage even above zero with a sufficient concentration of reactants, and the reaction would proceed spontaneously. Nevertheless, the question whether this would be feasible in practice remains.

Additional Topic – Hydrogen Economy

Before the end of this episode, let us briefly return to the motivation for studying electrochemistry and introduce one of its potentially most important applications, namely the *hydrogen economy*. This concept focuses on the production and use of hydrogen as an energy medium in industry, energy, and transportation.

Hydrogen is the most abundant element in the universe, yet on Earth, it is found almost exclusively in compounds. Nonetheless, it can be produced through water electrolysis using electricity and then combine it again with atmospheric oxygen back into water molecules, generating electric energy. If we use electricity from renewable sources, the entire cycle is completely emission-free and is one of the pathways to sustainable energy.

Within the hydrogen economy, we could balance the power grid – in times of overproduction of electricity from wind or solar power, we could store the energy by producing hydrogen, which can then be released anytime through the reverse reaction. Hydrogen can also be used it as fuel for transportation. Today, hydrogen is already an essential part of some industrial processes and in ammonia production, which is the basis for the fertilizer production. However, most of today's hydrogen production comes from fossil fuels, with this process being a significant contributor to carbon dioxide emissions. Electrochemical production of hydrogen via water electrolysis could therefore become an essential part of the global economy, similar to its use in galvanic cells for electricity generation.

There are several types of electrolyzers and fuel cells, which differ in their efficiency, the materials required for their operation, and applications (large stationary electrolyzers or, on the other hand, fuel cells in hydrogen-powered vehicles). The electrochemical reactions in all of them are governed by the laws we discuss in this year's series. Research and advancement in this field could be one of the key factors in the transition to a decarbonized society. Nevertheless, there are still many challenges to overcome, such as safety, storage, transport, or cost and efficiency of hydrogen production, making this area of electrochemistry still open to new discoveries. We will discuss the efficiency of the entire cycle in the next episode of our series, while you will calculate how much energy is hidden in 1 kg of hydrogen in the third part of the series problem statement.

A Few Concluding Words

In this part, we returned to the electrochemical cells and how to write the reactions that occur in them. From this notation, as well as directly from electrochemical equations, we can see what is being reduced and what is being oxidized. This information is enough to determine whether the reaction occurs spontaneously or not, and even by using standard reduction potentials, we can determine the cell voltage. Finally, we went even further, and now we can determine

cell voltage depending on concentration. Along the way, we also touched on thermodynamic potentials.

All of today's insights stem from thermodynamics and the structure of given substances, but they do not describe the *reaction kinetics*, that is, how many reactions can occur per unit of time. After this episode, we know the voltage required for electrolysis, but in practice, we need to use a voltage even several tenths of a volt higher to achieve the desired current. Exploring reaction kinetics and how the current depends on the cell voltage will be part of the next episode of the series, so there is much to look forward to.

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