Problem I.S ... electrochemistry 1 – reactions and electrolysis

10 points; průměr 7,77; řešilo 99 studentů

1. *To get well acquainted with concepts such as oxidation or cathode, we should solve a few chemical equations on our own. For the following chemical equations, determine the oxidation numbers of the individual atoms, determine, what oxidizes and what reduces, write both of the half-reactions, balance them out, and write the total equation of the reaction:*
   - *a)* $Cu^{2+}(aq) + Cr(s) \longrightarrow Cu(s) + Cr^{3+}(aq)$,
   - *b)* $Fe(s) + O_2(g) \longrightarrow Fe^{2+}(aq) + H_2O(l)$ *in an acidic solution,*
   - *c)* $Pb(s) + PbO_2(s) + H_2SO_4(aq) \longrightarrow PbSO_4(s)$,
   - *d)* $(MnO_4)^-(aq) + Cr(OH)_3(s) \longrightarrow MnO_2(s) + (CrO_4)^{2-}(aq)$ *in a basic solution.*
   - *e)* Bonus: *Determine the same for the reaction* $CH_3OH(l) + O_2(g) \longrightarrow H_2O + CO_2(g)$.
2. *Let us consider the production of gas chlorine from* $26\,\mathrm{wt\%}$ *concentrated kitchen salt solution. Through the circuit, a current of* $6\,\mathrm{kA}$ *is flowing under a voltage of* $3.4\,\mathrm{V}$.
   - *a) Determine, what will be the weight of the chlorine produced in the device after one day.*
   - *b) Considering that the reaction also produces* H_2 *and* $NaOH$, *write the total reaction of this process and determine by what amount the weight of the water decreases after one day.*
   - *c) How long would it take to fill a* $50\,\mathrm{l}$ *bottle with the produced chlorine, if stored inside under normal conditions?*
   - *d) The amount of chlorine in the bottle felt low, so before filling the bottle, we have isothermically pressed it to a pressure of* $8\,\mathrm{bar}$. *What is the amount of work necessary (for the electrolysis and the pressing) to fill the mentioned* $50\,\mathrm{l}$ *bottle?*
   - *e) Another option for chlorine production is the electrolysis of melted salt, which produces liquid sodium as well. Why is this type of chlorine production less common?*

Jarda has confused a seminar.

Part 1

Subproblem 1a) Half-reactions are obvious in this case. We split the equation by the elements and calculate the number of electrons from the oxidation number

$$Cu^{2+} + 2\,e^- \longrightarrow Cu^0\,,$$
$$Cr^0 \longrightarrow Cr^{3+} + 3\,e^-\,.$$

Copper gains electrons and is therefore reduced, a process that occurs at the cathode. In contrast, chromium loses electrons and is oxidized, a reaction that takes place at the anode.

However, the number of electrons in the half-reactions is not the same, so we must multiply both reactions to get the lowest possible common multiple of the number of electrons in each equation. We arrive at

$$3\,Cu^{2+} + 6\,e^- \longrightarrow 3\,Cu^0\,,$$
$$2\,Cr^0 \longrightarrow 2\,Cr^{3+} + 6\,e^-\,.$$

We add both reactions and subtract $6\,e^-$ from both sides of the equation. The total balanced equation is then

$$3\,Cu^{2+}(aq) + 2\,Cr(s) \longrightarrow 3\,Cu(s) + 2\,Cr^{3+}\,.$$

Let's keep in mind that if the substance is solid, its oxidation number is zero.

Subproblem 1b) Again, the half-reaction for iron is obvious

$$Fe^0 \longrightarrow Fe^{2+} + 2\,e^-\,.$$

Iron oxidation takes place at the anode. In this reaction, the reduced particle must be present on both sides of the equation. Hydrogen appears only on the right side; thus, it must be the oxygen that is reduced at the cathode in the half-reaction

$${O_2}^0 + 4\,e^- \longrightarrow 2\,{H_2}^{+I}O^{-II}\,.$$

There is hydrogen on the right side of the reaction, but none on the left side. Hydrogen does not change its oxidation state, as it is absent from the original reaction from the problem statement. To balance the half-reaction, we will add the required number of H^+ ions to the left side

$$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,{H_2}^{+I}O^{-II}(l)\,.$$

During the reduction of oxygen, twice the number of electrons is needed compared to the oxidation of iron. Therefore, it is necessary to multiply the reaction by two. The total reaction is then

$$2\,Fe^0(s) + {O_2}^0(g) + 4\,H^+(aq) \longrightarrow 2\,Fe^{2+}(aq) + 2\,{H_2}^{+I}O^{-II}(l)\,.$$

Subproblem 1c) In this equation, we observe that the lead atoms transition from different compounds into a single compound. To identify what is being reduced and what is being oxidized, we will assign oxidation numbers to each atom in the equation

$$Pb^0(s) + Pb^{+IV}{O_2}^{-II}(s) + {H_2}^{+I}S^{+VI}{O_4}^{-II}(aq) \longrightarrow Pb^{+II}S^{+VI}{O_4}^{-II}(s) + {H_2}^{+I}O^{-II}(l)\,.$$

The oxidation numbers only change for the lead atoms. At the cathode, the (still unbalanced) equation takes place

$$Pb^{+IV}{O_2}^{-II} + 2\,e^- \longrightarrow Pb^{+II}S^{+VI}{O_4}^{-II}\,,$$

as the atoms of lead in the lead oxide are reduced. At the anode, the reaction taking place is

$$Pb^0 \longrightarrow Pb^{+II}S^{+VI}{O_4}^{-II} + 2\,e^-\,.$$

We need to add the anion $(SO_4)^{2-}$ to the left side of both equations, as it forms the basis of the resulting sulfate. Since the problem involves a solution of sulfuric acid, the ions H^+ and $(SO_4)^{2-}$ can move independently within the solution.

Therefore, the half-reaction at the anode is already balanced

$$Pb^0 + (SO_4)^{2-} \longrightarrow Pb^{+II}S^{+VI}{O_4}^{-II} + 2\,e^-\,.$$

At the cathode, the lead oxide must lose its oxygen atoms, ideally forming water in the process. Additionally, there is an excess of H^+ ions from the sulfuric acid present in the solution. We write this half-reaction with all the reactants and products

$$\mathrm{Pb^{+IV}O_2{}^{-II} + (SO_4)^{2-} + 4\,H^+ + 2\,e^- \longrightarrow Pb^{+II}S^{+VI}O_4{}^{-II} + 2\,H_2O}\,.$$

Now, this reaction is balanced as well, and we can add the two half-reactions together to obtain

$$\mathrm{Pb(s) + PbO_2(s) + 2\,H_2SO_4(aq) \longrightarrow 2\,PbSO_4(s) + 2\,H_2O(l)}\,.$$

This reaction forms the foundation of lead-acid accumulators commonly used in devices such as car batteries.

Subproblem 1d) We write the oxidation numbers for each atom

$$\mathrm{Mn^{+VII}O_4{}^{-II}(aq) + Cr^{+III}\,(OH)\,_3{}^{-I}(s) \longrightarrow Mn^{+IV}O_2{}^{-II}(s) + Cr^{+VI}O_4{}^{-II}(aq)}\,.$$

The half-reactions are as follows

$$\mathrm{Mn^{+VII}O_4{}^{-II} + 3\,e^- \longrightarrow Mn^{+IV}O_2{}^{-II}}\,,$$
$$\mathrm{Cr^{+III}\,(OH)\,_3{}^{-I} \longrightarrow Cr^{+VI}O_4{}^{-II} + 3\,e^-}\,.$$

Manganese is reduced at the cathode, while chromium is oxidized at the anode. The $(OH)^-$ ion can participate as a reactant since the reaction occurs in an alkaline environment. At the cathode, the oxygen level decreases, so no $(OH)^-$ ions are added. Conversely, at the anode, we add one $(OH)^-$ ion to balance the (4) oxygen atoms on both sides of the reaction. After that, the reaction at the anode takes the form of

$$\mathrm{Cr^{+III}\,(OH)\,_3{}^{-I} + \,(OH)\,^- \longrightarrow Cr^{+VI}O_4{}^{-II} + 3\,e^- + 4\,H^+}\,.$$

At the cathode, we have

$$\mathrm{Mn^{+VII}O_4{}^{-II} + 3\,e^- + 4\,H^+ \longrightarrow Mn^{+IV}O_2{}^{-II} + 2\,H_2O}\,.$$

The half-reactions are now balanced from both the perspective of the atoms and the charge. The number of electrons on both electrodes is the same. Therefore, we can add them, subtract H^+ and electrons from both sides, and we get the total reaction

$$\mathrm{Mn^{+VII}O_4{}^{-II} + Cr^{+III}\,(OH)\,_3{}^{-I} + (OH)^- \longrightarrow Cr^{+VI}O_4{}^{-II} + Mn^{+IV}O_2{}^{-II} + 2\,H_2O}\,.$$

Subproblem 1e) Let us write the equation with the oxidation numbers

$$\mathrm{C^{-II}H_3{}^{+I}O^{-II}H^{+I} + O_2{}^0 \longrightarrow C^{+IV}O_2{}^{-II} + H_2{}^{+I}O^{-II}}\,.$$

We see that the oxidation numbers of carbon and oxygen atoms change. At the anode, the reaction is

$$\mathrm{C^{-II}H_3{}^{+I}O^{-II}H^{+I} \longrightarrow C^{+IV}O_2{}^{-II} + 6\,e^-}\,,$$

because the carbon loses its electrons. At the cathode, the half-reaction is

$$\frac{1}{2}\mathrm{O_2{}^0 + 2\,e^- \longrightarrow H_2{}^{+I}O^{-II}}\,.$$

You might wonder why we separated the substances in this way. The oxygen in CO_2 cannot originate from O_2 because O_2 would undergo reduction. During the formation of CO_2, it is the carbon that is oxidized. However, CO_2 contains two oxygen atoms per carbon atom, while CH_3OH has only one. Therefore, we need to add a substance containing O^{-II} to the left side of the half-reaction at the anode.

Since we are unsure what to add as a reactant at the anode, let us focus on balancing the cathode half-reaction. We must add H^+ ions generated at the anode. That leads us to a simplified reaction

$$\frac{1}{2}{O_2}^{0} + 2\,e^- + 2\,H^+ \longrightarrow {H_2}^{+I}O^{-II}\,.$$

Because our reactant is O_2, it is more natural to write

$${O_2}^{0} + 4\,e^- + 4\,H^+ \longrightarrow 2\,{H_2}^{+I}O^{-II}\,.$$

Water is created at the cathode. Therefore, the only possible reactant at the anode is the water produced at the cathode. We will add it to our half-reaction, which we can balance out

$$C^{-II}{H_3}^{+I}O^{-II}H^{+I} + {H_2}^{+I}O^{-II} \longrightarrow C^{+IV}{O_2}^{-II} + 6\,H^+ + 6\,e^-\,.$$

Now that both half-reactions are balanced, we can combine them to obtain the total reaction. To do this, we must ensure the number of electrons is the same on both sides. We multiply the cathode half-reaction by a factor of three and the anode half-reaction by a factor of two, resulting in

$$2\,CH_3OH + 3\,O_2 + 2\,H_2O \longrightarrow 2\,CO_2 + 6\,H_2O\,,$$

or after subtracting $2\,H_2O$ from both sides

$$2\,CH_3OH + 3\,O_2 \longrightarrow 2\,CO_2 + 4\,H_2O\,.$$

Part 2

Subproblem 2a) Chlorine is a gas (under standard temperature and pressure) in the form of two-atom molecules Cl_2, whose molar mass is $M_{Cl_2} = 2 \cdot M_{Cl} \doteq 70.9\,\mathrm{g{\cdot}mol^{-1}}$. Two Cl^- ions are necessary per one molecule of the produced chlorine, while each one loses an electron during its oxidation. Thus, two electrons per Cl_2 molecule are necessary, so $z = 2$.

By substituting the relation from the serial text, we arrive at

$$m_{Cl_2} = \frac{M_{Cl_2} I t}{zF} \doteq 190\,\mathrm{kg}\,,$$

where F is the Faraday constant, $I = 6\,000\,\mathrm{A}$ is the current from the problem statement, and we have substituted $t = 86\,400\,\mathrm{s}$ for the time t.

Subproblem 2b) The products of the reaction are Cl_2, H_2 and NaOH, while the reactants include Cl^-, Na^+ and water. The unbalanced equation with oxidation numbers is

$$Na^+ + Cl^- + {H_2}^{+I}O^{-II} \longrightarrow {Cl_2}^{0} + {H_2}^{0} + Na^{+I}\,(OH)^{-I}\,.$$

The oxidation state changes for chlorine and hydrogen – chlorine is oxidized, and hydrogen is reduced. We can balance the equation into the form of

$$2\,Na^+ + 2\,Cl^- + 2\,{H_2}^{+I}O^{-II} \longrightarrow {Cl_2}^{0} + {H_2}^{0} + 2\,Na^{+I}\,(OH)^{-I}\,,$$

where we tried setting the number of ions Cl^- to 2. By that, we had to adjust the number of Na^+ and subsequently of NaOH. The number of oxygen atoms must correspond to the number of water molecules, which is also 2. Now, the number of atoms is correct for each element.

There is one water molecule per every chlorine atom and one electron flowing through the circuit per every chlorine atom. There are It/e electrons in total. The mass of water consumed for the given reactions is therefore

$$m_{\mathrm{H_2O}} = \frac{M_{\mathrm{H_2O}} It}{F} \doteq 97\,\mathrm{kg}\,,$$

where we have substituted $M_{\mathrm{H_2O}} = 18\,\mathrm{g{\cdot}mol^{-1}}$. Thus, we consume a substantial amount of water during this process.

Subproblem 2c) The state equation of an ideal gas is

$$pV = nRT\,,$$

where $p \doteq 1 \cdot 10^5\,\mathrm{Pa}$ is the chlorine pressure, in our case equal to atmospheric, $V = 50\,\mathrm{l}$ is the volume of the bottle, n is the molar amount of the chlorine in the bottle, $R = 8.31\,\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ is the molar gas constant and $T = 298\,\mathrm{K}$ is the standard temperature. By a simple modification, we get

$$n = \frac{pV}{RT}\,.$$

The amount of substance can also be derived from the equation for the mass of the produced chlorine

$$n = \frac{m_{\mathrm{Cl_2}}}{M_{\mathrm{Cl_2}}} = \frac{It}{zF}\,.$$

By substituting from the previous equation, we get the time

$$t = \frac{pVzF}{RTI} \doteq 65\,\mathrm{s}\,.$$

Subproblem 2d) First and foremost, let us find the amount of chlorine stashed in $V = 50\,\mathrm{l}$ bottle under pressure of $p_1 = 8\,\mathrm{bar}$. From the state equation, it is $n_1 = p_1V/(RT)$. According to the previous subproblem, it took a time of $t_1 = p_1vzF/(RTI)$ to produce this amount.

The input power of the electrolyzer is

$$P = UI\,,$$

where $U = 3.4\,\mathrm{V}$ is the voltage from the problem statement. We can calculate the work necessary for the electrolysis of the amount n_1 of chlorine as a product of input power and time

$$W_{\mathrm{el}} = Pt_1 = UIt_1 = U\frac{p_1vzF}{RT} \doteq 10.6\,\mathrm{MJ}\,.$$

The result does not depend on current or time but on their product, which is proportional to the required amount of the produced substance.

During an isothermal compression of a given amount of gas, the temperature remains constant. Consequently, according to the state equation, the product $pV = nRT$ remains unchanged. Initially, after electrolysis, the gas pressure was $p_0 = 1\,\mathrm{bar}$ and its volume

$$V_0 = v\frac{p_1}{p_0}\,.$$

The work done during an isothermal compression of a gas volume of $\mathrm{d}V$ is therefore

$$\mathrm{d}W_{\mathrm{com}} = -p\,\mathrm{d}v = -p_0 V_0 \frac{\mathrm{d}V}{V}\,,$$

where the negative sign represents the reduction in volume (compression). Therefore, we can determine the total work done during the compression from V_0 to V as

$$W_{\mathrm{com}} = -\int_{V_0}^{V} p_0 V_0 \frac{\mathrm{d}V}{V} = -p_0 V_0 \left[\ln v\right]_{V_0}^{V} = p_0 V_0 \ln\!\left(\frac{V_0}{V}\right) = p_1 v \ln\!\left(\frac{p_1}{p_0}\right) = 0.08\,\mathrm{MJ}\,.$$

Therefore, the compression to the required pressure comprises only an insignificant fraction of the total work necessary to fill the bottle.

Let us write the sum of both the works and divide them by the product $p_1 vzF/(RT)$ to arrive at

$$\frac{W}{\frac{p_1 vzF}{RT}} = U + \frac{RT}{nF}\ln\!\left(\frac{p_1}{p_0}\right)\,.$$

The expression on the left side is the voltage we would need for the electrolysis if we collected the chlorine straight into a bottle with a pressure of 8 bar (eliminating the need for subsequent mechanical compression). On top of that, this equation reminds us of the *Nernst equation*, one of the foundational relations in electrochemistry, which will be one of the topics in the second part of this series.

Subproblem 2e) Electrolysis of a salt solution is preferred over molten salt for chlorine production for several reasons. One major factor is the technological challenge of constructing an electrolyzer capable of handling the high melting temperature of salt, which is 801 °C. Although adding chlorine calcite lowers this temperature, resulting in calcium as a byproduct, the process still operates at approximately 600 °C.

Other reasons are more economical. The yearly chlorine consumption in the year 2006 was about $60 \cdot 10^6$ t[1] and $50 \cdot 10^6$ t,[2] for NaOH while only $0.1 \cdot 10^6$ t.[3] for pure sodium. Sodium hydroxide is in significantly higher demand than sodium itself, making it much easier for chlorine manufacturers to sell as a secondary product.

The final reason we will mention is energy demand. In the problem statement, we noted that electrolysis occurs at 3.4 V, though this voltage can vary, affecting the current passing through the electrolyte. The minimum voltage required for chlorine production in a salt solution is approximately 2.2 V, whereas for molten salt, it is around 4.1 V. Hence, producing chlorine from molten salt consumes nearly twice the electrical energy per chlorine molecule! The difference

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[1] `https://en.wikipedia.org/wiki/Chlorine`

[2] `https://en.wikipedia.org/wiki/Sodium_hydroxide`

[3] `https://en.wikipedia.org/wiki/Sodium`

arises from the products formed at the other electrode. In the second part of this series, we will explore how to calculate this voltage.

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