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Problem II.S ... electrochemistry 2 — potentials řešilo 66 studentů

1. Determine the voltage of the following electrochemical reactions under standard conditions. Does the reaction occur spontaneously? (2 points)

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(a) \operatorname{CaCl}_2(l) \longrightarrow \operatorname{Ca}(s) + \operatorname{Cl}_2(g),
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- (b) $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l).$
- 2. Determine which of the following electrochemical half-cells will reduce and what will be the voltage after they combine. (2 points)
 - (a) $Ni^{2+}(aq)|Ni(s) a Au^{3+}(aq)|Au(s),$
 - (b) $(NO_3)^-(aq)|NO(g)|Pt(s)$ in an acidic solution and $Fe^{2+}Fe^{3+}|Pt$
- 3. Let us consider a fuel cell which, under standard conditions, produces electric energy during the water-producing reaction $2 H_2(g) + O_2(g) \longrightarrow 2 H_2O(g)$. Determine the energy density in relation to the mass of hydrogen (in $J \cdot kg_{H_2}^{-1}$) that is released in this situation. Determine the constant of equilibrium K for this reaction and discuss its value. (2 points)
- 4. Now, let us consider a electrochemical cell Cu|Cu²⁺(aq)||Ag⁺(aq)|Ag. The initial concentration of copper in the solution is [Cu²⁺] = 0.40 M while the concentration of silver is [Ag⁺] = 0.50 M. What is the concentration of silver when the cell's voltage is equal to 0.40 V? (4 points)

Special motivation: You might encounter a problem like this on the electrochemistry exam during your master's studies at MFF. Can you solve it already in high school?

Jarda has a great potential.

Subproblem 1a) Individual half-equations are

$$\operatorname{Ca}^{2+} + 2 e^{-} \longrightarrow \operatorname{Ca},$$

 $2 \operatorname{Cl}^{-} \longrightarrow \operatorname{Cl}_{2} + 2 e^{-}$

assuming molten CaCl₂; the ions are free in the liquid state. Calcium is formed at the cathode because it is reduced, while chlorine is formed at the anode because it is oxidized. The standard reduction potentials of the reactions are $E_{\rm red}(\text{cathode}) = -2.84 \,\text{V}$ and $E_{\rm red}(\text{anode}) = 1.40 \,\text{V}^1$.

We substitute the values into the equation from the series text and get

$$E_{\text{cell}} = E_{\text{red}}(\text{cathode}) - E_{\text{red}}(\text{anode}) = -2.84 \text{ V} - 1.40 \text{ V} = -4.24 \text{ V}.$$

The voltage is negative; the reaction therefore does not occur spontaneously under standard conditions. It is an electrolytic cell.

¹https://chem.libretexts.org/Ancillary_Materials/Reference/Reference_Tables/Electrochemistry_Tables

Subproblem 1b) We already encountered this equation in the first part of the series. Let us remind ourselves of the half-equations:

$$\begin{split} \mathrm{Pb}^{0} + (\mathrm{SO}_{4})^{2-} &\longrightarrow \mathrm{Pb}^{+\mathrm{II}} \mathrm{S}^{+\mathrm{VI}} \mathrm{O}_{4}^{-\mathrm{II}} + 2 \, \mathrm{e}^{-} \,, \\ \mathrm{Pb}^{+\mathrm{IV}} \mathrm{O}_{2}^{-\mathrm{II}} + (\mathrm{SO}_{4})^{2-} + 4 \, \mathrm{H}^{+} + 2 \, \mathrm{e}^{-} &\longrightarrow \mathrm{Pb}^{+\mathrm{II}} \mathrm{S}^{+\mathrm{VI}} \mathrm{O}_{4}^{-\mathrm{II}} + 2 \, \mathrm{H}_{2} \mathrm{O} \,. \end{split}$$

The first half-reaction is oxidation and it occurs at the anode, whereas the second one is reduction at the cathode. We find the tabled values of standard reduction potential for both reactions, obtaining $E_{\rm red}(\text{anode}) = -0.36 \text{ V}$ and $E_{\rm red}(\text{cathode}) = 1.69 \text{ V}$.

The total voltage across the cell is therefore

$$E_{\text{cell}} = E_{\text{red}}(\text{cathode}) - E_{\text{red}}(\text{anode}) = 1.69 \text{ V} - (-0.36 \text{ V}) = 2.05 \text{ V}$$

The voltage is positive and the reaction therefore occurs spontaneously. Six cells connected in series give us about 12 V; they are used as car batteries, for example.

Problem 2

Subproblem 2a) The individual half-reactions in a reduction form are:

$$\begin{split} \operatorname{Ni}^{2+}(\operatorname{aq}) &+ 2 \operatorname{e}^{-} \longrightarrow \operatorname{Ni}^{0}(\operatorname{s}) \,, \\ \operatorname{Au}^{3+}(\operatorname{aq}) &+ 3 \operatorname{e}^{-} \longrightarrow \operatorname{Au}^{0}(\operatorname{s}) \,. \end{split}$$

For nickel, we have the standard reduction potential $E_{\rm red}^{\circ}({\rm Ni}^{2+} \longrightarrow {\rm Ni}^{0}) \doteq -0.26 \,{\rm V}$; for gold, it is $E_{\rm red}^{\circ}({\rm Au}^{3+} \longrightarrow {\rm Au}^{0}) \doteq 1.52 \,{\rm V}$. Gold has the higher standard reduction potential, so ${\rm Au}^{3+}$ is reduced at the cathode while ${\rm Ni}^{0}$ is oxidized at the anode. The total voltage across the cell is therefore

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ}(\text{cathode}) - E_{\text{red}}^{\circ}(\text{anode}) = 1.52 \,\text{V} - (-0.26 \,\text{V}) = 1.78 \,\text{V}$$

The complete reaction takes the form

$$2 \operatorname{Au}^{3+}(aq) + 3 \operatorname{Ni}^{0}(s) \longrightarrow 2 \operatorname{Au}^{0}(s) + 3 \operatorname{Ni}^{2+}(aq)$$

Subproblem 2b) The reduction reactions are:

$$\begin{split} & Fe^{3+}(aq) + e^{-} \longrightarrow Fe^{2+}(aq) \,, \\ (N^{+V}O_{3}^{-II})^{-}(aq) + 4\,H^{+} + 3\,e^{-} \longrightarrow N^{+II}O^{-II}(g) + 2H_{2}O(l) \,. \end{split}$$

For iron, the reduction potential is $E_{\rm red}^{\circ}({\rm Fe}^{3+} \longrightarrow {\rm Fe}^{2+}) \doteq 0.77 \, {\rm V}$; for the nitrate reduction $E_{\rm red}^{\circ}(({\rm NO}_3)^- \longrightarrow {\rm NO}) \doteq 0.96 \, {\rm V}$. The reaction with nitrate has a higher reduction potential; the iron is therefore being oxidized at the anode. The voltage across the cell for a spontaneous reaction is then

$$E_{\text{cell}}^{\circ} = 0.96 \,\text{V} - (0.77 \,\text{V}) = 0.19 \,\text{V}$$

The whole reaction takes the form

$$3 \operatorname{Fe}^{2+}(\mathrm{aq}) + (\mathrm{NO}_3)^-(\mathrm{aq}) + 4 \operatorname{H}^+ \longrightarrow 3 \operatorname{Fe}^{3+}(\mathrm{aq}) + \operatorname{NO}(\mathrm{g}) + 2 \operatorname{H}_2 \operatorname{O}(\mathrm{l}).$$

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Problem 3

In a fuel cell, electrical energy is created, so the voltage across the cell should be positive. For now, we will denote it as E_{cell} . For one electron, we can obtain the work $W = E_{\text{cell}}e$. To solve the problem, we only need to determine E_{cell} and the number of electrons that will travel throughout the circuit if we let a kilogram of hydrogen react.

To begin, we calculate the voltage. We will write the (unbalanced) chemical reaction first; we will then determine the oxidation numbers and find out what is oxidized and what is reduced

$$\mathrm{H_2}^0 + \mathrm{O_2}^0 \longrightarrow \mathrm{H_2}^{+\mathrm{I}}\mathrm{O}^{-\mathrm{II}}$$

Oxygen is reduced and hydrogen is oxidized. There are multiple options as to what individual half-reactions take place depending on the fuel cell type; however, the voltage across the cell must stay the same, as we have the same reactants and products. At the anode, there is a possibility of a reaction

$$\mathrm{H_2}^0 \longrightarrow 2 \mathrm{H}^+ + 2 \mathrm{e}^-,$$

which has a standard reduction potential $E_{\rm red}(\text{anode}) = 0.00 \,\text{V}$; as is obvious from the definition of this scale.

At the cathode, this reaction takes place:

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

for this reaction, we find the tabled potential $E_{\rm red}(\text{cathode}) = 1.23 \text{ V}$. Now, we only substitute into our equation for the calculation of voltage across the cell and get

$$E_{\text{cell}} = E_{\text{red}}(\text{cathode}) - E_{\text{red}}(\text{anode}) = 1.23 \,\text{V}.$$

The complete electrochemical reaction is then

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

For one atom of hydrogen, a single electron travels through the circuit. If the released energy for one electron is 1.23 eV, then we need to determine the number of particles in one kilogram of hydrogen. The number of moles of hydrogen atoms in a kilogram is

$$n = \frac{m}{M_{\rm H}} \doteq 992 \,\mathrm{mol}\,,$$

where we substituted $M_{\rm H} = 1.00784 \,\mathrm{g \cdot mol^{-1}}$ as molar mass of a hydrogen atom. Our wanted energy is then

$$E_{\mathrm{H}_{2}} = nN_{A}eE_{\mathrm{cell}} = nFE_{\mathrm{cell}} \doteq 118 \,\mathrm{MJ \cdot kg_{H_{2}}^{-1}}$$

No other fuel has such high gravimetric energy density as hydrogen.

In the second half of the problem, we were tasked with describing a similar situation in which the total voltage across the cell is zero (i.e., Q = K). In that case, the Nernst equation is simplified into

$$E_{\rm cell}^{\circ} = \frac{RT}{zF} \ln K \;\; ,$$

from where

$$K = \exp\left(\frac{zF}{RT}E_{\text{cell}}^{\circ}\right) = 1.6 \cdot 10^{83}.$$

This number is extremely high and unfeasible in practice. Even if we considered only one oxygen or hydrogen molecule as a reactant, it would still have to be allotted about as many water molecules as there are atoms in the whole observable universe. The exact value greatly differs based on the precision with which we substitute the quantities in the exponent.

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Problem 4

Consider the direction of this reaction

$$\operatorname{Cu}^{0}(s) + \operatorname{Ag}^{+}(aq) \longrightarrow \operatorname{Cu}^{2+}(aq) + \operatorname{Ag}^{0}(s).$$

In this direction, copper is being oxidized and silver is reduced. For the reaction

$$\operatorname{Ag}^+(\operatorname{aq}) + \operatorname{e}^- \longrightarrow \operatorname{Ag}^0(\operatorname{s}),$$

the standard reduction potential is $E^{\circ}_{red}(Ag^+(aq) \longrightarrow Ag^0) = 0.80 \text{ V}$; this reaction will take place at the cathode.

At the anode, the reaction

$$Cu^{0}(s) \longrightarrow Cu^{2+}(aq) + 2e^{-}$$

takes place, in which copper oxidized. For this reaction, the standard reduction potential is $E_{\rm red}^{\circ}({\rm Cu}^{2+} \longrightarrow {\rm Cu}^{0}) = 0.34 \,{\rm V}$. The reaction with the higher reduction potential occurs as a reduction; silver is indeed reduced and copper is oxidized. The voltage across the cell is then

$$E_{\rm cell}^{\circ} = E_{\rm red}^{\circ}({\rm cathode}) - E_{\rm red}^{\circ}({\rm anode}) = 0.80 \,{\rm V} - 0.34 = 0.46 \,{\rm V}$$

We have to determine Q when the voltage across the cell is $E_{cell} = 0.40 \text{ V}$. We will do so utilizing the Nernst equation

$$Q = \exp\left(\frac{zF}{RT} \left(E_{\text{cell}}^{\circ} - E_{\text{cell}}\right)\right) \doteq 107.$$

Next, we have to express Q as a function of concentrations of the individual reactants and products. We also need to balance the whole equation to the form of

$$\operatorname{Cu}^{0}(s) + 2\operatorname{Ag}^{+}(aq) \longrightarrow \operatorname{Cu}^{2+}(aq) + 2\operatorname{Ag}^{0}(s).$$

We solve for Q as

$$Q = \frac{\left[\mathrm{Cu}^{2+}\right]}{\left[\mathrm{Ag}^{+}\right]^{2}}.$$

The concentration of the reactants and products is, according to our convention, numerically always equal to 1 in the solid state. We, therefore, do not need to consider them in the previous equation. We still have two unknown concentrations. It is true that

$$\left[\mathrm{Ag}^{+}\right] + 2\left[\mathrm{Cu}^{2+}\right] = \left[\mathrm{Ag}^{+}\right]_{0} + 2\left[\mathrm{Cu}^{2+}\right]_{0},$$

where lower index $_0$ denotes the initial concentration given in the problem statement. For every released copper atom, two silver atoms are adsorbed. Concentrations are tightly tied to the initial conditions according to the equation above.

We substitute the concentration of copper into the equation with Q and get

$$Q = \frac{\left[\mathrm{Ag^+}\right]_0 + 2\left[\mathrm{Cu^+}\right]_0 - \left[\mathrm{Ag^+}\right]}{2\left[\mathrm{Ag^+}\right]^2} \,.$$

We solve for $\left[Ag^+\right]$

$$\begin{bmatrix} Ag^{+} \end{bmatrix}^{2} + \begin{bmatrix} Ag^{+} \end{bmatrix} - \left(\begin{bmatrix} Ag^{+} \end{bmatrix}_{0} + 2 \begin{bmatrix} Cu^{+} \end{bmatrix}_{0} \right) = 0,$$
$$\begin{bmatrix} Ag^{+} \end{bmatrix} = \frac{-1 + \sqrt{1 + 8Q \left(\begin{bmatrix} Ag^{+} \end{bmatrix}_{0} + 2 \begin{bmatrix} Cu^{+} \end{bmatrix}_{0} \right)}}{4Q} \doteq 0.076 \,\mathrm{M},$$

where the sign convention comes from the idea that the silver atom concentration should not be negative. The final equation is not correct in terms of units; we, however, made our peace with this fact the moment we substituted the number 1 as the concentration on the electrode, instead of calculating with those values until the end.

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