## Solution for exercise series 2

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1. Write down explanations of the following terms or answers on the queries
   (a) What is the EMF of a galvanic cell? Specify the relation between the maximum reversible work of a reaction and the EMF.

*The maximum potential of a cell that could be put at work in order to move electrons from anode to cathode through the external wiring,*

$$E_{\mathrm{el}}^{\mathrm{C}} - E_{\mathrm{el}}^{\mathrm{A}} = E_{\mathrm{cell}} = \varphi^{\mathrm{C}} - \varphi^{\mathrm{A}}$$

*It is directly proportional to the reaction Gibbs free energy,* $E_{\mathrm{cell}} = -\frac{\Delta_{\mathrm{r}} G}{|v_{\mathrm{e}}| F}$

*i.e. it is only determined by the thermodynamic properties of the cell. Ideally, it could only be harvested, if no current were flowing through the cell, i.e. under open circuit conditions. Under real conditions, i.e. in an operating electrochemical cell, a finite current will be drawn, electrons will perform work and the cell will operate at a certain power density, given by* $P = j \cdot \Delta V$, *where* $\Delta V$ *is the actual potential difference between cathode and anode that forces electrons to move. Finite currents always imply irreversible voltage losses and thus,* $\Delta V < E_{\mathrm{cell}}$.

   (b) Why can Galvani potentials between distinct phases not be measured?

*The two contacting phases will have distinct chemical composition. Therefore, upon transferring charged particles (which could be seen as test particles for probing the local Galvani potentials) between these phases not only electrostatic work but also chemical work will have to be performed (in other words: there will also be a difference in chemical potentials, look up definitions of chemical potentials and electrochemical potentials). Moreover, charges will have to be moved across the metal surface which possesses a rather nonuniform charge distribution, resulting in the so-called surface potential (look up definitions of Volta potential and Galvani potential).*

   (c) What are the properties of a good reference electrode?

*An ideal reference electrode should have a stable, well-defined (i.e. reproducible) electrochemical potential. Common reference electrodes (SCE, Ag/AgCl,* $Cu/CuSO_4$*) meet this criterion when they are functioning properly. An ideal reference electrode should also have zero impedance.*

(d) Specify the known “standard conditions” as complete as possible.

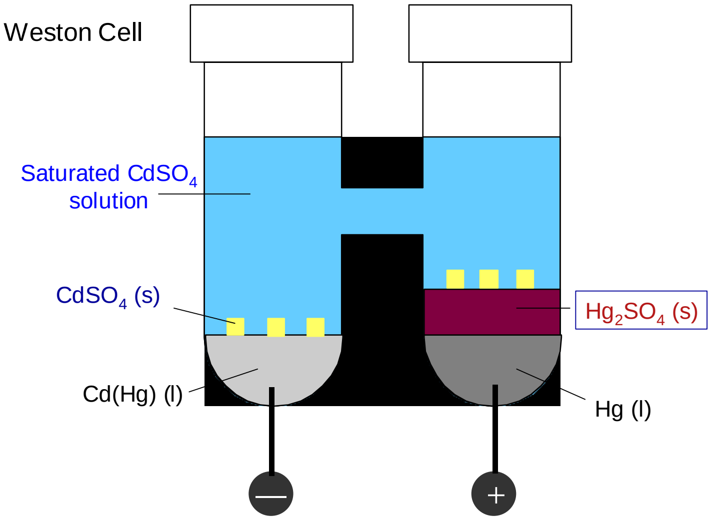
***T = 25°C,***
***gas pressures 1 atm***
***concetrations 1 mol/l***
***activities a = 1***

(e) What is an ideally polarizable electrode?

*An electrode at which no charge transfer processes occur in the considered range of electrode potentials. There will be no Faradaic currents, only double layer charging effects, i.e. only capacitive currents. Such electrodes are needed for instance in supercapacitors. Now you already know that this situation reaquires that the exchange current density of this electrode has to be extremely small.*

**2.** The **Weston cell**, invented by Edward Weston in 1893, is an electrochemical cell. Due to its highly stable voltage it is suitable as a laboratory standard for calibration of voltmeters. It was adopted as the Int. Standard for EMF in 1911.

The Weston Cell



The anode is an amalgam of cadmium with mercury, the cathode is of pure mercury, and the electrolyte is a solution of cadmium sulphate. The overall cell reaction is

$$\mathbf{Cd(Hg) + Hg_2SO_4(s) \leftrightarrow 2\,Hg(l) + Cd^{2+}(aq) + SO_4^{2-}(aq.)}$$

(a) What are the half reactions of this cell?

Anode: $Cd \rightarrow Cd^{2+}(aq) + 2e^-$

Cathode: $Hg_2SO_4(s) + 2e^- \rightarrow 2Hg(l) + SO_4^{2-}(aq)$

(b) Write the Nernst-equation for the cell reaction.

$$E_{\text{cell}} = \varphi^{\text{C}} - \varphi^{\text{A}} = E^0 - \frac{RT}{2F} \ln a_{\text{Cd}^{2+}} a_{\text{SO}_4^{2-}}$$

(c) The EMF is $E = 1.0180$ **V (at 25°C)**. What is the corresponding reaction Gibbs free energy? What is the corresponding rate constant.

$$E_{\text{cell}} = -\frac{\Delta_{\text{r}} G}{2F} \quad \Rightarrow \quad \Delta_{\text{r}} G = -2FE_{\text{cell}} = -196.4\ kJ/mol$$

*Equilibrium rate constant*

$$K = \exp\left(-\frac{\Delta_{\text{r}} G}{RT}\right) = 2.71 \cdot 10^{34}$$

The reaction proceeds spontaneous. The rate constant is >>> 1.

(d) The EMF given in (c) is not the standard EMF, but it is nevertheless very stable. Can you explain why (hint: you can assume that the solution remains saturated, what about other parameters)?

*Consider a variation in cell potential. In general form this is given by*

$$\Delta E_{\text{cell}} = -\frac{RT}{2F} \Delta \ln a_{\text{Cd}^{2+}} a_{\text{SO}_4^{2-}}$$

*Since the solution remains saturated*

$$\Rightarrow \Delta \ln a_{\text{Cd}^{2+}} a_{\text{SO}_4^{2-}} \approx 0$$

$\Rightarrow \Delta E_{\text{cell}} \approx 0$ *is very stable. Even fluctuations in temperature will not significantly affect the cell potential.*

**3.** Consider the cell **Pt | H₂(g, 1 atm) | $\mathbf{H^+}$(aq, a=1) | $\mathbf{Fe^{3+}}$(aq),$\mathbf{Fe^{2+}}$ | Pt,** given that $\mathbf{Fe^{3+} + e^- \rightarrow Fe^{2+}}$ and $E^0 = 0.771$ **V**

(a) If the cell potential is $E = 0.712$ **V (at 25°C)**, what is the ratio of concentrations of $Fe^{3+}$(aq) and $Fe^{2+}$(aq)? Could you determine the absolute values of concentrations or just their ratio?

$H_2(g) \rightarrow 2H^+(aq) + 2e^-$

$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$

*Overall:* $H_2(g) + 2Fe^{3+}(aq) + 2e^- \rightarrow 2H^+(aq) + 2Fe^{2+}(aq) + 2e^-$

$$E_{\text{cell}} = E^{\text{C}}_{\text{el}} - E^{\text{A}}_{\text{el}} = 0.771\ V - \frac{RT}{2F}\ln Q$$

$$= 0.771\ V - \frac{RT}{2F}\ln\frac{a^2_{\text{H}^+}c^2_{\text{Fe}^{2+}}}{P_{\text{H}_2}c^2_{\text{Fe}^{3+}}}$$

***T = 298K,*** $a_{\text{H}^+} = 1$, $P_{\text{H}_2}$ ***=1atm***

$$0.712\ V = 0.771\ V - \frac{RT}{2F}\ln\frac{c^2_{\text{Fe}^{2+}}}{c^2_{\text{Fe}^{3+}}}$$

$$E_{\text{cell}} - E^0 = -0.059\ V$$

$$\frac{c_{\text{Fe}^{2+}}}{c_{\text{Fe}^{3+}}} = 10$$

*Only the ratio can be calculated*

(b) What is the ratio of these concentrations if the cell potential is $E = 0.830$ **V (at 25°C)**?

$$E_{\text{cell}} - E^0 = +0.059V$$

*Note: this is the same absolute value as in (a)!*

$$\Rightarrow \frac{c_{\text{Fe}^{2+}}}{c_{\text{Fe}^{3+}}} = 0.1$$ (the reciprocal of the ratio found in (a))

4. Nernst equation demonstrates that the electrode potential depends upon concentration. A cell made of the same materials, but with different concentrations, will also produce a potential difference. Consider a cell

**Cu | Cu2+ (0.001 M) || Cu2+ (1.00 M) | Cu**

(a) What is standard potential of this cell?

$$E^0 = E^{0\text{C}} - E^{0\text{A}} = \varphi^{0\text{C}} - \varphi^{0\text{A}} = 0$$

(b) Write down the Nernst-equation (using for simplicity concentrations of ions in solution instead of activities). What is the number $\nu_{\text{e}}$ of electrons being transferred?

$$E = E^0 - \frac{RT}{2F}\ln\frac{0.001M}{1.0M} = -\frac{RT}{2F}\ln 0.001 = 0.089V\ ,\ |\nu_e| = 2$$

(c) Calculate $E$ at 25°C for the specified concentrations – see (b)

5. Living cells maintain a small voltage drop across their membrane in its resting state due to the directed transport of sodium ions from inside to outside and the transport of potassium ions in the opposite direction (driven by pumping mechanisms). The inside of the cell is negative with respect to the outside. Consider a mammalian muscle cell with the internal and external ion concentrations:

| **inside** | **outside** |
|---|---|
| $[\mathrm{K}]_\mathrm{i}$ = 140 mM | $[\mathrm{K}]_\mathrm{o}$ = 2.5 mM |
| $[\mathrm{Na}]_\mathrm{i}$ = 10 mM | $[\mathrm{Na}]_\mathrm{o}$ = 115 mM |
| $[\mathrm{Cl}]_\mathrm{i}$ = 15 mM | $[\mathrm{Cl}]_\mathrm{o}$ = 140 mM |

*Two separate compartments (inside & outside), different potential on each side.*

*Separate reactions → mixed potential.*

*Electrode chemical equilibrium:*

$$\tilde{\mu}_\mathrm{i}^\mathrm{in} = \tilde{\mu}_\mathrm{i}^\mathrm{out}$$

$$\tilde{\mu}_i = \mu_i + z_i F \varphi, \;\; \mu_i = \mu_i^0 + RT \ln c_i$$

$$\mu_i^0 + RT \ln c_i^\mathrm{in} + z_i F \varphi^\mathrm{in} = \mu_i^0 + RT \ln c_i^\mathrm{out} + z_i F \varphi^\mathrm{out}$$

$$\Rightarrow \Delta\varphi = \varphi^\mathrm{in} - \varphi^\mathrm{out} = \frac{RT}{z_i F} \ln \frac{c_i^\mathrm{out}}{c_i^\mathrm{in}}$$

*3 species, specified concentrations*
$\Rightarrow$ *over determined system of egs. (only 2 unknowns!* $\varphi^{in}, \varphi^{out}$ *)*
*Not all species in equilibrium*

(a) What are the equilibrium potentials for each of these ions?

$$K^+ : \quad \Delta\varphi_{\mathrm{K^+}} = \frac{RT}{z_i F} \ln \frac{[K^+]^\mathrm{out}}{[K^+]^\mathrm{in}} = \frac{RT}{F} \ln \frac{2.5}{140} = -0.104V$$

$$Na^+ : \quad \Delta\varphi_{\mathrm{Na^+}} = \frac{RT}{z_i F} \ln \frac{[Na^+]^\mathrm{out}}{[Na^+]^\mathrm{in}} = \frac{RT}{F} \ln \frac{115}{10} = 0.063V$$

$$Cl^- : \quad \Delta\varphi_{\mathrm{Cl^-}} = \frac{RT}{z_i F} \ln \frac{[Cl^-]^\mathrm{out}}{[Cl^-]^\mathrm{in}} = -\frac{RT}{F} \ln \frac{140}{15} = -0.058V$$

(b) Calculate the total molar Gibbs free energy of reaction and the corresponding voltage across the cell membrane.

$$\Delta_r G = \Delta_r G_{K^+} + \Delta_r G_{Na^+} + \Delta_r G_{Cl^-}$$

$$\Delta_r G_{K^+} = -F\Delta\varphi_{K^+} = +9.984 \cdot 10^3 J \cdot mol^{-1}$$
$$\Delta_r G_{Na^+} = -F\Delta\varphi_{Na^+} = -6.048 \cdot 10^3 J \cdot mol^{-1}$$
$$\Delta_r G_{Cl^-} = -F\Delta\varphi_{Cl^-} = -5.53 \cdot 10^3 J \cdot mol^{-1}$$

$$\Rightarrow \Delta_r G = -1.586 \cdot 10^3 J \cdot mol^{-1}$$

$$\Delta\varphi = -\frac{\Delta_r G}{F} = +0.0165 V$$