

**Problem III.S ... electrochemistry 3 – kinetics and efficiency**

10 points;

průměr 4,61; řešilo 38 studentů

1. In previous parts, we used a model where Gibbs free energy increases linearly and then decreases depending on the reaction coordinate to calculate the change in activation barriers for both the forward and the reverse reaction. Consider the slopes of these straight lines in figure 4 of this part of the series to be  $s_f > 0$  for the forward reaction and  $s_b < 0$  for the reverse reaction. Find the relationship between  $\alpha$  and  $s_f$  and  $s_b$ . – 3 points
2. It is possible to use an electrochemical cell to compress gases instead of mechanical pistons. Consider a simplified model of such a cell for hydrogen compression. Assume we have two standard hydrogen electrodes in beakers, filled with a solution of concentration  $[H^+] = 1$  M. One electrode is connected to a reservoir (i.e., an infinite volume) of gaseous hydrogen with a pressure of 1 bar, and the other is also connected to hydrogen of the same pressure, but only a volume of 10 l. We apply a voltage of 25 mV to the cell, causing gaseous hydrogen to start forming at the second electrode. We reached a pressure of 2 bar in the bottle at time  $t_{2\text{ bar}} = 1.2$  h. How long did it take for the pressure to increase to 90 % of its maximum value? Assume the beakers with  $H^+$  are large enough that their concentrations remain constant during the process, and everything occurs at a temperature of 25 °C. – 5 points
3. Consider a Carnot heat engine with the corresponding efficiency, where the cooler temperature is  $T_c = 40$  °C. What is the temperature  $T_h$  from which would this heat source achieve higher efficiency than the electrochemical reaction of hydrogen forming water, which also occurs at temperature  $T_h$ ? For water vapor, use  $\Delta G_{100} = 225 \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta H_{100} = 248 \text{ kJ}\cdot\text{mol}^{-1}$ , both valid at a temperature of 100 °C. – 2 points

*Jarda thinks the 3rd part of the series should be the hardest.*

**Commentary on the submitted solutions**

In the original wording of *subproblem 3*, the temperature of the reaction for the formation of water was not specified, nor was it stated to which temperature the values of  $\Delta G_{100}$  and  $\Delta H_{100}$  refer. Almost all solvers compared the efficiency of the Carnot engine with a reaction of water formation at given  $\Delta G_{100}$  and  $\Delta H_{100}$ , i.e., at 100 °C. Due to the ambiguity of the problem statement, we accepted this solution with  $T_h \doteq 3400$  K as correct.

However, in our sample solution, we also account for the reduction in efficiency arising from the relationship used to calculate Gibbs free energy from enthalpy. We apologize for the imprecise formulation of the problem.

The second subproblem was designed so that we could work with a standard hydrogen electrode, which is defined for a hydrogen pressure of 1 bar, but at one of the electrodes, the pressure increases. The pressure, therefore, affects the concentration of products and shifts the potential in the Nernst equation, so the applied voltage ultimately compensates for the pressure difference. By similar reasoning, we can conclude that in the Butler-Volmer equation, we should use the pressure at the individual electrodes instead of the concentrations. Some solvers correctly estimated the dependence of the pressure in the bottle as exponential, but the reasoning via the Butler-Volmer equation was missing.

*Subproblem 1*

We will start from Figure 4 in the series, which we will redraw in our solution. Let us first consider a situation when  $\Delta E = 0$ , meaning we are working under standard conditions. Let the activation energy for the forward reaction be  $E_{a,f}(0)$  and for the reverse reaction  $E_{a,f}(0) - \Delta G^\circ$ , regardless of whether the reaction is spontaneous or not.

Let us denote the reaction coordinate as  $x$  regardless of its physical meaning. Let the Gibbs energy  $G$  of the reactants be zero for  $x < 0$ , and starting from  $x = 0$ , let it increase linearly according to the definition as  $G = s_f x$  until it reaches the value  $E_{a,f}(0)$ . This occurs for

$$x_1 = \frac{E_{a,f}(0)}{s_f}.$$

Then,  $G$  begins to decrease linearly, following the relation

$$G(x) = s_b(x - x_1) + E_{a,f}(0),$$

until it reaches the value  $-\Delta G^\circ$ , where it becomes constant.

Now, we lower the energy of the reactants by  $nF\Delta E$ , just as we did in the series. The rising part of  $G$  in the energy barrier region now becomes

$$G_{\Delta E}(x) = s_f x - nF\Delta E,$$

while the descending part remains unchanged. Therefore, the intersection point, and thus the maximum value of  $G$ , has shifted. The coordinate with the peak value of the energy barrier now lies at

$$s_f x_2 - nF\Delta E = s_b(x_2 - x_1) + E_{a,f}(0) \quad \Rightarrow \quad x_2 = \frac{E_{a,f}(0) + nF\Delta E - s_b x_1}{s_f - s_b}.$$

All of this is clearly illustrated in Figure 1.

The height of the forward energy barrier is therefore

$$\begin{aligned} E_{a,f}(\Delta E) &= G_{\Delta E}(x_2) - G_{\Delta E}(0) = s_f x_2 - nF\Delta E - (-nF\Delta E) = s_f x_2 = \\ &= s_f \frac{E_{a,f}(0) + nF\Delta E - s_b x_1}{s_f - s_b} = \frac{(s_f - s_b) E_{a,f}(0) + s_f nF\Delta E}{s_f - s_b} \\ &= E_{a,f}(0) + \frac{s_f}{s_f - s_b} nF\Delta E. \end{aligned}$$

In the series, we considered the height of the barrier to be

$$E_{a,f}(\Delta E) = E_{a,f}(0) + \alpha nF\Delta E,$$

so when comparing these two expressions, we obtain the relation we are looking for

$$\alpha = \frac{s_f}{s_f - s_b}.$$

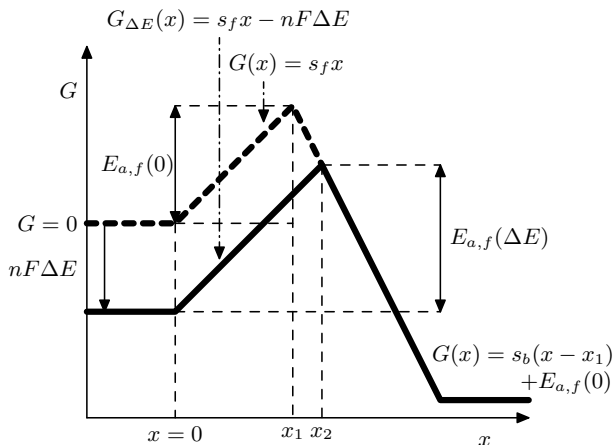
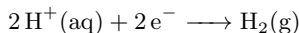


Figure 1: Specific dependence of the free energy on the reaction coordinate with the activation barrier for the forward direction marked.

### Subproblem 2

The following reaction takes place in the second beaker



with hydrogen gas bubbling out of the solution and into a collection bottle. Since hydrogen ions are being reduced at this electrode, it functions as the cathode. At the first electrode, the opposite reaction occurs as hydrogen from the reservoir decomposes into water in the form of ions. Here, hydrogen is being oxidized, making this the anode. According to this equation, we will assume  $z = 2$  throughout the rest of the text.

The standard reduction potential of the cell is

$$E_{\text{cell}}^{\circ} = E_{\text{red}}(\text{cathode}) - E_{\text{red}}(\text{anode}) = 0 \text{ V} - 0 \text{ V} = 0 \text{ V},$$

since both electrodes are, by definition, standard hydrogen electrodes under the given standard conditions. This result is unsurprising, as the reactant and the product are the same substance,  $\text{H}_2$ .

However, once some hydrogen is formed at the cathode, the pressure in the bottle increases, and we are no longer under standard conditions. The cell voltage then changes according to the Nernst equation

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

where  $Q$  corresponds to

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

The concentration of reactants ( $\text{H}_2$  at the anode) is proportional to the pressure, which is  $p_{\text{a}} = 1 \text{ bar}$ . The situation is similar at the cathode, and we can denote the pressure here as  $p$ .

The voltage across the cell depends on the pressure in the bottle at the cathode according to the Nernst equation as

$$E_{\text{cell}} = -\frac{RT}{zF} \ln\left(\frac{p}{p_a}\right).$$

It is negative when  $p > p_a$ , meaning that the reaction does not proceed spontaneously in this direction, and an external voltage must be applied to drive it. This voltage is used to push more and more hydrogen into a confined volume to compress it. For this, we must supply the energy from the outside. If we apply a voltage of  $U = -25$  mV that is greater in absolute value than  $|E_{\text{cell}}|$ , the pressure will increase until

$$U = -\frac{RT}{zF} \ln\left(\frac{p}{p_a}\right).$$

The maximum pressure at voltage  $U$  is thus

$$p_{\text{max}} = p_a \exp\left(-\frac{UzF}{RT}\right) \doteq 7 \text{ bar}.$$

That concludes the thermodynamic analysis. Since we are now interested in the time dependence, we must examine the kinetics and determine the current flowing through the circuit—that is, the rate of hydrogen evolution at the cathode. To do this, we will use the Butler–Volmer equation, but we must first select the appropriate form for our analysis. Although the total cell voltage  $U$  is known and the standard reduction potential is  $E_{\text{cell}}^\circ = 0$  V, suggesting the use of the basic Butler–Volmer form, the overpotential  $\eta = U - E_{\text{cell}}$  is not constant, as the cell potential varies with pressure. Furthermore, the exchange current density  $j_0$  cannot be treated as constant either because it depends on concentrations (and pressures).

Therefore, we use the Butler–Volmer equation in the general form

$$j = zFk^\circ \left( c_r \exp\left(-\frac{\alpha zF}{RT} \Delta E\right) - c_p \exp\left(\frac{(1-\alpha) zF}{RT} \Delta E\right) \right),$$

where  $\Delta E = U - E_{\text{react}}^\circ = U = -25$  mV.

The current above determines how fast the number of particles in the bottle at the cathode increases, and, therefore, how the pressure inside increases. According to the ideal gas law, the number of particles  $N$  in a space with volume  $V$ , at temperature  $T$  and pressure  $p$  is equal to

$$N = \frac{pV}{kT}.$$

The concentration is simply  $c = p/(kT)$ . The change in pressure per unit of time is therefore

$$\frac{dp}{dt} = \frac{kT}{V} \frac{dN}{dt} = \frac{kT}{V} \frac{I}{ze}.$$

The last equation follows from the number of electrons transferred by the current  $I$  through the circuit, which is proportional to the number of molecules formed.

We use a simple relation relating the current density  $j$  and the current  $I$  as  $I = jA$ , where  $A$  is the area of the electrode. Let us substitute from the Butler-Volmer equation

$$\begin{aligned} \frac{dp}{dt} &= \frac{kT}{V} \frac{AF}{e} k^\circ \left( c_r \exp\left(-\frac{\alpha zF}{RT} \Delta E\right) - c_p \exp\left(\frac{(1-\alpha) zF}{RT} \Delta E\right) \right) = \\ &= \frac{AF}{Ve} k^\circ \left( p_a \exp\left(-\frac{\alpha zF}{RT} \Delta E\right) - p \exp\left(\frac{(1-\alpha) zF}{RT} \Delta E\right) \right), \end{aligned}$$

where we substituted pressures for concentrations in the second step. The first term on the right side is constant because we have a pressure reservoir. The second is proportional to the pressure at the cathode. Therefore, we have to solve this differential equation to get the time dependence.

For clarity, let us define constants

$$B_a = \frac{AF}{Ve} k^\circ p_a \exp\left(-\frac{\alpha zF}{RT} \Delta E\right), \quad b_c = \frac{AF}{Ve} k^\circ \exp\left(\frac{(1-\alpha) zF}{RT} \Delta E\right).$$

Our differential equation takes a simple form

$$\frac{dp}{dt} = B_a - b_c p.$$

We solve this using the separation of variables. With a simple rearrangement, we get

$$\frac{dp}{B_a - b_c p} = dt,$$

where we integrate both sides, using substitution  $x = B_a - b_c p$ ,  $dx = -b_c dp$  giving us

$$-\frac{1}{b_c} \frac{dx}{x} = dt.$$

The integral of  $dx/x$  is a standard result  $\ln x$ . After substituting back for  $x$ , we have

$$-\frac{1}{b_c} \ln(B_a - b_c p) = t + C_1,$$

where  $C$  is the integration constant. Solving for pressure as a function of time, after several algebraic steps, it gives us

$$p = \frac{1}{b_c} (B_a - C_2 \exp(-b_c t)).$$

At time  $t = 0$  we have  $p = p_a$ , from which we calculate the constant  $C_2$  as

$$C_2 = B_a - p_a b_c.$$

Substituting back for  $B_a$  and  $b_c$  we get

$$p = p_a \exp\left(-\frac{zF}{RT} \Delta E\right) \left(1 - \left(1 - \exp\left(\frac{zF}{RT} \Delta E\right)\right) \exp(-b_c t)\right).$$

The pressure increases over time, as expected, and approaches the maximum pressure  $p_{\max} = p_a \exp(-zF/(RT)\Delta E)$ .

The only unknown in the equation is the constant  $b_c$ . However, we can find it using the condition that at time  $t_{2 \text{ bar}}$ , the pressure is  $p = p_2 = 2 \text{ bar}$ . We substitute this condition into our expression and obtain

$$b_c = \frac{1}{t_{2 \text{ bar}}} \ln \left( \frac{1 - \exp\left(\frac{zF}{RT} \Delta E\right)}{1 - \frac{p_2}{p_{\max}}}\right).$$

Here, it is useful to realize that we would get the same expression using the pair  $p_{90 \%} = 0.9p_{\max}$  and  $t_{90 \%}$

$$b_c = \frac{1}{t_{90 \%}} \ln \left( \frac{1 - \exp\left(\frac{zF}{RT} \Delta E\right)}{1 - \frac{p_{90 \%}}{p_{\max}}}\right).$$

By comparing these two expressions, we arrive at the following ratio

$$t_{90 \%} = t_{2 \text{ bar}} \frac{\ln \left( \frac{1 - \exp\left(\frac{zF}{RT} \Delta E\right)}{1 - \frac{p_{90 \%}}{p_{\max}}}\right)}{\ln \left( \frac{1 - \exp\left(\frac{zF}{RT} \Delta E\right)}{1 - \frac{p_2}{p_{\max}}}\right)}.$$

Now, it is enough to substitute  $p_{90 \%} = 0.9p_{\max}$  yielding the final expression

$$t_{90 \%} = t_{2 \text{ bar}} \frac{\ln(10 (1 - \exp\left(\frac{zF}{RT} \Delta E\right)))}{\ln \left( \frac{1 - \exp\left(\frac{zF}{RT} \Delta E\right)}{1 - \frac{p_2}{p_{\max}}}\right)} \doteq 14 \text{ h},$$

which we can rewrite into a more elegant form

$$t_{90 \%} = t_{2 \text{ bar}} \frac{\ln \left( \frac{p_{\max} - p_a}{p_{\max} - p_{90 \%}} \right)}{\ln \left( \frac{p_{\max} - p_a}{p_{\max} - p_2} \right)}.$$

By substituting another pressure instead of  $p_{90 \%}$ , we would get the time for that specific pressure.

### Subproblem 3

For the Carnot cycle, the efficiency is given by the well-known relationship

$$\eta_C = 1 - \frac{T_c}{T_h}.$$

This efficiency increases with rising  $T_h$ . Let us compare it with the ratio of  $\Delta G$  and  $\Delta H$  in our reaction

$$\eta_{H_2} = \frac{\Delta G}{\Delta H} = \frac{\Delta H - T_h \Delta S}{\Delta H},$$

where, in contrast, the efficiency decreases with increasing temperature. In both cases, the expression represents the efficiency of extracting useful work from a thermodynamic system.

We know the values of  $\Delta H_{100} = 248 \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta G_{100} = 225 \text{ kJ}\cdot\text{mol}^{-1}$  at  $T_{100} = 100 \text{ }^\circ\text{C}$ . To find the  $\Delta G$  for all the other temperatures, we need to calculate  $\Delta S$ . We express it as

$$\Delta S_{100} = \frac{\Delta H_{100} - \Delta G_{100}}{T_{100}} \doteq 0.048 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}.$$

We get

$$1 - \frac{T_c}{T_h} = \frac{\Delta H_{100} - T_h \Delta S_{100}}{\Delta H_{100}} \Rightarrow T_h = \sqrt{\frac{\Delta H_{100}}{\Delta S_{100}}} T_c.$$

After substituting for  $\Delta S$ , we can finally express the temperature we are looking for

$$T_h = \sqrt{\frac{\Delta H_{100}}{\Delta H_{100} - \Delta G_{100}}} T_c T_{100} \doteq 1\,120\text{ K} = 850\text{ }^\circ\text{C}.$$

At very high temperatures, the electrochemical efficiency becomes so low that using hydrogen directly as a fuel for heat production is more effective. However, this is a purely theoretical consideration that neglects practical constraints, as implementing such a system would be technically challenging. In practice, it is generally more efficient to reconvert the hydrogen into water electrochemically to generate electricity.

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