Homework 2, solution

In this homework you train your skills on theoretical treatment and calculations of the temperature and pressure dependence of the reversible cell voltage of a fuel cell.

Problem:

Let's assume that our hydrogen/oxygen fuel cell has reversible voltage $E = E_1$ when the partial pressure of oxygen at the cathode side is $p_{O2} = p_{O2,1}$, the partial pressure of hydrogen at the anode side is $p_{H2} = p_{H2,1}$ and the fuel cell is operated at temperature $T = T_1$.

  a) What would the partial pressures of the reactant gases ($p_{O2,2}$ and $p_{H2,2}$) need to be, to keep the cell voltage at its initial value ($E = E_2 = E_1$), when we increase the cell temperature from T_1 to T_2? Note: this can be accomplished by adjusting the partial pressure of either O_2, H_2, or both.
  b) Consider a hydrogen/oxygen fuel cell that is operated initially at $T_1 = 45$ °C, while supplying air at 1 atm pressure to the cathode and hydrogen at 1 atm pressure to the anode. Keeping the hydrogen pressure constant ($p_{H2,2} = p_{H2,1} = 1$ atm), what would the partial pressure of oxygen at the cathode need to be, to keep the same reversible cell voltage, when the temperature of the fuel cell is increased to 85 °C?
  c) If we did not do the pressure adjustment in the previous case, how much would the reversible cell voltage change?

Supporting reading from the course book (O'Hayre et al., Fuel cell fundamentals, 2016):

  • Sections 2.4.1 – 2.43, p. 47 – 50
  • Nernst equation for H_2/O_2 fuel cell: eq. (2.90) – (2.93), p. 53
  • "Pressure, temperature, and Nernst equation" box, p. 53 - 54

Solution:

a)

At arbitrary temperature T and activities (partial pressures) the reversible cell voltage of a fuel cell is given by (O´Hayre eqs. 2.95 and 2.96):

$$E = E_T - \frac{RT}{nF} \ln \frac{\Pi a_{products}^{v_i}}{\Pi a_{reactants}^{v_i}} \tag{1}$$

$$E = E^0 + \frac{\Delta s}{nF}(T - T_0) - \frac{RT}{nF} \ln \frac{\Pi a_{products}^{v_i}}{\Pi a_{reactants}^{v_i}} \tag{2}$$

where entropy of the reaction Δs (= Δs_{rxn}, a simplified notation is used here) has been assumed independent of temperature (an approximation), and E^0 is the reversible cell voltage at the standard state condition, namely when the reactants and products are present at unit activities and temperature is $T = T_0 = 298.15$ K.

For a H_2/O_2 fuel cell, which has the total cell reaction $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ and $n = 2$, equation (2) becomes

$$E = E^0 + \frac{\Delta s}{2F}(T - T_0) - \frac{RT}{2F}\ln\left[\frac{1}{\left(\frac{p_{H_2}}{p_0}\right)\left(\frac{p_{O_2}}{p_0}\right)^{\frac{1}{2}}}\right] \tag{3}$$

$$E = E^0 + \frac{\Delta s}{2F}(T - T_0) + \frac{RT}{2F}\ln\left[\left(\frac{p_{H_2}}{p_0}\right)\left(\frac{p_{O_2}}{p_0}\right)^{\frac{1}{2}}\right] \tag{4}$$

where the activities of H_2 and O_2 in eq. (2) were expressed as the ratio of their partial pressures and the standard state pressure $p_0 = 1$ bar. To simplify the equations, it is customary to redefine the partial pressure ratios with relative (normalized) pressure as $p_i \equiv p_i/p_0$ (i.e. measured as multiples of 1 bar):

$$E = E^0 + \frac{\Delta s}{2F}(T - T_0) + \frac{RT}{2F}\ln\left[p_{H_2}p_{O_2}^{\frac{1}{2}}\right] \tag{5}$$

You often see the Nernst equation written with these relative standard pressures directly.

Using this equation, the reversible cell voltage in state 1 (T_1, $p_{O2,1}$, $p_{H2,1}$) and state 2 (T_2, $p_{O2,2}$, $p_{H2,2}$) are

$$E_1 = E^0 + \frac{\Delta s}{2F}(T_1 - T_0) + \frac{RT_1}{2F}\ln\left[p_{H_2,1}p_{O_2,1}^{\frac{1}{2}}\right] \tag{7a}$$

$$E_2 = E^0 + \frac{\Delta s}{2F}(T_2 - T_0) + \frac{RT_2}{2F}\ln\left[p_{H_2,2}p_{O_2,2}^{\frac{1}{2}}\right] \tag{7b}$$

In the problem we require that $E_2 = E_1$, which guides us to the solution. Equating eq. 7a and 7b we get

$$E_1 = E_2 \tag{8}$$

$$E^0 + \frac{\Delta s}{2F}(T_2 - T_0) + \frac{RT_2}{2F}\ln\left[p_{H_2,2}p_{O_2,2}^{\frac{1}{2}}\right] = E^0 + \frac{\Delta s}{2F}(T_1 - T_0) + \frac{RT_1}{2F}\ln\left[p_{H_2,1}p_{O_2,1}^{\frac{1}{2}}\right] \tag{9}$$

The terms containing E^0 and T_0 cancel out

$$\frac{\Delta s}{2F}T_2 + \frac{RT_2}{2F}\ln\left[p_{H_2,2}p_{O_2,2}^{\frac{1}{2}}\right] = \frac{\Delta s}{2F}T_1 + \frac{RT_1}{2F}\ln\left[p_{H_2,1}p_{O_2,1}^{\frac{1}{2}}\right] \tag{10}$$

Also the factor $1/2F$ cancels out, and we can collect the temperatures at both sides as a common factor

$$T_2\left(\Delta s + R\ln\left[p_{H_2,2}p_{O_2,2}^{\frac{1}{2}}\right]\right) = T_1\left(\Delta s + R\ln\left[p_{H_2,1}p_{O_2,1}^{\frac{1}{2}}\right]\right) \tag{11}$$

Rearranging we can solve for the partial pressures at state 2

$$\ln\left[p_{H_2,2}p_{O_2,2}^{\frac{1}{2}}\right] = \frac{T_1}{T_2R}\left(\Delta s + R\ln\left[p_{H_2,1}p_{O_2,1}^{\frac{1}{2}}\right]\right) - \frac{\Delta s}{R} \tag{12}$$

$$p_{H_2,2}p_{O_2,2}^{\frac{1}{2}} = e^{\frac{1}{R}\left[\frac{T_1}{T_2}\left(\Delta s + R\ln\left[p_{H_2,1}p_{O_2,1}^{\frac{1}{2}}\right]\right) - \Delta s\right]} \tag{13}$$

This is our result. (We could work the logarithm out from the exponent, to simplify further). We can see that the reversible cell voltage can be maintained constant either by changing the partial pressure of oxygen, hydrogen, or both, so that their product $p_{H_2,2}p_{O_2,2}^{\frac{1}{2}}$ takes the value given by the right hand side of equation 13. The required partial pressures depend on the ratio of the two temperature levels (T_1/T_2), the partial pressured of the gases at state 2, and the entropy change of the cell reaction (which was assumed constant).

b)

In this example calculation, we have $T_1 = 45\ °C = 318.15\ K$, $p_{H2,1} = 1$ (atm ≈ bar), and $p_{O2,1} = 0.21 p_{air,1} = 0.21$. Note: we are using air instead of pure oxygen at the cathode, and air contains 21 % oxygen. We do the pressure adjustment with oxygen only, keeping the hydrogen pressure constant: $p_{H2,2} = p_{H2,1} = 1$ (1 bar). The partial pressure of oxygen, $p_{O2,2}$, required to keep the cell voltage constant when temperature is increased to $T_2 = 85$ °C = 358.15 K, can be obtained by solving for $p_{O2,2}$ in equation 13:

$$p_{H_2,2}p_{O_2,2}^{\frac{1}{2}} = e^{\frac{1}{R}\left[\frac{T_1}{T_2}\left(\Delta s + R\ln\left[p_{H_2,1}p_{O_2,1}^{\frac{1}{2}}\right]\right)-\Delta s\right]} \tag{13}$$

$$p_{O_2,2} = \left[\frac{1}{p_{H_2,2}}e^{\frac{1}{R}\left[\frac{T_1}{T_2}\left(\Delta s + R\ln\left[p_{H_2,1}p_{O_2,1}^{\frac{1}{2}}\right]\right)-\Delta s\right]}\right]^2 \tag{14}$$

This is pretty hairy expression, but we are almost finished. From the problem statement we know the values of all the other quantities on the right hand side, except the *entropy change of the reaction* Δs. Since we assumed it constant, we can used its value at the standard state conditions: $\Delta s = \Delta s^0$. To get a value for Δs^0 we have to consult thermodynamic tables, where it might be found already calculated for us for the H_2/O_2 fuel cell reaction, or, we can calculate it from the standard state entropies of the reactants and products, in the same way as the *standard state enthalpy of reaction* is calculated from the formation enthalpies of the reactants and products (see O'Hayre (2016), section 2.2.1, page 35).

The total cell reaction being $H_2 + ½O_2 \rightarrow H_2O$, the standard state entropy of reaction is

$$\Delta s^0 = [s^0(H_2O_{liq}] - [s^0(H_2) + \frac{1}{2}s^0(O_2)] \tag{15}$$

$$\Delta s^0 = [69.95\frac{J}{molK}] - [130.68\frac{J}{molK} + \frac{1}{2}\cdot 205.00\frac{J}{molK}] \tag{16}$$

$$\Delta s^0 = -163.53\frac{J}{molK} \qquad\qquad \text{298.15 K)} \tag{17}$$

Now we have all that is needed to calculate equation 14 with values

$$p_{O_2,2} = \left[\frac{1}{1}e^{\frac{1}{8.314\frac{J}{mol\ K}}\cdot\left[\frac{318.15\ K}{358.15\ K}\cdot\left(\text{-163.58}\frac{J}{mol\ K}+8.314\frac{J}{mol\ K}\cdot\ln\left[1\cdot 0.21^{\frac{1}{2}}\right]\right)+163.58\frac{J}{mol\ K}\right]}\right]^2 \tag{18}$$

$$p_{O_2,2} = 20.25\ \text{bar} = 20\ \text{bar}$$

The partial pressure of oxygen has to be increased to 20 bar, which could be achieved by pressurizing the air at the cathode side to 20 bar / 0.21 = **95 bar**. This a huge pressure, which the cell would hardly sustain mechanically. We must ask, is there really need for this pressure adjustment in practice?

c)

If the pressure adjustment was not done, the cell voltage would change from the initial value. The change in the reversible cell voltage can be calculated from equations (7a,b) with $T_0 = 298.15$ K, $T_1 = 318.15$ K, $T_2 = 358.15$ K, $p_{O2,1} = p_{O2,1} = 0.21$, and $p_{H2,1} = p_{H2,1} = 1$)

$$E_2 - E_1$$

$$= \left[\frac{\Delta s}{2F}(T_2 - T_0) + \frac{RT_2}{2F} \ln\left[0.21^{\frac{1}{2}}\right] \right] - \left[\frac{\Delta s}{2F}(T_1 - T_0) + \frac{RT_1}{2F} \ln\left[0.21^{\frac{1}{2}}\right] \right]$$

$$= \frac{\Delta s}{2F}(T_2 - T_1) + \frac{R(T_2 - T_1)}{2F} \ln\left[0.21^{\frac{1}{2}}\right]$$

$$= \frac{T_2 - T_1}{2F} \left(\Delta s + R \ln\left[0.21^{\frac{1}{2}}\right] \right)$$

$$= \frac{358.15\,\text{K} - 318.15\text{K}}{2 \cdot 96485 \frac{\text{C}}{\text{mol}}} \left(-163.53 \frac{\text{J}}{\text{mol K}} + 8.314 \frac{\text{J}}{\text{mol K}} \ln\left[0.21^{\frac{1}{2}}\right] \right)$$

$$= \frac{40\,\text{K}}{2 \cdot 96485 \frac{\text{C}}{\text{mol}}} \left(-163.53 \frac{\text{J}}{\text{mol K}} - 6.488 \frac{\text{J}}{\text{mol K}} \right)$$

$$0.032\,\text{V} = 32\,\text{mV}$$

Increasing the cell temperature from 45 °C to 85 °C would decrease the reversible cell voltage by ca. 32 mV, i.e. on by ca. 2 %, with respect to the reversible cell voltage. It is therefore not worth the trouble to compensate it by increasing the air pressure at the cathode side.

Note that the pressure-dependent term in the above calculation brings only $6.488/136.23 = 5$ % contribution to the result. Moreover, the oxygen partial pressure is inside a square root and logarithm, which makes the term highly insensitive to it, as can be seen from the figure below. We can conclude that compensating for temperature-induced decrease in the reversible cell voltage by increasing the air pressure is not a practically feasible solution, nor is it really necessary either, because the voltage decrease is quite small thanks to a relative small temperature increase in this case.
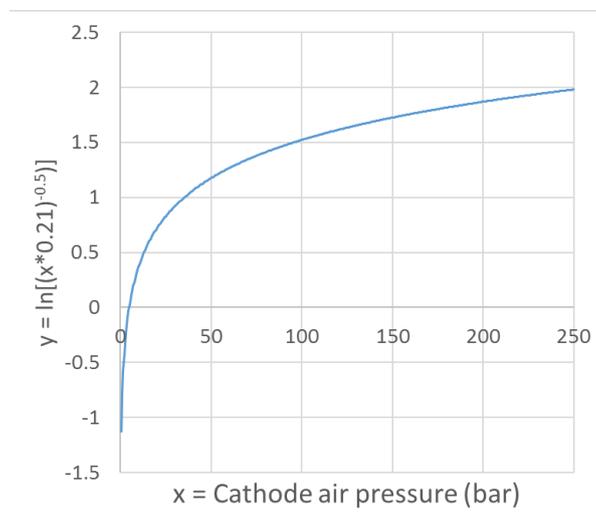
Alternative solutions

1. **Using gaseous instead of liquid water as the product (an incorrect solution)**

In equation (15) we assumed that the water is formed in liquid state. This is correct because the cell temperature is below the boiling point of water. Had we assumed water to be formed in gaseous state, the entropy of water would have been much higher $s^0(H_2O_{(g)})$ = 188.84 J/(mol K) (at standard state), and as a result, the entropy of reaction would have been only -17.34 J/(mol K) and the required oxygen partial pressure only 0.398, i.e. pressurizing the air to 0.398/0.21 = 1.896 = **1.9 bar** would have done the job. When the entropy of reaction is small, temperature increase has smaller effect in the reversible cell voltage, which can be seen directly from eq. (2). Smaller pressure increase was therefore enough to compensate for the temperature increase. However, we should use the entropy of liquid water in this case.

2. **Using Δs value between T_1 and T_2 instead of at T_0 (a more accurate solution)**

In the calculations it was assumed that Δs is temperature-independent and we used its standard state (T_0) value. However, it would make more sense the use Δs value that is taken from the actual temperature range in question, because it would increase the accuracy of the calculation. Calculating the entropy of reaction at the average temperature $(T_1 + T_2)/2 = (318.15$ K $+ 358.15$ K$)/2 = 338.15$ K ≈ 340 K, using the data in Appendix B of O 'Hayre (2016), we get:

$$\Delta s^0 = \left[s^0(H_2O_{(liq)}) \right] - \left[s^0(H_2) + \tfrac{1}{2} s^0(O_2) \right]$$

$$\Delta s^0 = \left[79.85 \, \tfrac{J}{mol \, K} \right] - \left[134.48 \, \tfrac{J}{mol \, K} + \tfrac{1}{2} \cdot 208.92 \, \tfrac{J}{mol \, K} \right]$$

$$\Delta s^0 = -159.09 \, \tfrac{J}{mol \, K} \qquad \text{(at 340 K)}$$

This is 17 % higher value than at 298.15 K, resulting to $p_{O2,2}$ = 17.96 = 18, corresponding to air pressure of 18/0.21 = **86 bar**.

3. **Using thermodynamic tables to account for the temperature dependence directly (the most accurate solution)**

Note that Nernst equation describes change in the reversible cell voltage upon deviation of the reactant and product activities from their unit value at the standard state, which here means unit activity of water and 1 bar pressure for hydrogen and air. We can therefore simply calculate the reversible cell voltage at each temperature from the Gibbs free energy change of the reaction at that temperature as E_T = $-\Delta G_T/nF$. Taking G_T directly from thermodynamic tables allows us to avoid the use any approximate expressions for the temperature-dependence of the reversible cell voltage, which improves the accuracy of the solution.

$$E = -\frac{\Delta G_T}{nF} - \frac{RT}{nF} \ln \frac{\Pi \, a_{products}^{v_i}}{\Pi \, a_{reactants}^{v_i}} \qquad (1)*$$

$$E = -\frac{\Delta G_T}{2F} + \frac{RT}{2F} \ln \left[p_{H_2} p_{O_2}^{\frac{1}{2}} \right] \qquad (5)*$$

Requiring that $E_2 = E_1$, we get

$$-\frac{\Delta G_{T_2}}{2F} + \frac{RT_2}{2F} \ln \left[p_{H_2,2} p_{O_2,2}^{\frac{1}{2}} \right] = -\frac{\Delta G_{T_1}}{2F} + \frac{RT_1}{2F} \ln \left[p_{H_2,1} p_{O_2,1}^{\frac{1}{2}} \right]$$

$$-\Delta G_{T_2} + RT_2 \ln\left[p_{H_2,2}p_{O_2,2}^{\frac{1}{2}}\right] = -\Delta G_{T_1} + RT_1 \ln\left[p_{H_2,1}p_{O_2,1}^{\frac{1}{2}}\right]$$

$$\ln\left[p_{H_2,2}p_{O_2,2}^{\frac{1}{2}}\right] = \frac{(\Delta G_{T_2}-\Delta G_{T_1})}{RT_2} + \frac{T_1}{T_2}\ln\left[p_{H_2,1}p_{O_2,1}^{\frac{1}{2}}\right]$$

$$p_{H_2,2}p_{O_2,2}^{\frac{1}{2}} = e^{\frac{(\Delta G_{T_2}-\Delta G_{T_1})}{RT_2}+\frac{T_1}{T_2}\ln\left[p_{H_2,1}p_{O_2,1}^{\frac{1}{2}}\right]}$$

$$p_{H_2,2}p_{O_2,2}^{\frac{1}{2}} = e^{\frac{(\Delta G_{T_2}-\Delta G_{T_1})}{RT_2}} e^{\frac{T_1}{T_2}\ln\left[p_{H_2,1}p_{O_2,1}^{\frac{1}{2}}\right]}$$

$$p_{H_2,2}p_{O_2,2}^{\frac{1}{2}} = e^{\frac{(\Delta G_{T_2}-\Delta G_{T_1})}{RT_2}} \left(p_{H_2,1}p_{O_2,1}^{\frac{1}{2}}\right)^{\frac{T_1}{T_2}}$$

$$p_{O_2,2} = \left[e^{\frac{(\Delta G_{T_2}-\Delta G_{T_1})}{RT_2}} \left(p_{H_2,1}p_{O_2,1}^{\frac{1}{2}}\right)^{\frac{T_1}{T_2}} p_{H_2,2}^{-1}\right]^2 \qquad (p_{H_2,1} = p_{H_2,1} = 1,\ p_{O_2,1} = 0.21)$$

$$p_{O_2,2} = \left[e^{\frac{(\Delta G_{T_2}-\Delta G_{T_1})}{RT_2}} \left(0.21^{\frac{1}{2}}\right)^{\frac{T_1}{T_2}}\right]^2$$

$$p_{O_2,2} = e^{\frac{2(\Delta G_{T_2}-\Delta G_{T_1})}{RT_2}} 0.21^{\frac{T_1}{T_2}}$$

The Gibbs free energy change at temperatures $T_1 = 318.15$ K ≈ 320 K and $T_2 = 358.15$ K ≈ 360 K can be calculated using the values tabulated in Appendix B of O´Hayre (2016):

$$\Delta G_T = \left[G_T(H_2O_{(liq)})\right] - \left[G_T(H_2) + \frac{1}{2}G_T(O_2)\right]$$

$$\begin{cases} \Delta G_{T_1} = \left[-308.27\,\frac{kJ}{mol}\right] - \left[-41.84\,\frac{kJ}{mol} + \frac{1}{2}\left(-65.66\,\frac{kJ}{mol}\right)\right] = -233.6\,\frac{kJ}{mol} \\ \Delta G_{T_2} = \left[-309.82\,\frac{kJ}{mol}\right] - \left[-47.22\,\frac{kJ}{mol} + \frac{1}{2}\left(-74.02\,\frac{kJ}{mol}\right)\right] = -225.6\,\frac{kJ}{mol} \end{cases}$$

$$\Delta G_{T_2} - \Delta G_{T_1} = 8.0\,\frac{kJ}{mol}$$

The partial pressure of oxygen required for the compensation is therefore

$$p_{O_2,2} = e^{\frac{2\left(8.0\frac{kJ}{mol}\right)}{8.314\frac{J}{mol\,K}\cdot 358.15K}} \cdot 0.21^{\frac{318.15K}{358.15K}} = e^{5.37}\cdot 0.21^{0.8883} = 53.89 = 54$$

This would require pressurizing air to 53.89/0.21 = **257 bar**, which is even higher value than in the previous calculations.

It becomes clear that the solution is highly sensitive to the approximations made in the calculations. Depending on the approach the air should be pressurized to 46, 86 or 257 bar! The reason for so large variation is that the pressure has much weaker effect on the reversible cell voltage than temperature. For this reason, small errors (approximations) in the calculation of the temperature-induced change in it, produce large differences in the pressure difference needed to produce equal but opposite effect (See the figure above).