Redox potential — Influence of the gases' composition

1. *Standard* redox potential $E^{\ominus}$ at 800°C

Reminder:

The *standard* redox potential *does not take into account the concentration of gases*, since it is determined for unit concentration.

The procedure is the same as in ex. 1 of series 2, except that 800°C is considered instead of 100°C. In summary, the redox reaction being $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$, Hess' law is applied to compute $\Delta_{\mathrm{r}}\tilde{h}^{\ominus}_{25°\mathrm{C}\,(g)}$ and $\Delta_{\mathrm{r}}\tilde{s}^{\ominus}_{25°\mathrm{C}\,(g)}$. Gibbs' relation is then used to get $\Delta_{\mathrm{r}}\tilde{g}^{\ominus}_{25°\mathrm{C}\,(g)}$, which is linked to the standard redox potential according to $\Delta_{\mathrm{r}}\tilde{g}^{\ominus}_{(T)} = -\nu_{\mathrm{e}}\mathcal{F}E^{\ominus}_{(T)}$. Finally, a linearization of Gibb's relation allows estimating its slope.

Hess' law: $\Delta_{\mathrm{r}}\tilde{h} = \sum_j \nu_j\, \Delta_{\mathrm{f}}\tilde{h}_j - \sum_i \nu_i\, \Delta_{\mathrm{f}}\tilde{h}_i$ (with *j* products and *i* reactants)

Gibbs' relation: $\Delta_{\mathrm{r}}\tilde{g}_{(T)} = \Delta_{\mathrm{r}}\tilde{h}_{(T)} - T\Delta_{\mathrm{r}}\tilde{s}_{(T)}$

$$E^{\ominus}_{25°\mathrm{C}\,(g)} = 1.184\ \mathrm{V} \quad \text{and} \quad \left.\frac{\partial E^{\ominus}(T)}{\partial T}\right|_{25°\mathrm{C}\,(g)} \cong \frac{\Delta_{\mathrm{r}}\tilde{s}^{\ominus}_{25°\mathrm{C}\,(g)}}{\nu_{\mathrm{e}}\mathcal{F}} = -230\ \mu\mathrm{V/K}$$

The value at 800°C can be computed in one step, from **25°C *(g)*** → 800°C *(g)*:

$$E^{\ominus}_{800°\mathrm{C}} = 1.184 - 230 \cdot 10^{-6} \cdot (800 - 25) = 1.006\ \mathrm{V}$$

Rigorously correct calculations —involving integration of Kirchoff's law— gave 0.978 V, hence the error of the approximation at 800°C is around 3%.

Remark:

The aforementioned linearization is equivalent to consider $\Delta_{\mathrm{r}}\tilde{h}$ and $\Delta_{\mathrm{r}}\tilde{s}$ independent of temperature (which is a fair assumption when there is *no phase-change*). By injecting the term with entropy in the estimation of the slope, it can be shown that this procedure is equivalent to using the following approximation:

$$\Delta_{\mathrm{r}}\tilde{g}_{800°\mathrm{C}} \cong \Delta_{\mathrm{r}}\tilde{h}_{25°\mathrm{C}\,(g)} - 1073.15 \cdot \Delta_{\mathrm{r}}\tilde{s}_{25°\mathrm{C}\,(g)}$$

2. Redox potential *E* as a function of fuel utilization, Υ_{f}

The (non-standard) redox potential takes into account the concentration of the compounds participating in the reaction. It is computed thanks to Nernst's equation.

Nernst's equation:

$$E(T, p_k) = E^{\ominus}(T) - \frac{\mathcal{R}T}{\nu_{\mathrm{e}}\mathcal{F}} \ln(Q_{\mathrm{r}})$$

The quotient of a redox reaction is:

$$Q_{\mathrm{r}} = \frac{\prod_j a_j^{\nu_j}}{\prod_i a_i^{\nu_i}}$$

With *j* and *i* the index of respectively the products and reactants, *a* their activity, and *ν* their stoichiometric coefficient. In the case of gases, activities are equivalent to the partial pressures with respect to the standard pressure, which in their turn can be written in function of molar fractions.

$$Q_\mathrm{r} = \frac{\prod_j a_j^{\nu_\mathrm{j}}}{\prod_i a_i^{\nu_i}} = \frac{\prod_j \left(\frac{p_j}{p^\ominus}\right)^{\nu_j}}{\prod_i \left(\frac{p_i}{p^\ominus}\right)^{\nu_i}} = \frac{\prod_j \left(\tilde{c}_j \frac{p_{\mathrm{mix} \ni j}}{p^\ominus}\right)^{\nu_j}}{\prod_i \left(\tilde{c}_i \frac{p_{\mathrm{mix} \ni i}}{p^\ominus}\right)^{\nu_j}}$$

In this case, the operating pressure p_0 in both the anode and cathode compartments is atmospheric pressure (1 atm). Furthermore, it is assumed the change of pressure along the cell is negligible, so that the pressure is constant. The standard pressure $p^\ominus$ corresponding to the data is 1 bar ≃ 1 atm.[1] Therefore, the pressure of the mixes has no additional effect with respect to the standard pressure. Only the molar fractions (partial pressures) enter into considerations.

The quotient of the reaction for this SOFC is then:

$$Q_\mathrm{r} = \frac{\prod_j \tilde{c}_j^{\nu_\mathrm{j}}}{\prod_i \tilde{c}_i^{\nu_i}} = \frac{\tilde{c}^{\mathrm{an}}_{\mathrm{H_2O}}}{\tilde{c}^{\mathrm{an}}_{\mathrm{H_2}} \left(\tilde{c}^{\mathrm{cat}}_{\mathrm{O_2}}\right)^{1/2}}$$

It is therefore necessary to compute the molar fractions of the species.

a) Molar fractions at anode

The definition of the molar fraction is:

$$\tilde{c}_k = \frac{N_k}{N_\mathrm{mix}} = \frac{\dot{N}_k}{\dot{N}_\mathrm{mix}} \qquad \text{with} \qquad \textstyle\sum_k \tilde{c}_k = 1 \;\;,\;\; k \in \mathrm{mix},\;\; \forall\,\mathrm{mix}$$

Although no indication is given in this exercise regarding the flow rates, it will be shown that it is possible to express numerators and denominators in function of the hydrogen injected, so that it cancels out. This quantity will therefore be considered known (constant) in the following reasoning.

Generally speaking, the molar fractions of hydrogen and steam are, respectively:

$$\tilde{c}^{\mathrm{an}}_{\mathrm{H_2}} = \frac{\dot{N}_{\mathrm{H_2}}}{\dot{N}_\mathrm{an}} \qquad \text{and} \qquad \tilde{c}^{\mathrm{an}}_{\mathrm{H_2O}} = \frac{\dot{N}_{\mathrm{H_2O}}}{\dot{N}_\mathrm{an}} \qquad \text{with} \qquad \dot{N}_\mathrm{an} = \dot{N}_{\mathrm{H_2}} + \dot{N}_{\mathrm{H_2O}} = \mathrm{cst} = \dot{N}^{\mathrm{in}}_{\mathrm{H_2}}$$

Observe that *in this case, the molar rate at anode remains constant.* Indeed, according to the electrochemical reaction, for 1 mole of hydrogen consumed, 1 mole of steam is produced; besides, steam is generated on the anode-side in the case of SOFCs, so that the amount of mole is conserved at anode.

In addition, the molar fraction of steam can be obtained knowing that of hydrogen, since both must sum to unity. It is therefore only necessary to express the flow rate of hydrogen as a function of the fuel utilization, which is simply the amount of hydrogen injected minus the hydrogen that is consumed at (or up to) that fuel utilization:

$$\dot{N}_{\mathrm{H_2}}(\Upsilon_\mathrm{f}) = \dot{N}^{\mathrm{in}}_{\mathrm{H_2}} - \dot{N}^{\mathrm{c}}_{\mathrm{H_2}}(\Upsilon_\mathrm{f})$$

Using the definition of the fuel utilization (for pure hydrogen):

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[1] From 1982, IUPAC recommends using a standard pressure of 1 bar. The previous value of 1 atm is however still used by several other organisms (e.g., NIST). In practice, this makes little difference.

$$\Upsilon_\mathrm{f} = \frac{I_\mathrm{actual}}{I_\mathrm{max}} = \frac{\dot{N}_{\mathrm{H}_2}^\mathrm{c}}{\dot{N}_{\mathrm{H}_2}^\mathrm{in}} = \frac{1}{\lambda_\mathrm{f}}$$

Finally, the molar fractions at anode in function of the fuel utilization are simply given by:

$$\tilde{c}_{\mathrm{H}_2}^\mathrm{an}(\Upsilon_\mathrm{f}) = \frac{\dot{N}_{\mathrm{H}_2}(\Upsilon_\mathrm{f})}{\dot{N}_\mathrm{an}} = \frac{\dot{N}_{\mathrm{H}_2}^\mathrm{in} - \dot{N}_{\mathrm{H}_2}^\mathrm{c}(\Upsilon_\mathrm{f})}{\dot{N}_{\mathrm{H}_2}^\mathrm{in}} = \frac{\dot{N}_{\mathrm{H}_2}^\mathrm{in}(1-\Upsilon_\mathrm{f})}{\dot{N}_{\mathrm{H}_2}^\mathrm{in}} = (1-\Upsilon_\mathrm{f})$$

$$\tilde{c}_{\mathrm{H}_2\mathrm{O}}^\mathrm{an.}(\Upsilon_\mathrm{f}) = 1 - \tilde{c}_{\mathrm{H}_2}^\mathrm{an.}(\Upsilon_\mathrm{f}) = \Upsilon_\mathrm{f}$$

b) Molar fractions at cathode

At cathode, only the molar fraction of oxygen enters in the computation of the reaction's quotient:

$$\tilde{c}_{\mathrm{O}_2}^\mathrm{cat} = \frac{\dot{N}_{\mathrm{O}_2}}{\dot{N}_\mathrm{cat}} \qquad \text{with} \qquad \dot{N}_{\mathrm{O}_2} = \dot{N}_{\mathrm{O}_2}^\mathrm{in} - \dot{N}_{\mathrm{O}_2}^\mathrm{c} \qquad \text{and} \qquad \dot{N}_\mathrm{cat} = \dot{N}_\mathrm{air}^\mathrm{in} - \dot{N}_{\mathrm{O}_2}^\mathrm{c} \neq \mathrm{cst}$$

Pay attention that the consumption of oxygen appears both at the numerator and denominator: *the molar rate at cathode is* not *constant in this case*. Indeed, according to the electrochemical reaction, for 1 mole of oxygen consumed, 2 mole of steam are produced; besides, steam is generated on the anode-side in the case of SOFCs, so that the amount of mole is decreasing at cathode.

Using the definition of the air excess ratio, the molar flow rate of oxygen injected is: $\dot{N}_{\mathrm{O}_2}^\mathrm{in} = \lambda \dot{N}_{\mathrm{O}_2}^\mathrm{st}$

The stoichiometric molar flow rate of oxygen is linked to the hydrogen injected: $\dot{N}_{\mathrm{O}_2}^\mathrm{st} = 0.5\dot{N}_{\mathrm{H}_2}^\mathrm{in}$

The consumption of oxygen is linked to the consumption of hydrogen: $\dot{N}_{\mathrm{O}_2}^\mathrm{c} = 0.5\dot{N}_{\mathrm{H}_2}^\mathrm{c}$

Caution: *stoichiometric* ($^\mathrm{st}$) *and consumed* ($^\mathrm{c}$) are *not interchangeable terms!*

Reusing the definition of the fuel utilization: $\dot{N}_{\mathrm{H}_2}^\mathrm{c} = \Upsilon_\mathrm{f}\dot{N}_{\mathrm{H}_2}^\mathrm{in}$

Using the previous expressions, the molar flow rate of oxygen for a given fuel utilization becomes:

$$\dot{N}_{\mathrm{O}_2}(\Upsilon_\mathrm{f}) = 0.5\lambda\dot{N}_{\mathrm{H}_2}^\mathrm{in} - 0.5\Upsilon_\mathrm{f}\dot{N}_{\mathrm{H}_2}^\mathrm{in} = 0.5\dot{N}_{\mathrm{H}_2}^\mathrm{in}(\lambda - \Upsilon_\mathrm{f})$$

The molar flow rate of air injected can be expressed as:

$$\dot{N}_\mathrm{air}^\mathrm{in} = \frac{\dot{N}_{\mathrm{O}_2}^\mathrm{in}}{\tilde{c}_{\mathrm{O}_2}} = \frac{\lambda\dot{N}_{\mathrm{O}_2}^\mathrm{st}}{\tilde{c}_{\mathrm{O}_2}} = \frac{0.5\lambda\dot{N}_{\mathrm{H}_2}^\mathrm{in}}{\tilde{c}_{\mathrm{O}_2}}$$

So that the total (i.e., of mix) molar flow rate at the cathode for a given fuel utilization becomes:

$$\dot{N}_\mathrm{cat} = \dot{N}_\mathrm{air}^\mathrm{in} - \dot{N}_{\mathrm{O}_2}^\mathrm{c} = \frac{0.5\lambda\dot{N}_{\mathrm{H}_2}^\mathrm{in}}{\tilde{c}_{\mathrm{O}_2}} - 0.5\Upsilon_\mathrm{f}\dot{N}_{\mathrm{H}_2}^\mathrm{in} = \frac{0.5\dot{N}_{\mathrm{H}_2}^\mathrm{in}(\lambda - \tilde{c}_{\mathrm{O}_2}\Upsilon_\mathrm{f})}{\tilde{c}_{\mathrm{O}_2}}$$

Finally, an expression independent of flow rate is found for the molar fraction of oxygen:

$$\tilde{c}_{\mathrm{O}_2}^\mathrm{cat}(\Upsilon_\mathrm{f}) = \frac{0.5\dot{N}_{\mathrm{H}_2}^\mathrm{in}\,\tilde{c}_{\mathrm{O}_2}\,(\lambda - \Upsilon_\mathrm{f})}{0.5\dot{N}_{\mathrm{H}_2}^\mathrm{in}(\lambda - \tilde{c}_{\mathrm{O}_2}\Upsilon_\mathrm{f})} = \frac{\tilde{c}_{\mathrm{O}_2}(\lambda - \Upsilon_\mathrm{f})}{\lambda - \tilde{c}_{\mathrm{O}_2}\Upsilon_\mathrm{f}}$$

If the consumption of oxygen is neglected in the expression of $\dot{N}_{\mathrm{cat}}$, then it becomes:

$$\tilde{c}_{\mathrm{O}_2}^{\mathrm{cat}}(\Upsilon_{\mathrm{f}}) = \frac{\tilde{c}_{\mathrm{O}_2}(\lambda - \Upsilon_{\mathrm{f}})}{\lambda} = \tilde{c}_{\mathrm{O}_2}\left(1 - \frac{\Upsilon_{\mathrm{f}}}{\lambda}\right)$$

Remark:

At low fuel utilization and/or high air excess ratio, the consumption of oxygen is negligible relative to the amount injected. But for, e.g., $\Upsilon_{\mathrm{f}} = 0.9$ and $\lambda = 3$, the residual oxygen is 15.7% from an initial 21% (the approximation above gives 14.7%).

c) Back to Nernst's equation

Replacing the molar fractions by their expression, the quotient of the reaction finally becomes:

$$Q_{\mathrm{r}} = \frac{\tilde{c}_{\mathrm{H_2O}}^{\mathrm{an}}}{\tilde{c}_{\mathrm{H}_2}^{\mathrm{an}}\left(\tilde{c}_{\mathrm{O}_2}^{\mathrm{cat}}\right)^{1/2}} = \frac{\Upsilon_{\mathrm{f}}}{(1 - \Upsilon_{\mathrm{f}})\left(\frac{\tilde{c}_{\mathrm{O}_2}(\lambda - \Upsilon_{\mathrm{f}})}{\lambda - \tilde{c}_{\mathrm{O}_2}\Upsilon_{\mathrm{f}}}\right)^{1/2}}$$

The expression of the redox potential can therefore be computed as a function of the fuel utilization. It is analyzed below.

3. Intermediate terms of Nernst's equation and plot of $E(\Upsilon_{\mathrm{f}})$

$$E(T, p_k) = E^{\ominus}(T) - \Delta E_{\mathrm{composition}} = E^{\ominus}(T) - \frac{\mathcal{R}T}{\nu_{\mathrm{e}}\mathcal{F}}\ln(Q_{\mathrm{r}})$$

At 800°C, $\lambda = 3$ and assuming dry air (~21%-mol oxygen), table 1 and figure 1 are obtained.

Table 1 — Intermediate terms of Nernst's equation in function of the fuel utilization Υ_{f}

Υ_{f} (%)	$\tilde{c}_{\mathrm{O}_2}$ (%)	Q_{r}	$\ln(Q_{\mathrm{r}})$	$\Delta E_{\mathrm{composition}}$	E
0.01	20.999	$2.18 \cdot 10^{-4}$	–8.43	–0.390	1.396
0.1	20.994	$2.18 \cdot 10^{-3}$	–6.13	–0.283	1.289
1	20.944	$2.21 \cdot 10^{-2}$	–3.81	–0.176	1.182
2	20.889	$4.47 \cdot 10^{-2}$	–3.11	–0.144	1.150
5	20.723	$1.16 \cdot 10^{-1}$	–2.16	–0.100	1.106
10	20.443	$2.46 \cdot 10^{-1}$	–1.40	–0.065	1.071
20	19.878	$5.61 \cdot 10^{-1}$	–0.58	–0.027	1.033
50	18.135	$2.35 \cdot 10^{0}$	0.85	0.039	0.966
80	16.314	$9.90 \cdot 10^{0}$	2.29	0.106	0.900
90	15.688	$2.27 \cdot 10^{1}$	3.12	0.144	0.861
95	15.372	$4.85 \cdot 10^{1}$	3.88	0.179	0.826
98	15.181	$1.26 \cdot 10^{2}$	4.83	0.224	0.782
99	15.118	$2.55 \cdot 10^{2}$	5.54	0.256	0.750
99.90	15.060	$2.57 \cdot 10^{3}$	7.85	0.363	0.643
99.99	15.054	$2.58 \cdot 10^{4}$	10.16	0.470	0.536

Observations:

- The variation of the molar fraction of oxygen is small with respect to the changes in the molar fractions of hydrogen and steam (Υ_f).
- The quotient of the reaction changes by several orders of magnitude, but its effect is "damped" by the logarithmic function.
- At high fuel utilization, the (Nernst) redox potential is significantly lower than the standard redox potential (e.g., 18% at $\Upsilon_\mathrm{f} = 95\%$)
- However, the redox potential can actually also take *bigger* values than the standard redox potential!

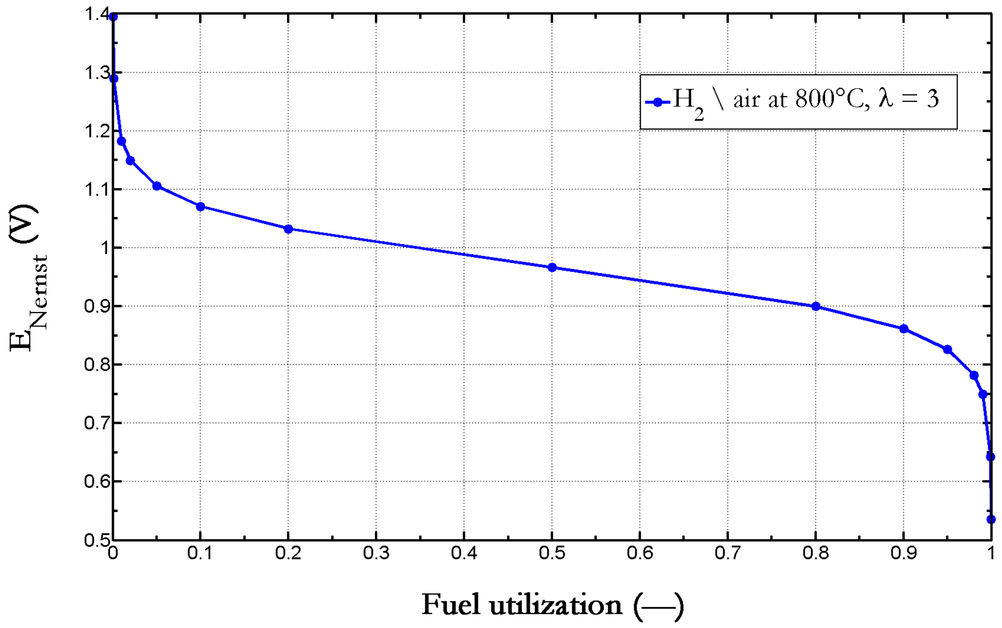

Figure 1 — Redox potential in function of the fuel utilization $E(\Upsilon_\mathrm{f})$ for H_2 & air at 800°C, $\lambda = 3$

4. Is an SOFC operable at 100% fuel utilization without recirculation?

No. The redox potential E (no net external current) strongly drops at high product concentration (= steam), for this fuel cell type (SOFC). In practice, the operation of SOFCs is limited in a single pass at $\Upsilon_\mathrm{f} < 100\%$, 100% being impossible because E would reach $\ln(0) = -\infty$. Recirculation of the anode outlet to its inlet can be carried out in order to convert all of the injected fuel into electricity.

Thinking further:

- What is the domain of validity of Nernst's equation?

Nernst's equation as expressed above is valid for any physical value of its terms, except for $\lambda < 1$. It shows limit at extreme values ($\lambda = 0$, $\lambda = 1$, $\Upsilon_\mathrm{f} = 0$, $\Upsilon_\mathrm{f} = 1$, $\tilde{c}_{O_2} = 0$), though these represent actual physical limits. It is indefinite for $Q_\mathrm{r} < 1$, although this is usually due to a calculation error… However, Nernst's equation is *not* valid (sufficient) to compute the cell voltage (see below).

- What is the redox potential for "dry" hydrogen (pure H_2)?

In theory, the redox potential for pure H_2 would be infinite.

Indeed, $\tilde{c}_{\mathrm{H_2}}^{\mathrm{an}} \to 1$ implies $\tilde{c}_{\mathrm{H_2O}}^{\mathrm{an}} \to 0 \quad \Longrightarrow \quad Q_\mathrm{r} \to 0 \quad \Longrightarrow \quad \ln(Q_\mathrm{r}) \to -\infty \quad \Longrightarrow \quad E \to \infty$. Somehow, this is evidence that it is not manageable to get perfectly dry hydrogen.

- What can be said about the electrical current in this exercise?

The value of the electrical current cannot be computed, since no flow rate is given (neither current-density and active area). However, for a same fuel flow rate, the current (-density) increases with the global fuel utilization, according to its definition. Moreover, it is known $I \geq 0$.

- In which case the cell voltage equals the redox potential E?

The cell voltage equals the redox potential E when no electrical current is drawn from the cell (open circuit voltage, OCV). As soon as an electrical current is drawn from the cell, various losses of potential arise (e.g., ohmic loss RI^2), lowering the cell voltage.

- How would you interpret the fuel utilization here?

The fuel utilization in this exercise can be interpreted in at least two different ways:

i) Global fuel utilization: Υ_f, E, $\tilde{c}_k$, and T are values at the end of the active area.
ii) Local fuel utilization: Υ_f, E, $\tilde{c}_k$, and T are values at the position along the active area where the fuel has been consumed up to Υ_f %.

In the latter case, if global $\Upsilon_\mathrm{f} = 1$ and if the rate of reaction is assumed constant along the active area, then the x-axis in figure 1 can also be interpreted as the normalized length of the active area.

- Which situations can be modeled and understood with this exercise?

Evolution of concentrations and redox potential with fuel utilization, which can also be thought of as the distance along the fuel cell.

- What flow configuration of the fuel cell has been (implicitly) assumed?

The quotient of the reaction is defined according to the local concentrations. The molar fraction of oxygen was computed assuming that its consumption is “synchronous” with that of hydrogen, i.e., air and fuel flow in the same direction (*co-flow* configuration).