Exercise 2 solution

1. Spontaneity of chemical reactions

Problem

What can you say about the spontaneity of a chemical reaction if:

a) $\Delta h < 0$ and $\Delta s > 0$
b) $\Delta h < 0$ and $\Delta s < 0$
c) $\Delta h > 0$ and $\Delta s < 0$
d) $\Delta h > 0$ and $\Delta s > 0$

Solution

Reaction (at constant temperature and pressure) is spontaneous if $\Delta g = \Delta h - T\Delta s < 0$.

a) $\Delta h < 0$ and $\Delta s > 0 \rightarrow \Delta h - T\Delta s < 0 \rightarrow$ Spontaneous
b) $\Delta h < 0$ and $\Delta s < 0$
    a. If $\Delta h/\Delta s < T \rightarrow \Delta h - T\Delta s > 0 \rightarrow$ Not spontaneous
    b. If $\Delta h/\Delta s > T \rightarrow \Delta h - T\Delta s < 0 \rightarrow$ Spontaneous
c) $\Delta h > 0$ and $\Delta s < 0 \rightarrow \Delta h - T\Delta s < 0 \rightarrow$ Not spontaneous
d) $\Delta h > 0$ and $\Delta s > 0$
    a. If $\Delta h/\Delta s < T \rightarrow \Delta h - T\Delta s < 0 \rightarrow$ Spontaneous
    b. If $\Delta h/\Delta s > T \rightarrow \Delta h - T\Delta s > 0 \rightarrow$ Not spontaneous

For example of a practical case, see Example 2.2. on section 2.3.1, page 38, in O'Hayre et al., Fuel cell fundamentals, 2016:

Example 2.2 Determine the approximate temperature at which the following reaction is no longer spontaneous:

$$CO + H_2O_{(g)} \rightarrow CO_2 + H_2 \tag{2.40}$$
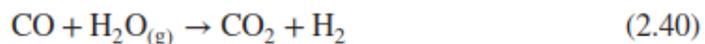
Solution: To answer this question, we need to calculate the Gibbs free energy for this reaction as a function of temperature and then solve for the temperature at which the Gibbs free energy for this reaction goes to zero:

$$\Delta \hat{g}_{rxn}(T) = \Delta \hat{h}_{rxn}(T) - T\,\Delta \hat{s}_{rxn}(T) = 0 \tag{2.41}$$

To get an approximate answer, we can assume that $\Delta \hat{h}_{rxn}$ and $\Delta \hat{s}_{rxn}$ are independent of temperature (heat capacity effects are ignored). In this case, the temperature dependence of $\Delta \hat{g}_{rxn}$ is approximated as

$$\Delta \hat{g}_{rxn}(T) = \Delta \hat{h}_{rxn}^0 - T\Delta \hat{s}_{rxn}^0 \tag{2.42}$$

From Appendix B, the $\Delta\hat{h}_f^0$ and $\hat{s}^0$ values for CO, CO_2, H_2, and H_2O are given in the table below.

Chemical Species	$\Delta\hat{h}_f^0$ (kJ/mol)	$\hat{s}^0$ [J/(mol·K)]
CO	−110.53	197.66
CO_2	−393.51	213.79
H_2	0	130.68
H_2O(g)	−241.83	188.84

Following Equation 2.31, $\Delta\hat{h}_{rxn}^0$ is calculated as

$$\Delta\hat{h}_{rxn}^0 = \left[\Delta\hat{h}_f^0(CO_2) + \Delta\hat{h}_f^0(H_2)\right] - \left[\Delta\hat{h}_f^0(CO) + \Delta\hat{h}_f^0(H_2O)\right]$$

$$= [(-393.51) + (0)] - [(-110.53) + (-241.83)]$$

$$= -41.15 \text{ kJ/mol} \tag{2.43}$$

Similarly, $\Delta\hat{s}_{rxn}^0$ is calculated as

$$\Delta\hat{s}_{rxn}^0 = \left[\hat{s}^0(CO_2) + \hat{s}^0(H_2)\right] - \left[\hat{s}^0(CO) + \hat{s}^0(H_2O)\right]$$

$$= [(213.79) + (130.68)] - [(197.66) + (188.84)]$$

$$= -42.03 \text{ J/(mol} \cdot \text{K)} \tag{2.44}$$

This gives

$$\Delta\hat{g}_{rxn}(T) = -41.15 \text{ kJ/mol} - T[-0.04203 \text{ kJ/(mol} \cdot \text{K)}] \tag{2.45}$$

Examining this expression, it is apparent that at low temperatures the enthalpy term will dominate over the entropy term, and the free energy will be negative. However, as the temperature increases, entropy eventually wins and the reaction ceases to be spontaneous. Setting this equation equal to zero and solving for T give us the temperature where the reaction ceases to be spontaneous:

$$-41.15 \text{ kJ/mol} + T[0.04203 \text{ kJ/(mol} \cdot \text{K)}] = 0 \quad T \approx 979\text{K} \approx 706°\text{C} \tag{2.46}$$

This reaction is known as the water gas shift reaction. It is important for high-temperature internal reforming of direct hydrocarbon fuel cells. These fuel cells run on simple hydrocarbon fuels (such as methane) in addition to hydrogen gas. Since these fuels contain carbon, carbon monoxide is often produced. The water gas shift reaction allows additional H_2 fuel to be created from the CO stream. However, if the fuel cell is run above 700°C, the water gas shift reaction is thermodynamically unfavorable. Therefore, operating a high-temperature direct hydrocarbon fuel cell requires a delicate balance between the thermodynamics of the reactions (which are more favorable at lower temperatures) and the kinetics of the reactions (which improve at higher temperatures). This balance is discussed in greater detail in Chapter 11.

2. Definition and interpretation of the practical fuel cell efficiency

Problem

The real (practical) fuel cell efficiency can be written as

$$\varepsilon_{real} = \varepsilon_{thermo} \times \varepsilon_{voltage} \times \varepsilon_{fuel} \tag{1}$$

where ε_{thermo} = reversible thermodynamic efficiency
$\varepsilon_{voltage}$ = voltage efficiency
ε_{fuel} = fuel utilization efficiency

Define these three partial efficiencies, giving for their defining equation and explanation, and show that equation (1) can written also as

$$\varepsilon_{real} = P_{elec,out} / P_{fuel,in} \tag{2}$$

where $P_{elec,out}$ = electrical output power of the fuel cell
$P_{fuel,in}$ = rate at which chemical energy of the fuel cell reaction is consumed by operating the fuel cell

Solution

See O'Hayre et al., Fuel cell fundamentals, 2016, section 2.5.2. For definition and explanations.
The defining equations are

$$\varepsilon_{thermo,\,fc} = \frac{\Delta \hat{g}}{\Delta \hat{h}} \qquad \varepsilon_{voltage} = \frac{V}{E} \qquad \varepsilon_{fuel} = \frac{i/nF}{v_{fuel}}$$

Equation (1) can therefore be written as

$$\varepsilon_{real} = \left(\frac{\Delta \hat{g}}{\Delta \hat{h}_{HHV}} \right) \left(\frac{V}{E} \right) \left(\frac{i/nF}{v_{fuel}} \right)$$

This can be rearranged to

$$\varepsilon_{real} = \left(\frac{\Delta g}{-nFE} \right) \left(\frac{iV}{-\Delta h_{HHV} v_{fuel}} \right) = \frac{P_{elec,out}}{P_{fuel,in}}$$

where $P_{elec,out} = iV$, is the electrical output power of the fuel cell, i.e. current times voltage delivered by the fuel cell to the external circuit (units: A x V = W), and $P_{fuel,in} = -\Delta h_{HHV} v_{fuel}$, is the rate at which chemical energy of the fuel cell reaction is consumed in the cell, i.e. the reaction enthalpy per mole of fuel (J/mol) times the rate of fuel consumption (mol/s) by the cell operation, including possible fuel losses, i.e. fuel that is fed in the cell but is not used in the fuel cell reaction and therefore does not produce current (units: J/mol x mol/s = J/s = W). Note that the first term is unity based on the relation between reversible cell voltage E and Gibbs free energy change of the fuel cell reaction $\Delta g = -nFE$.

3. Effect of fuel utilization on the fuel cell efficiency

Problem

a) Why does the shape of the current - efficiency curve follow the shape of the $j–V$ curve, the efficiency being highest at low current density and lowest at high current density, when the fuel cell is operated under *constant stoichiometry condition*?

b) Why the fuel cell efficiency is poor at low current densities, zero at highest current density, and reaches a maximum at some intermediate high current density, when the cell is operated at a *constant fuel flow rate condition*?

Solution

See O'Hayre et al., Fuel cell fundamentals, 2016, section 2.5.2. and Figure 2.9 for qualitative explanations. For theoretical analysis, recall from the text the two ways of writing the practical fuel cell efficiency:

Combining effects of thermodynamics, irreversible kinetic losses, and fuel utilization losses, we can write the practical efficiency of a real fuel cell as

$$\varepsilon_{real} = \left(\frac{\Delta \hat{g}}{\Delta \hat{h}_{HHV}}\right)\left(\frac{V}{E}\right)\left(\frac{i/nF}{v_{fuel}}\right) \tag{2.124}$$

For a fuel cell operating under a constant-stoichiometry condition, this equation simplifies to

$$\varepsilon_{real} = \left(\frac{\Delta \hat{g}}{\Delta \hat{h}_{HHV}}\right)\left(\frac{V}{E}\right)\left(\frac{1}{\lambda}\right) \tag{2.125}$$

From eq. 2.125 we can see that under **constant stoichiometry condition** (λ = constant), and at constant temperature and pressure, the fuel cell efficiency is proportional to the cell voltage while all other quantities in the equation are constant, i.e. $\varepsilon_{real} \propto V$. **The $i − \varepsilon$ curve therefore follows the shape of the $i − V$ curve**, and the efficiency is therefore highest at lowest current densities. In practice, this is because part of the useful work is lost to voltage losses that are larger at higher current densities. Although fuel is utilized equally effectively in reactions, smaller fraction comes out as electrical power to the external circuit.

From eq. 2.124 we can see that under **constant fuel flow rate condition** (v_{fuel}= constant), the fuel cell efficiency is proportional to the product of current and cell voltage (iV), which is the electrical power output of the cell, while all other quantities in the equation are constant, i.e. $\varepsilon_{real} \propto iV = P_{elec}$. **The $i − \varepsilon$ curve therefore follows the shape of the $i − P$ curve**. In practice, this is because at low current densities, large fraction of the fuel is not used, but flows though unreacted. On the other hand, at maximum current density the cell voltage is zero (short circuit condition), which means that also the electrical output power is zero (all useful electrical work is consumed in the internal voltage losses of the cell, producing heat).

4. A simple practical fuel cell efficiency calculation

Problem (O'Hayre et al., Fuel cell fundamentals, 2016, calculation exercise 2.12)

A typical H_2–O_2 PEMFC might operate at a voltage of 0.75 V and $\lambda = 1.10$. At STP, what is the efficiency of such a fuel cell (use HHV and assume pure oxygen at the cathode)?

Solution

A H_2/O_2 fuel cell, operating at STP, at cell voltage $V = 0.75$ V when H_2 is supplied with $\lambda = 1.1$ stoichiometry (i.e. 10 % more than is used in the FC reaction).

From problem 3: (O'Hayre eq. 2.125)

The FC real efficiency can be expressed as:

$$\varepsilon_{real} = \left(\frac{\Delta g}{\Delta h_{HHV}}\right)\left(\frac{V}{E}\right)\left(\frac{1}{\lambda}\right) \qquad (1)$$

Using $\Delta g = -h\,FE \iff \dfrac{\Delta g}{E} = -hF$

Eq (1) becomes:

$$\varepsilon_{real} = \frac{-hF}{\Delta h_{HHV}} \cdot \frac{V}{\lambda}$$

$h_{HHV} = -285.83 \dfrac{kJ}{mol}$

(O'Hayre or thermodynamic tables)

$$= \frac{-2.96485\ C/mol}{-285.83\ \frac{kJ}{mol}} \cdot \frac{0.75V}{1.1}$$

$$= 0.4603 = \underline{\underline{46\%}}$$

5. Mass balance in fuel cell – theoretical exercise

Problem (O'Hayre et al., Fuel cell fundamentals, 2016, review question 2.8)

Assume x moles per second of methanol and y moles per second of air are supplied to a direct methanol fuel cell (DMFC) generating a current of i amperes at a voltage V (volts). (a) Write expressions for the output mass flux (mol/s) of methanol ($v_{MeOH, out}$), air ($v_{air, out}$), water ($v_{H_2O, out}$), and carbon dioxide ($v_{CO_2, out}$) using the given variables. (b) Write expressions for the stoichiometric factors for methanol (λ_{MeOH}) and air (λ_{air}) using the given variables. (Clearly indicate numeric values for n in all cases.)

Solution

A DMFC operates using a mixture of methanol (MeOH) and water as the fuel at anode and air at cathode, generating current i and voltage V.

The Fuel cell reactions are:

Anode: $\quad CH_3OH_{(l)} + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$

Cathode: $\quad \frac{3}{2}(O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O)$

Total: $\quad CH_3OH_{(l)} + \frac{3}{2}O_2 \longrightarrow CO_2 + 2H_2O$
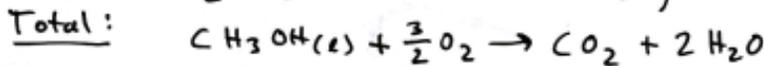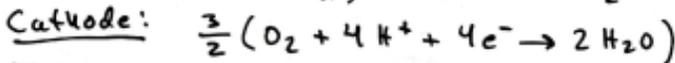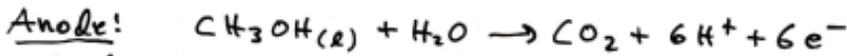
(See book chapter 8.7.1 for more info on DMFC)
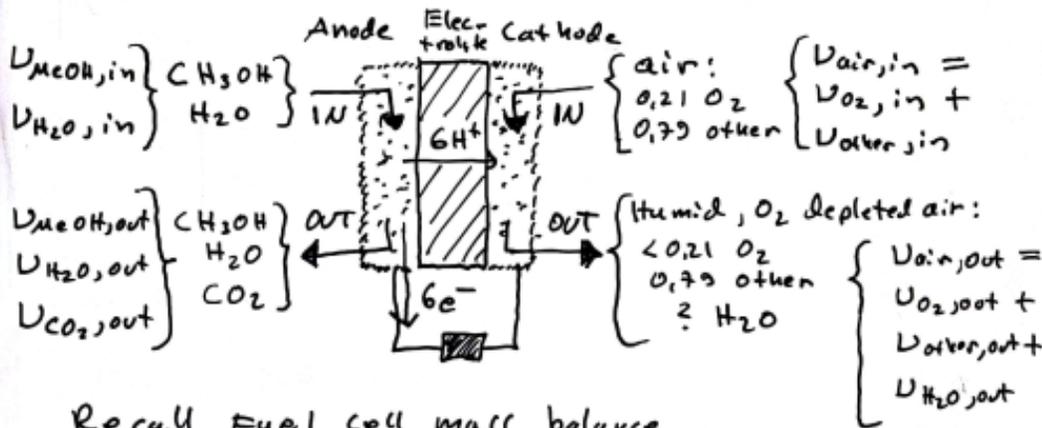
Recall Fuel cell mass balance
From the book (eq. 2.129):

$$\boxed{v_{i, out} = v_{i, in} \pm \frac{i}{nF}}$$

(units mol/s)

where n is the moles of electrons transferred in the reactions (to external circuit) per mole of reactant consumed or product produced in the reaction.

The stoichiometric Factor
is defined as

$$\boxed{\lambda = \frac{v_{i, in}}{v_{i, reacted}} = \frac{v_{i, in}}{(i/nF)}} \quad (\text{O'Hayre eq. 2.123})$$

The molar flow rates (mol/s) of the different species can be related to the current (A) generated in the fuel cell (half cell) reactions as follows.

One mole of MeOH is consumed per six moles of electrons generated.

$$\Rightarrow n_{MeOH} = 6 \quad, \quad \underline{v_{MeOH,out}} = v_{MeOH,in} - \frac{i}{6F} = x - \underline{\frac{i}{6F}}$$

One mole of CO_2 is produced per six moles of electrons generated.

$$\Rightarrow n_{CO_2} = 6 \quad, \quad \underline{v_{CO_2,out}} = \underbrace{v_{CO_2,in}}_{=0} + \frac{i}{6F} = \underline{\frac{i}{6F}}$$

(We pay no interest to the consumption of H_2O at the anode.)

At the cathode, ~~two~~ moles of H_2O is produced per ~~4~~ moles of electrons consumed.

$$\Rightarrow n_{H_2O} = \frac{4}{2} = 2, \quad \underbrace{v_{H_2O,out}}_{Cathode} = \underbrace{v_{H_2O,in}}_{\underbrace{}_{=0}} + \frac{i}{2F} = \underline{\frac{i}{2F}}$$

(dry air)

One mole of O_2 per 4 moles of electrons.

$$\Rightarrow n_{O_2} = 4 \quad, \quad \underline{v_{O_2,out}} = v_{O_2,in} - \frac{i}{4F} = \underline{0.21\, y - \frac{i}{4F}}$$

(air is 21% O_2)

The cathode out flow is humid, oxygen depleted air:

$$v_{air,out} = v_{O_2,out} + v_{H_2O,out} + v_{other,out}$$

$$= \left(0.21\, y - \frac{i}{4F}\right) + \frac{i}{2F} + 0.79\, y$$

$$= y + \frac{i}{4F}$$

b)

$$\underline{\lambda_{MeOH}} = \frac{v_{MeOH,in}}{(i/6F)} = \underline{\frac{6FX}{i}}$$

$$\underline{\lambda_{air}} = \lambda_{O_2} = \frac{v_{O_2,in}}{(i/4F)} = \frac{0.21\,Y}{(i/4F)} = \underline{\frac{0.84\,FY}{i}}$$

"Stoichiometry" of fuel cell mass flow relates only to reactants, which in the case of air and DMFC is only O_2. If we want λ_{O_2} we need to supply air in the same proportion.

6. Mass and heat balance in fuel cell – calculation exercise

Problem (O'Hayre et al., Fuel cell fundamentals, 2016, calculation exercise 2.13)

A direct methanol fuel cell generates 1000 A at 0.3 V at STP. Methanol and air are supplied to the fuel cell at 0.003 and 0.03 mol/s, respectively. Calculate (a) the output mass flux (mol/s) of methanol ($v_{MeOH, out}$), air ($v_{air, out}$), water ($v_{H_2O, out}$), and carbon dioxide ($v_{CO_2, out}$); (b) the stoichiometric factors for methanol (λ_{MeOH}) and air (λ_{air}); and (c) the heat generation rate (J/s) for this fuel cell assuming $\Delta \hat{h}_{rxn} = -719.19$ kJ/mol for methanol combustion at STP.

Solution

6. a) and b) are numerical calculations using expressions derived in problem 5.

Given:
$$\begin{cases} v_{MeOH, in} = X = 3 \text{ mmol/s} \\ v_{air, in} = Y = 30 \text{ mmol/s} \\ i = 1000 \text{ A} \quad, \quad V = 0,3 \text{ V} \quad, \quad \Delta h_{rxn} = -719.19 \frac{kJ}{mol} \text{ (STP)} \end{cases}$$

a) $v_{MeOH, out} = X - \frac{i}{6F} = 3 \text{ mmol/s} - \frac{1000 \text{ A}}{6 \cdot 96485 \text{ C/mol}} = \underline{1.27 \text{ mmol/s}}$

$v_{air, out} = Y + \frac{i}{4F} = 30 \text{ mmol/s} + \frac{1000 \text{ A}}{4 \cdot 96485 \text{ C/mol}} = \underline{32.6 \text{ mmol/s}}$

$v_{H_2O, out}^{Cathode} = \frac{i}{2F} = \frac{1000 A}{2 \cdot 96485 \text{ C/mol}} = \underline{5,18 \text{ mmol/s}}$

b) $\lambda_{MeOH} = \frac{6FX}{i} = \frac{6 \cdot 96485 \text{ C/mol} \cdot 3 \text{ mmol/s}}{1000 \text{ A}} = \underline{1,74}$

$\lambda_{air} = \frac{0,84 FY}{i} = \frac{0,84 \cdot 96485 \text{ C/mol} \cdot 30 \text{ mmol/s}}{1000 \text{ A}} = \underline{2,43}$

c) From O'Hayere (2016) eq. 2.128:

$$P_h = P_{in} - P_e = |\Delta h_{rxn}| v_{MeOH} - iV \qquad \left(\lambda = \frac{v}{(i/nF)} \right)$$

$$= \left(\frac{\lambda |\Delta h_{rxn}|}{nF} - V \right) i \qquad \Leftrightarrow v = \frac{\lambda i}{nF}$$

$$= \left(\lambda E^H - V \right) i \qquad ; \quad \boxed{E^H = \frac{|\Delta h_{rxn}|}{nF}} = \text{thermoneutral voltage}$$

$$= \left(1,74 \cdot 1,242 \text{ V} - 0,3V \right) \cdot 1000A \qquad \boxed{= \frac{719.19 \text{ kJ/mol}}{6 \cdot 96485 \text{ C/mol}} = 1,242 \text{ V}}$$

$$= \underline{1861 W \simeq 1860 W}$$

(According to the book, appendix 8, the answer is 942 W. Let me know if you find an error in these calculations, or derivations of problem 5.)

— Janne Halme