

Just another

Fuel Cell Formulary

by Dr. Alexander Kabza

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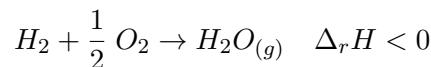
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1 Fundamentals

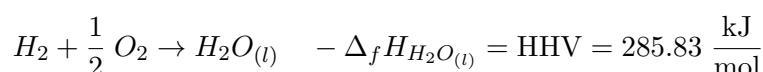
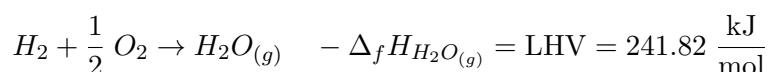
This is a collection of relevant formulas, calculations and equations for designing a fuel cell system (FCS).

1.1 Thermodynamic of H₂/O₂ electrochemical device

In an H₂/O₂ electrochemical device hydrogen is oxidized by oxygen to water in an exothermic reaction:



The *reaction enthalpy* $\Delta_r H$ is equal to the *enthalpy of water formation* $\Delta_f H$. The (chemical) energy content of any fuel is called *heating value* (for more information on thermodynamics see chapter 4.1). The heating value of hydrogen is equal to the absolute value of the reaction enthalpy. Because product water is produced either as gaseous or liquid phase, we distinguish between the *lower heating value* (LHV) and the *higher heating value* (HHV) of hydrogen:



Please note that LHV and HHV have positive signs whereas ΔH is negative. All thermodynamic potentials are dependent on temperature and pressure, but are defined at thermodynamic standard conditions (25°C and 100 kPa, standard ambient temperature and pressure SATP, see also section 4.4).

The difference between LHV and HHV of 44.01 kJ/mol is equal to the molar latent heat of water vaporization at 25°C.

The (thermodynamic) *electromotive force (EMF)* or *reversible open cell voltage (OCV)* E^0 of any electrochemical device is defined as:

$$E^0 = \frac{\Delta G}{n \cdot F}$$

where n is the amount of exchanged electrons and F is Faraday's constant (see chapter 5). For more information see chapter 4.1. For the hydrogen oxidation or water formation $n = 2$. The free enthalpies $\Delta_f G$ of water formation is either

$$\Delta_f G_{H_2O(g)} = -228.57 \text{ kJ/mol} \quad \text{or} \quad \Delta_f G_{H_2O(l)} = -237.13 \text{ kJ/mol}$$

Therefore the corresponding EMFs are:

$$E_g^0 = \frac{-\Delta_f G_{H_2O(g)}}{2F} = 1.184 \text{ V} \quad E_l^0 = \frac{-\Delta_f G_{H_2O(l)}}{2F} = 1.229 \text{ V} \quad (1.1)$$

These voltages are the maximum voltages which can (theoretically) be obtained from the electrochemical reaction of H_2 and O_2 . Beside that it make sense to define two other voltages to simplify the efficiency calculations (see section 1.7). If all the chemical energy of hydrogen (i.e. its heating value) were converted into electric energy (which is obviously not possible!), the following voltage equivalents would result:

$$E_{LHV}^0 = \frac{LHV}{2F} = 1.253 \text{ V} \quad E_{HHV}^0 = \frac{HHV}{2F} = 1.481 \text{ V} \quad (1.2)$$

Those two values are the *voltage equivalent* to the enthalpy ΔH , also called *thermal cell voltage* (see [1], page 27) or *thermoneutral voltage*.

The thermodynamic potentials ΔH and ΔG are dependent on temperature; therefore also the corresponding voltage equivalents are functions of temperature. The temperature dependency (of absolute values) is shown in figure 1.1, values are calculated with HSC Chemistry 6.21.

1.2 Nernst equation

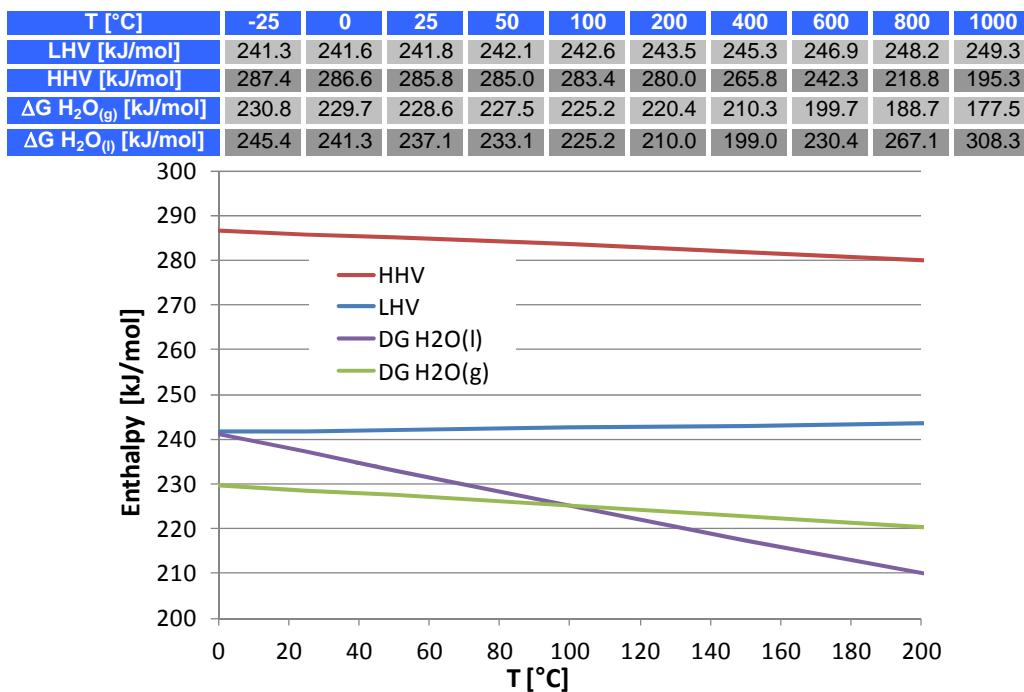
The theoretical cell potential or electromotive force (EMF) is not only depending on the temperature (as shown in the previous section), but also depending on the pressure. This dependency is in general described by the Nernst equation. For the H_2/O_2 electrochemical reaction the Nernst equation is:

$$E = E^0 + \frac{RT}{2F} \ln \left(\frac{p_{H_2} p_{O_2}^{1/2}}{p_{H_2O}} \right) \quad (1.3)$$

p is the partial pressure of H_2 , O_2 and H_2O .

Introducing a system pressure p_{Sys} and defining $p_{H_2} = \alpha p_{\text{Sys}}$, $p_{O_2} = \beta p_{\text{Sys}}$, $p_{H_2O} = \gamma p_{\text{Sys}}$, the Nernst equation simplifies to:

$$E = E^0 + \frac{RT}{2F} \ln \left(\frac{\alpha \beta^{1/2}}{\gamma} \right) + \frac{RT}{4F} \ln p_{\text{Sys}} \quad (1.4)$$

Figure 1.1: ΔH and ΔG as a function of temperature

If α , β and γ are constant, increasing the system pressure from p_1 to p_2 influences the cell potential as follows:

$$\Delta E = \frac{RT}{4F} \ln \frac{p_2}{p_1} \quad (1.5)$$

Assuming a cell runs at 80°C, then doubling the system pressure results in a potential increase of $\Delta E = 7.6 \text{ mV} \ln 2 = 5.27 \text{ mV}$. It is important to mention that due to other effects an increase in system pressure results in much higher cell voltage increases than just given by Nernst equation!

1.3 Reactant consumption and feed

The reactants H₂ and O₂ are consumed inside the fuel cell stack by the electrochemical reaction. Based on the *Faraday's laws* the molar flows \dot{n} for reactant consumptions are defined as follows:

$$\dot{n}_{\text{H}_2} = \frac{I \cdot N}{2F} \quad [\dot{n}_{\text{H}_2}] = \frac{\text{mol}}{\text{sec}} \quad (1.6)$$

$$\dot{n}_{\text{O}_2} = \frac{I \cdot N}{4F} = \frac{1}{2} \cdot \dot{n}_{\text{H}_2} \quad [\dot{n}_{\text{O}_2}] = \frac{\text{mol}}{\text{sec}}$$

I is the stack load (electric current, $[I] = A$), and N is the amount of single cells (cell count, $[N] = -$). 2 is again the amount of exchanged electrons per mole H_2 for the hydrogen oxidation; respectively 4 e^- per mole O_2 for the oxygen reduction. F is the Faraday constant.

The stoichiometry λ defines the ratio between reactant feed (into the fuel cell) and reactant consumption (inside the fuel cell). Due to fuel cell design and water management issues etc. the stoichiometry must always be more than one:

$$\lambda = \frac{\dot{n}_{\text{feed}}}{\dot{n}_{\text{consumed}}} > 1 \quad [\lambda] = -$$

The reactant feed for H_2 and air into the fuel cell stack are now defined by an anode and cathode stoichiometry λ :

$$\dot{n}_{H_2, \text{feed}} = \dot{n}_{H_2} \cdot \lambda_{\text{anode}} = \frac{I \cdot N}{2F} \cdot \lambda_{\text{anode}} \quad (1.7)$$

$$\dot{n}_{\text{air, feed}} = \frac{\dot{n}_{O_2}}{x_{O_2}} \cdot \lambda_{\text{cathode}} = \frac{I \cdot N}{4F \cdot x_{O_2}} \cdot \lambda_{\text{cathode}}$$

where x_{O_2} is the oxygen content in air.

The molar flows of unconverted (dry) reactants at the stack exhaust are given as:

$$\dot{n}_{H_2, \text{out}} = \dot{n}_{H_2, \text{feed}} - \dot{n}_{H_2} = \frac{I \cdot N}{2F} \cdot (\lambda_{\text{anode}} - 1)$$

$$\dot{n}_{\text{air, out}} = \dot{n}_{\text{air, feed}} - \dot{n}_{O_2} = \frac{I \cdot N}{4F} \cdot \left(\frac{\lambda_{\text{cathode}}}{x_{O_2}} - 1 \right)$$

It is very common to give the reactant feed either as a mass or volume flow. The mass flow \dot{m} is the product of molar flow \dot{n} and molar weight M :

$$\dot{m} = \dot{n} \cdot M \quad [\dot{m}] = \frac{\text{g}}{\text{sec}}$$

The mass flow for stack anode and cathode inlet are therefore:

$$\dot{m}_{H_2, \text{feed}} = \frac{IN}{2F} \cdot \lambda_{\text{anode}} \cdot M_{H_2} \quad (1.8)$$

$$\dot{m}_{\text{air, feed}} = \frac{IN}{4Fx_{O_2}} \cdot \lambda_{\text{cathode}} \cdot M_{\text{air}} \quad (1.9)$$

The dry mass gas flow at stack cathode outlet contains less oxygen than air and is calculated as:

$$\dot{m}_{\text{cathode, out}} = \dot{m}_{\text{air, feed}} - \dot{m}_{\text{O}_2, \text{ consumed}} = \frac{IN}{4F} \cdot \left(\frac{\lambda_{\text{cathode}}}{x_{\text{O}_2}} \cdot M_{\text{air}} - M_{\text{O}_2} \right) \quad (1.10)$$

The volume flow \dot{V} is calculated by the gas density ρ or the molar gas volume $V_{0, \text{mol}}$:

$$\dot{V} = \frac{\dot{m}}{\rho} = V_{0, \text{mol}} \cdot \dot{n} \quad [\dot{V}] = \frac{1}{\text{min}}$$

Both the gas density ρ and the molar gas volume $V_{0, \text{mol}}$ are temperature and pressure dependent! Therefor the referring temperature and pressure need to be defined. N or n indicates that the volume flow is normalized to a specific reference temperature and pressure (e.g. $[\dot{V}] = \text{Nl/min}$ or l_n/min). Physical standard temperature and pressure (STP) is defined as 0°C and 101.325 kPa (for more information see section 4.4). The molar gas volume at STP is $V_{0, \text{mol}} = 22.414 \frac{\text{Nl}}{\text{mol}}$.

The amount of product water is equal to hydrogen consumption (equation 1.6) and given by:

$$\dot{n}_{\text{H}_2\text{O, prod}} = \dot{n}_{\text{H}_2} = \frac{I \cdot N}{2F} \quad [\dot{n}_{\text{H}_2\text{O}}] = \frac{\text{mol}}{\text{sec}}$$

The product water mass flow is:

$$\dot{m}_{\text{H}_2\text{O, prod}} = \frac{I \cdot N}{2F} \cdot M_{\text{H}_2\text{O}} \quad [\dot{m}_{\text{H}_2\text{O}}] = \frac{\text{g}}{\text{sec}} \quad (1.11)$$

1.4 Hydrogen energy and power

Hydrogen is a chemical energy carrier with a specific (chemical) energy density, which is defined by either HHV or LHV. The *mass* specific chemical energy is:

$$W_{\text{H}_2, \text{HHV}} = \frac{\text{HHV}}{M} = \frac{285.83 \frac{\text{kJ}}{\text{mol}}}{2.02 \frac{\text{g}}{\text{mol}}} = 141.79 \frac{\text{kJ}}{\text{g}} \equiv 39.39 \frac{\text{kWh}}{\text{kg}}$$

$$W_{\text{H}_2, \text{LHV}} = \frac{241.82 \frac{\text{kJ}}{\text{mol}}}{2.02 \frac{\text{g}}{\text{mol}}} = 119.96 \frac{\text{kJ}}{\text{g}} \equiv 33.32 \frac{\text{kWh}}{\text{kg}}$$

The *volume* specific chemical energy (at STP) is:

$$W_{\text{H}_2, \text{HHV}} = \frac{\text{HHV}}{V_{0, \text{mol}}} = \frac{285.83 \frac{\text{kJ}}{\text{mol}}}{22.414 \frac{\text{l}_n}{\text{mol}}} = 12.75 \frac{\text{J}}{\text{ml}_n} = 3.54 \frac{\text{kWh}}{\text{m}_n^3}$$

$$W_{\text{H}_2, \text{LHV}} = \frac{241.82 \frac{\text{kJ}}{\text{mol}}}{22.414 \frac{\text{l}_n}{\text{mol}}} = 10.79 \frac{\text{J}}{\text{ml}_n} = 3.00 \frac{\text{kWh}}{\text{m}_n^3}$$

The chemical power of an H_2 flow is:

$$P_{H_2, \text{HHV}} = \text{HHV} \cdot \dot{n}_{H_2} \quad [P_{H_2, \text{HHV}}] = \frac{\text{J}}{\text{sec}} = \text{W} \quad (1.12)$$

Now the (chemical) power of H_2 consumed in a stack (with N cells at the stack load I) using equations 1.2 and 1.6 can easily be expressed as:

$$P_{H_2, \text{HHV consumed}} = 1.481 \text{ V} \cdot N \cdot I \quad (1.13)$$

And accordingly the (chemical) power of H_2 feed with equations 1.2 and 1.7 is:

$$P_{H_2, \text{HHV feed}} = 1.481 \text{ V} \cdot N \cdot I \cdot \lambda_{\text{anode}} \quad (1.14)$$

1.5 PolCurve (Current voltage dependency)

The current voltage dependency of a fuel cell is the most important property to express the performance of a fuel cell. This dependency is nonlinear due to kinetics of the electrochemical reaction of hydrogen and oxygen; it's called current voltage curve (I-U curve) or polarization curve (PolCurve) or performance characteristic.

1.5.1 Kinetic of the H_2/O_2 electrochemical device

The kinetics of electrochemical reaction is relevant as soon as the electric circuit of any electrochemical device is closed and it starts providing electric power. As soon as electrons and ions start moving we get voltage losses (overvoltage). This voltage losses are nonlinear functions of the load (or current density).

Voltage losses are the result of

- Oxygen reduction reaction (ORR) kinetics,
- Ohmic losses due to membrane ionic conductivity,
- Mass transport limitations at high load and
- Hydrogen oxidation reaction (HOR) kinetics (less relevant).

1.5.2 Butler-Volmer equation

The kinetics of ORR can be described with the Butler-Volmer equation. The Butler-Volmer equation defines the relation between current density j and overpotential φ of any electrochemical reaction:

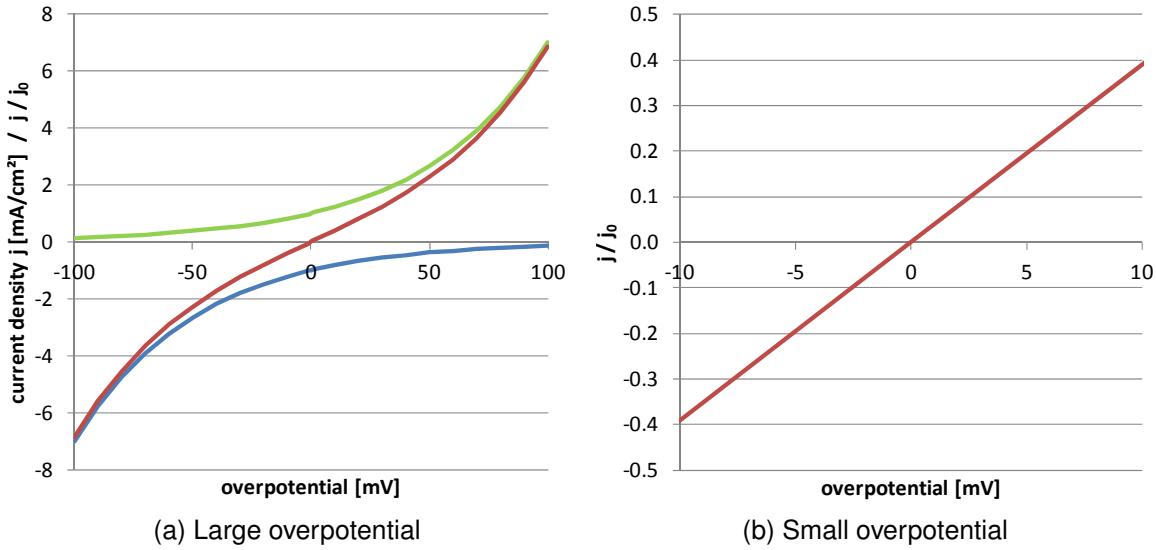


Figure 1.2: Butler Volmer

$$j(\varphi) = j_0 \left[\exp \left(\frac{\alpha nF}{RT} \varphi \right) - \exp \left(\frac{(1-\alpha)nF}{RT} \varphi \right) \right]$$

This is the sum of an anodic and cathodic current $j(\varphi) = j_a(\varphi) + j_c(\varphi)$ with:

$$j_a(\varphi) = j_0 \exp \left(\frac{\alpha nF}{RT} \varphi \right) \quad j_c(\varphi) = -j_0 \exp \left(\frac{(1-\alpha)nF}{RT} \varphi \right)$$

Side information: $e^x - e^{-x} = 2 \sinh x$

With $\alpha = 1/2$ the Butler-Volmer equation can be simplified to:

$$\frac{j(\varphi)}{j_0} = 2 \sinh \left(\frac{1}{2} \frac{nF}{RT} \varphi \right)$$

Figure 1.2a shows the anodic current (green line), the cathodic current (blue) and the Butler-Volmer equation itself (red). In case of low overpotentials ($|\varphi| < 10\text{mV}$, $\alpha = 1/2$) the Butler-Volmer equation simplifies to:

$$\frac{j(\varphi)}{j_0} = \frac{nF}{RT} \varphi$$

Figure 1.2b shows this linear relation between current density j and overpotential φ , with the slope $m = nF/RT$. In case of high overpotentials ($|\varphi| > 100\text{mV}$, $\alpha = 1/2$) the Butler-Volmer equation simplifies to:

$$\ln \frac{j(\varphi)}{j_0} = \frac{1}{2} \frac{nF}{RT} \varphi$$

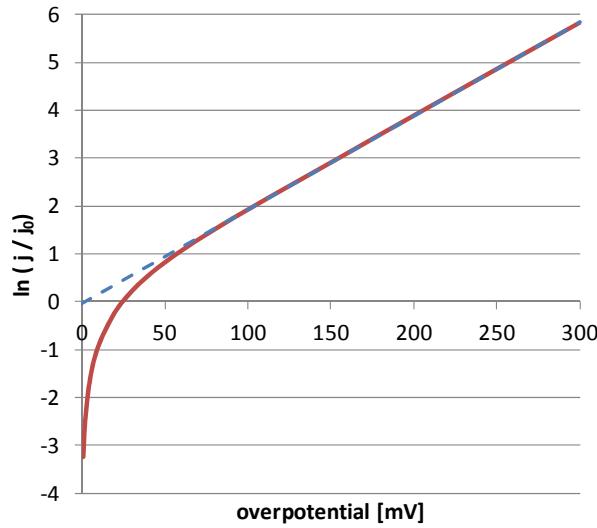


Figure 1.3: Butler Volmer logarithmic scale

This relation becomes linear by using a logarithmic y-axes like shown in figure 1.3. The slope of the blue dotted line $m = 1/2 nF/RT$ is the Tafel slope in the Tafel equation $\varphi = m \cdot j/j_0$.

1.5.3 Example PolCurve

The PolCurve plots the cell voltage versus current density of a single cell or stack. Figure 1.4 shows an theoretical PolCurve, including the electric and thermal power based on LHV or HHV (equation 1.17), and the electric efficiency based on LHV (1.18).

For simulation and modeling it is helpful to have a mathematical expression for the PolCurves. The following empirical equation with physical background describes the voltage current dependency quite well (see [2], [3]):

$$E = E_0 - b \cdot (\log j + 3) - Rj - m \cdot \exp^{nj} \quad (1.15)$$

The parameters are:

- E_0 : (measured) open cell voltage, $[E_0] = \text{V}$
- j : Current density, $[j] = \text{A/cm}^2$
- b : Tafel slope (voltage drop due to oxygen reduction reaction), $[b] = \text{V/dec}$
- R : Internal resistor, $[R] = \Omega \text{cm}^2$
- m, n : (Empirical) coefficients defining the voltage drop due to diffusion limitation, $[m] = \text{V}$, $[n] = \text{cm}^2/\text{A}$

The example PolCurve in the chart 1.4 is calculated with the following parameters: $E_0 = 1.0 \text{ V}$, $b = 0.08 \text{ V/dec}$, $R = 0.1 \Omega \text{cm}^2$, $m = 0.0003 \text{ V}$, and $n = 3.30 \text{ cm}^2/\text{A}$.

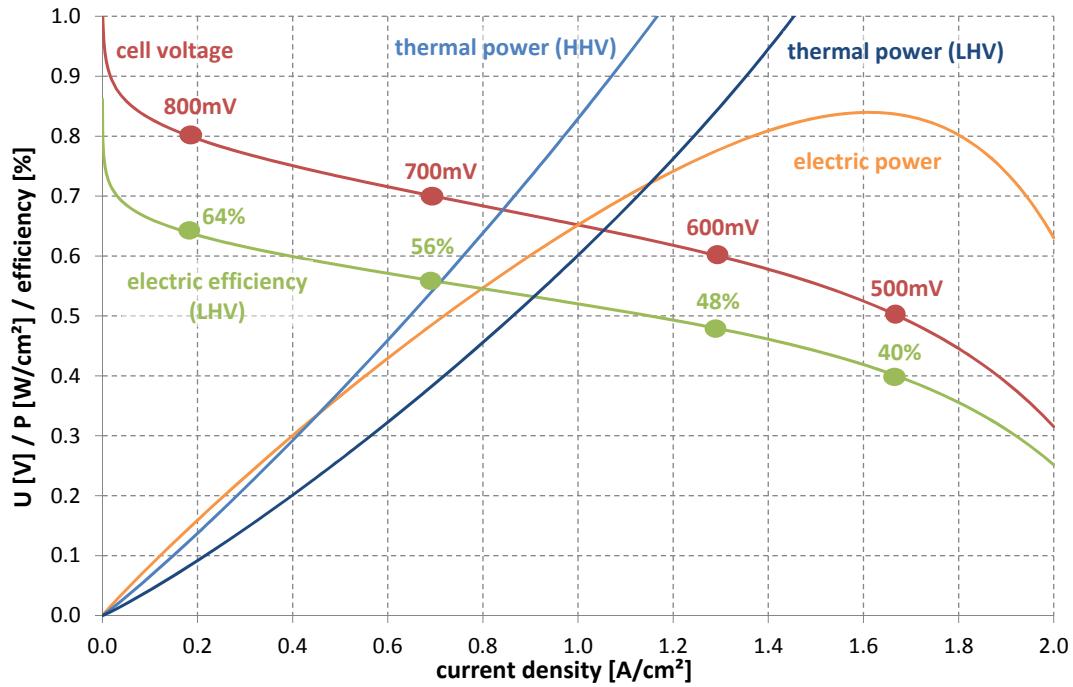


Figure 1.4: Polarization curve

1.6 Fuel cell stack power

Electric stack power P_{el} is the product of stack voltage and stack load, also called *gross power*:

$$P_{\text{el}} = U_{\text{Stack}} \cdot I = \text{AveCell} \cdot N \cdot I \quad (1.16)$$

where $\text{AveCell} = U_{\text{Stack}}/N$ is the average single cell voltage.

Thermal stack power P_{therm} is that part of the consumed chemical fuel power which is *not* converted into electric power:

$$P_{\text{therm}} = P_{\text{H}_2, \text{HHV}} - P_{\text{el}}$$

For the hydrogen fuel cell it is defined based on HHV as:

$$P_{\text{therm, HHV}} = (1.481 \text{ V} - \text{AveCell}) \cdot N \cdot I = P_{\text{el}} \left(\frac{1.481 \text{ V}}{\text{AveCell}} - 1 \right) \quad (1.17)$$

The voltage equivalent 1.481 V is defined by equation 1.2. To calculate the thermal power based on LHV this voltage equivalent needs to be replaced by 1.253 V.

Recovered heat The recovered heat is that part of the thermal stack power that is actually converted into usable heat. This is e.g. the heat transferred into the (liquid) coolant and can be calculated as follows:

$$P_{\text{recovered heat}} = \dot{V} \cdot c_p \cdot \Delta T \cdot \rho$$

Coolant parameters are: Volume flow \dot{V} , heat capacity c_p , temperature increase ΔT and density ρ .

Due to technical issues not all thermal power can be transferred to coolant; therefore:

$$P_{\text{recovered heat}} < P_{\text{therm, HHV}}$$

The unusable or waste heat:

$$P_{\text{waste heat}} = P_{\text{therm, HHV}} - P_{\text{recovered heat}}$$

This waste heat consists of two parts:

1. Heat rejected to ambient via stack surface (radiant heat).
2. Heat loss by cathode exhaust enthalpy; or more precise by the difference between air outlet and air inlet enthalpy.

1.7 Fuel cell efficiencies

1.7.1 Different efficiencies

There seems to be no commitment how to define or name the different efficiencies for fuel cells. Therefore the only thing I can do here is to clarify the differences; well knowing that in literature other definitions and wordings are used. *Don't talk about efficiency if you don't know what you are talking about!*

All efficiencies can be based on either LHV or HHV of the fuel. There is also no commitment to use LHV or HHV. Therefore be careful and keep in mind that the efficiency is higher if it refers to LHV!

In general the energy conversion efficiency η is defined as:

$$\eta = \frac{(\text{useful}) \text{ energy output}}{\text{energy input}} = \frac{(\text{useful}) \text{ power output}}{\text{power input}}$$

Thermodynamic efficiency The thermodynamic or *maximum* or *ideal* efficiency is the ratio between enthalpy (or heating value) ΔH and Gibbs free enthalpy ΔG (reflecting the maximum extractable work) of any electrochemical device:

$$\eta_{\text{el, max}} = \frac{\Delta G}{\Delta H}$$

For the hydrogen fuel cell it is:

$$\eta_{\text{el, TD, LHV}} = \frac{-\Delta_f G_{H_2O(g)}}{\text{LHV}} = \frac{E_g^0}{E_{\text{LHV}}^0} = \frac{1.184 \text{ V}}{1.253 \text{ V}} = 94.5\%$$

$$\eta_{\text{el, TD, HHV}} = \frac{-\Delta_f G_{H_2O(l)}}{\text{HHV}} = \frac{E_l^0}{E_{\text{HHV}}^0} = \frac{1.229 \text{ V}}{1.481 \text{ V}} = 83.1\%$$

The Handbook of Fuel Cells [1] calls this simply "ideal efficiency".

The Fuel Cell Handbook [4] calls this efficiency the "thermal efficiency of an ideal fuel cell operating *reversibly* on pure hydrogen and oxygen at standard conditions".

Fuel Cell Systems Explained [5] calls this efficiency "the maximum efficiency possible" or "maximum efficiency limit" which explains it also very well.

Electric efficiency The electric efficiency of a fuel cell (stack) is defined as:

$$\eta_{\text{el}} = \frac{P_{\text{el}}}{P_{\text{fuel, consumed}}}$$

P_{el} is the stack electric (gross) power and $P_{\text{fuel, consumed}}$ is the consumed fuel power (see equations 1.16 and 1.13).

The electric efficiency can easily be expressed as (more details see section 1.7.2):

$$\eta_{\text{el, LHV}} = \frac{\text{AveCell}}{1.253 \text{ V}} \quad \text{or} \quad \eta_{\text{el, HHV}} = \frac{\text{AveCell}}{1.481 \text{ V}} \quad (1.18)$$

How this efficiency is named in literature and codes & standards:

1. "Load efficiency" in the Handbook of Fuel Cells [1], refers to both LHV and HHV.
2. The Fuel Cell Handbook [4] refers to HHV and says "this efficiency is also referred to as the *voltage efficiency*".
3. "Cell efficiency" in Fuel Cell Systems Explained [5], and refers to LHV.
4. SAE J2617 [6] calls this efficiency "stack sub-system efficiency" and refers to LHV.

Fuel electric efficiency The fuel efficiency considers the amount of hydrogen feed to the stack (and not only the amount of consumed hydrogen). It is defined as:

$$\eta_{\text{fuel, el}} = \frac{P_{\text{el}}}{P_{\text{fuel, feed}}}$$

P_{el} is the stack electric gross power and $P_{\text{fuel, feed}}$ is the fuel feed power (see equations 1.16 and 1.14).

According to equation 1.18 it is:

$$\eta_{\text{fuel, el, LHV}} = \frac{\text{AveCell}}{1.253 \text{ V} \cdot \lambda_{\text{anode}}} \quad \text{or} \quad \eta_{\text{fuel, el, HHV}} = \frac{\text{AveCell}}{1.481 \text{ V} \cdot \lambda_{\text{anode}}}$$

Obviously, the relation between $\eta_{\text{fuel, el}}$ and η_{el} is the anode stoic:

$$\eta_{\text{fuel, el}} = \frac{\eta_{\text{el}}}{\lambda_{\text{anode}}}$$

How this efficiency is named in literature:

1. Fuel Cell Systems Explained [5] calls this efficiency simply “efficiency” (of either LHV or HHV).
2. Fuel Cell Handbook [4] calls it “*net* cell efficiency” and defines it as following: “To arrive at the *net* cell efficiency, the *voltage efficiency* must be multiplied by the fuel utilization.”

Voltage efficiency is the ratio between average and reversible cell voltage E^0 (see equation 1.1):

$$\eta_{\text{voltage}} = \frac{\text{AveCell}}{E^0}$$

Normally the voltage efficiency is based on $\Delta_f G_{H_2O(l)}$:

$$\eta_{\text{voltage}} = \frac{\text{AveCell}}{E_l^0} = \frac{\text{AveCell}}{1.229 \text{ V}}$$

$$\eta_{\text{voltage}} = \eta_{\text{el, HHV}} \cdot \eta_{\text{el, TD, HHV}} = \frac{\text{AveCell}}{1.481 \text{ V}} \cdot 83.1\%$$

Thermal efficiency η_{therm} can be calculated according the electric efficiency:

$$\eta_{\text{therm}} = \frac{P_{\text{therm}}}{P_{\text{fuel, consumed}}}$$

Based on HHV it is:

$$\eta_{\text{therm, HHV}} = \frac{1.481 \text{ V} - \text{AveCell}}{1.481 \text{ V}}$$

Recovered heat efficiency Due to the fact that not all thermal power P_{therm} is transferred into the coolant the recovery heat efficiency can be calculated:

$$\eta_{\text{recovered heat}} = \frac{P_{\text{recovered heat}}}{P_{\text{therm}}}$$

For HHV this is:

$$\eta_{\text{recovered heat, HHV}} = \frac{P_{\text{recovered heat}}}{P_{\text{therm, HHV}}} = \frac{\dot{V} \cdot c_p \cdot \Delta T \cdot \rho}{(1.481 \text{ V} - \text{AveCell}) \cdot N \cdot I}$$

Overall stack efficiency can be calculated as:

$$\eta_{\text{overall}} = \frac{P_{\text{el}} + P_{\text{therm}}}{P_{\text{fuel, consumed}}} = 1$$

This (thermodynamic) efficiency needs to be $\eta_{\text{overall}} = 1$, because the consumed hydrogen is converted completely in electric and thermal power:

$$P_{\text{fuel, consumed}} = P_{\text{el}} + P_{\text{therm}}$$

Therefore it is also:

$$\eta_{\text{overall}} = \eta_{\text{el}} + \eta_{\text{therm}}$$

Total efficiency is maybe more reasonable and defined as:

$$\eta_{\text{total}} = \frac{P_{\text{el}} + P_{\text{recovered heat}}}{P_{\text{fuel, feed}}} < 1$$

Obviously $\eta_{\text{total}} < 1$, because $P_{\text{recovered heat}} < P_{\text{therm}}$ and $P_{\text{fuel, feed}} > P_{\text{fuel, consumed}}$!

1.7.2 Electric efficiency calculation

How to convert $\eta_{\text{el, LHV}} = \frac{P_{\text{el}}}{P_{\text{fuel, consumed}}}$ to $\frac{\text{AveCell}}{1.253 \text{ V}}$?

With equations 1.2 and 1.6 it is:

$$\begin{aligned} \eta_{\text{el, LHV}} &= \frac{P_{\text{el}}}{P_{\text{fuel, consumed}}} \\ &= \frac{\text{AveCell} \cdot N \cdot I}{i_{\text{H}_2} \cdot \text{LHV}} = \frac{\text{AveCell} \cdot 2F}{\text{LHV}} \\ &= \frac{\text{AveCell}}{E_{\text{LHV}}^0} = \frac{\text{AveCell}}{1.253 \text{ V}} \end{aligned}$$

2 Fuel cell system (FCS)

IEC 62282-1:2005 [7] defines the main components of a fuel cell system and draws the system boundary around, see figure 2.1.

The main components are the fuel cell stack, an air processing system (e. g. a compressor and humidifier), the fuel gas supply, thermal management system etc. Other peripheral components are valves, pumps, electrical devices etc. Fuel like hydrogen (from a tank system) and air (ambient) are feed into the FCS.

Main FCS inputs are fuel (e.g. hydrogen), air and water, but also electric and thermal power. Main FCS outputs are the electric net and thermal power, the reactant exhaust gases and product water. The (electric) gross power is the stack electric power. The difference between gross and net is the electric power consumed by the peripheral electric components inside the FCS:

$$P_{\text{net}} = P_{\text{gross}} - P_{\text{peripheral}}$$

2.1 Anode subsystem

Hydrogen is feed into the fuel cell system from a tank system. The consumed hydrogen inside the fuel cell stack is based on the Faraday equation (equation 1.6) and dependent on the stack load. Actually always more hydrogen is feed into the FCS than is consumed inside the stack.

The anode flow shall on one hand be high enough to remove product water, but shall on the other hand be low to increase efficiency. This dilemma is often solved by an anode recirculation loop (see figure 2.2).

The anode recirculation is either realized with an Anode Recirculation Pump (ARP) or by one or more jet pumps. A water trapp shall remove liquid water at the anode exhaust. The purge valve opens with a specific frequency and duration to remove inert gases accumulated in the anode loop (mainly nitrogen from the cathode side). The anode loop ensures a high anode gas flow (e.g. $\lambda_{\text{gross}} > 2$) through the stack and allows a nearly complete utilization of hydrogen ($\lambda_{\text{net}} \ll 1.1$).

This stack anode off gas is finally purged either into the cathode exhaust or directly out of the FCS. This purged hydrogen is obviously lost for the electrochemical conversion, therefore the amount of anode purge losses shall be minimized.

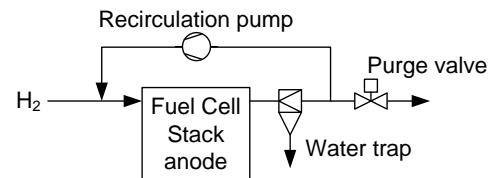


Figure 2.2: Anode loop

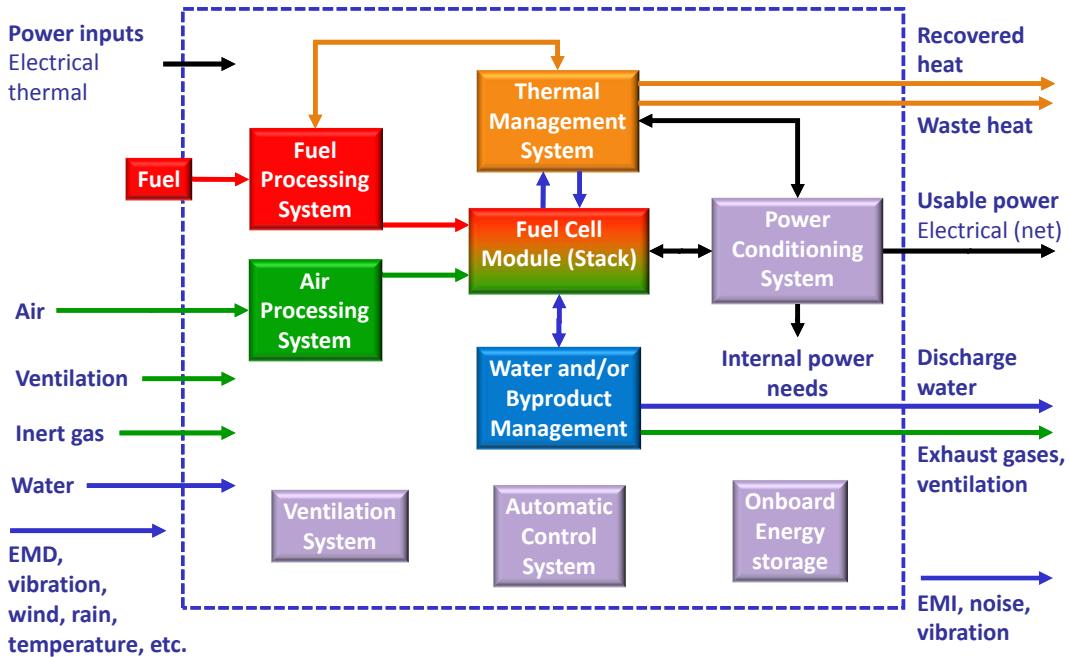


Figure 2.1: Fuel Cell System according to IEC 62282-1

The relation between hydrogen feed versus consumed hydrogen is called FCS fuel stoichiometry:

$$\lambda_{\text{net}} = \lambda_{\text{fuel,FCS}} = \frac{\text{fuel feed}}{\text{fuel consumed}} = \frac{\text{H}_2 \text{ feed}}{\text{H}_2 \text{ consumed}} \geq 1$$

The fuel efficiency (or fuel utilization) of a FCS is defined as:

$$\eta_{\text{fuel,FCS}} = 1/\lambda_{\text{fuel,FCS}}$$

The anode recirculation loop and its anode purge controls needs to be optimized regarding high fuel efficiency or low fuel losses. By doing this the fuel stoichiometry can be close to 1. One controls concept is the Amperehour counter. The anode purge is triggered when the integral of stack load reaches an Ah-threshold of e.g. 50 Ah. If the stack runs at 300 A constant load there is one purge every 10 min, calculated as following:

$$\frac{300 \text{ A}}{50 \text{ Ah}} = \frac{300 \text{ A}}{180,000 \text{ As}} = 0.00166 \text{ s}^{-1} = 0.1 \text{ min}^{-1}$$

2.2 Cathode subsystem

An air processing system or cathode submodule is e.g. a compressor and a gas-to-gas humidifier. Its purpose is to feed the conditioned (humidified) and required amount of air into the stack.

λ [-]	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5
Y.So.C [kg/kg]	0.224	0.206	0.191	0.178	0.167	0.157	0.148	0.140	0.133	0.126	0.120	0.115
T.So.C [°C]	66.6	65.2	63.9	62.7	61.6	60.6	59.5	58.6	57.8	56.8	56.0	55.2

Table 2.1: Specific humidity and temp. at stack outlet versus cathode stoichiometry

Ambient air has a specific relative humidity. Depending on the FCS design, this water input into the FCS may be neglected. More important is the pressure drop inside the stack and inside the FCS, and therefore the absolute pressure after the compressor and before the stack. The cathode stoichiometry is dependent on the system power level; typical values are between 1.8 (at higher load) to 3 (or more at low load).

2.2.1 Cathode pressure controls

In case of (low temperature) PEM fuel cell stacks it is essential to remove all product water from the stack. The stack operating conditions to fulfill this requirement can be calculated. Due to the fact that most water is removed via cathode exhaust; therefore we assume no water removal through anode exhaust. Based on this assumption we get the following equation to calculate the specific humidity at cathode exhaust (more details see chapter 7):

$$Y_{\text{out}} = \frac{\frac{\lambda}{x} \cdot Y_{\text{in}} + 2 \cdot \frac{M_{\text{water}}}{M_{\text{air}}}}{\frac{\lambda}{x} - \frac{M_{\text{O}_2}}{M_{\text{air}}}} \quad (2.1)$$

Y_{in} is the specific humidity at cathode inlet; according to equation 6.3 Y is a function of temperature, pressure and relative humidity at stack cathode inlet.

This equation allows to answer the following question: Under which stack operating conditions is water removal (via cathode side) maximized? Answer: The maximum amount of water can be removed if a) the inlet air is dry, b) under minimum pressure and c) is cathode exhaust is fully saturated.

- Criterion a) means no water input and therefore $Y_{\text{in}} = 0 \text{ kg/kg}$. Now the specific humidity at cathode outlet Y_{out} (or Y.So.C) just depends on cathode stoichiometry λ (all other parameters are constant).
- Criterion b) means lowest possible pressure at cathode exhaust, which is of course ambient pressure, and therefore $p_{\text{So.C}} = 101.325 \text{ kPa}$.
- Criterion c) means relative humidity at cathode exhaust shall be $\text{RH.So.C} = 100\%$ (fully saturated at cathode exhaust temperature T.So.C). In many fuel cell applications (e.g. automotive) the product water exits the stack as vapor and liquid water. Nevertheless this assumption allows first Fuel Cell System design considerations.

With these three criteria we get the dependencies shown in table 2.1.

This table now defines the lowest stack cathode exhaust temperature T.So.C under which (theoretically) all product water can be fully removed as a function of cathode stoichiometry.

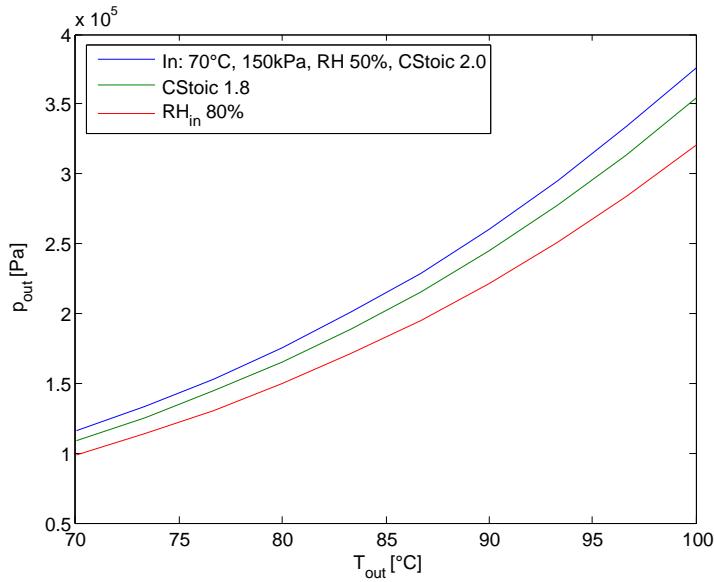


Figure 2.3: Cathode pressure controls as a function of temperature

try λ . If this temperature gets lower, the cathode stoichiometry must be increased to remove product water.

What happens if this temperature increases? On one hand the cathode stoichiometry may be decreased; but this is of course not doable for temperatures above 65°C corresponding to cathode stoichiometry below $\lambda < 1.5$. On the other hand either the inlet air may be humidified, or the cathode exhaust pressure may be increased, or both.

The dependency of cathode outlet pressure and temperature is also given by equation 2.1. The chart in figure 2.3 shows this pressure-temperature-dependency at three different stack operating conditions.

This chart shows the cathode exhaust pressure (p_{out} or p.So.C) as a function of cathode exhaust temperature (T_{out} or T.So.C). p.So.C is calculated based on equation 6.5 as:

$$p_{out} = \frac{\frac{M_w}{M_{air}} + Y_{out}}{Y_{out}} \cdot \varphi_{out} \cdot p_s(t_{out}) \quad (2.2)$$

This cathode exhaust pressure (p_{out} or p.So.C) in a function of stack cathode inlet RH, temperature and pressure, cathode stoichiometry λ , and cathode outlet temperature t_{out} and RH φ_{out} .

Further optimization of stack operating conditions is needed, but this may be a reasonable starting point for FCS pressure controls development. Especially as long as the stack temperature did not reach its desired operating temperature, product water needs to be removed also as liquid water! This is e.g. the case for automotive application during cold ambient temperatures (cold startup conditions). Under certain conditions the stack never warms up enough to reach the temperature needed for full vaporization!

The typically fully humidified cathode exhaust gas of a FCS contains a lot of energy in form of enthalpy (see also section 6.2).

The increasing enthalpy of process air inside the FCS cathode subsystem considers first the temperature increase (from cold inlet to warm outlet) and second the product water uptake.

As a first guess the energy loss via stack (not FCS!) cathode exhaust seems to be the difference between thermal power based on HHV and LHV. But in fact this energy loss is even higher! This is due to the fact that the air temperature increases inside the stack, while LHV and HHV are based on the thermodynamic standard temperature T_c .

2.2.2 Stack pressure drop

In the previous section the pressure at stack exhaust was calculated. To also calculate the pressure at stack inlet the cathode pressure drop through the stack is needed. Any gas flow through a pipe causes a specific pressure drop as a function of gas flow. A simplified assumption for the cathode air pressure drop of an air flow through a stack can be made with the orifice equation (more details see chapter 8).

For a given stack coefficient and cross sectional area αA (obtained by one measured pressure drop), the pressure drop Δp can be calculated as a function of air mass flow \dot{m} :

$$\Delta p = \frac{p_2 - p_0}{2} + \frac{\sqrt{(\alpha A \rho_0)^2 \cdot (p_0 + p_2)^2 + 2 \dot{m}^2 p_0 \rho_0}}{2 \alpha A \rho_0} - p_2 \quad \Delta p \propto \dot{m}^x \quad (2.3)$$

Here p_2 is the gauge pressure at the stack exhaust, and p_0 and ρ_0 are absolute pressure and air density at STP.

2.2.3 Cathode air compression

The theoretical work for gas compression can be calculated as following (for detailed information see chapter 6.3):

$$w_{\text{comp}} = c_{p, m} T_1 \cdot \left(\Pi^{\frac{\kappa-1}{\kappa}} - 1 \right) \quad \Pi = \frac{p_2}{p_1}$$

The gas is compressed from pressure p_1 to pressure p_2 , temperature before compression is T_1 . Constant values for air: Heat capacity at constant pressure $c_{p, m, \text{air}} = 1005.45 \frac{\text{J}}{\text{kg K}}$, $(\kappa - 1)/\kappa = 0.285$.

The units for the compression work can be expressed as follows:

$$[w_{\text{comp}}] = \frac{\text{kJ}}{\text{kg}} = \frac{\text{W}}{\text{g/sec}}$$

For dry air at room temperature (25°C) this compression work w_{comp} as a function of pressure ratio Π looks as follows:

Finally the required power for compression is:

$$P_{\text{comp}} = \dot{m} \cdot w_{\text{comp}}$$

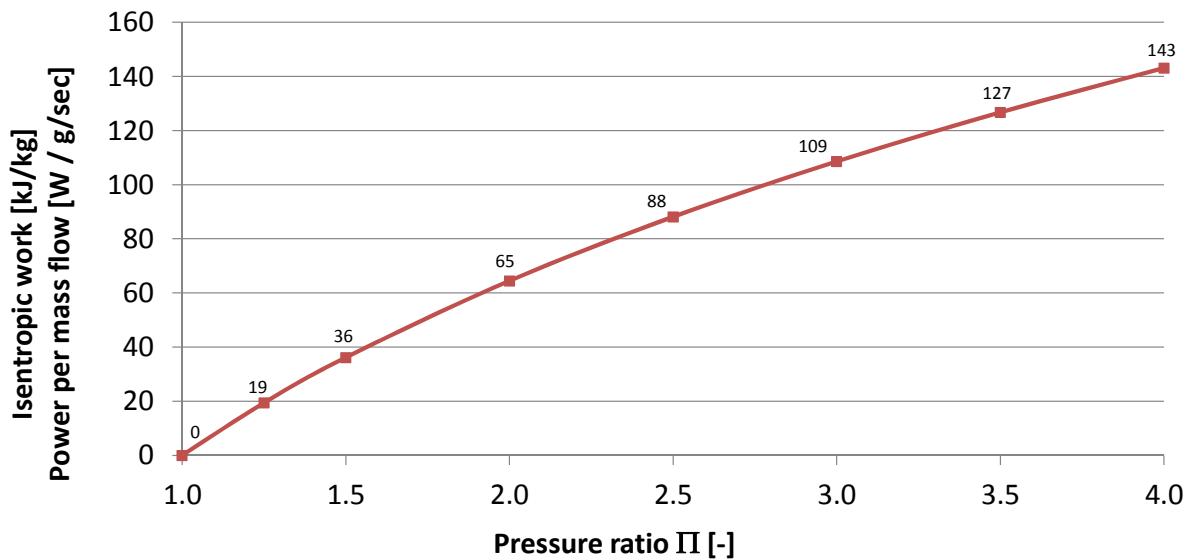


Figure 2.4: Isentropic work for air compression

Example: The theoretical (isentropic) power request to compress an (dry) air mass flow of 92 g/sec (from ambient temperature and pressure) to 250 kPaabs is:

$$P_{\text{comp}} = \dot{m} \cdot w_{\text{comp}} = 92 \text{ g/sec} \cdot 88 \frac{\text{W}}{\text{g/sec}} = 8.1 \text{ kW}$$

2.3 Coolant subsystem

Coolant (typically liquid, e.g. DI water or WEG) is feed by the coolant pump into the fuel cell stack. Other peripheral components (e.g. electric converters, compressor, etc.) inside the FCS may also be cooled in parallel to the stack or serial before or after the stack.

The coolant enters the stack at the stack inlet temperature and leaves the stack at the stack outlet temperature; leading to a specific temperature increase ΔT depending on stack load. Typical the temperature increase is $\Delta T \leq 10$ K. According to given ΔT requirements depending on stack load the coolant flow needs to be a function of the stack load, too.

The required coolant flow rate \dot{V} at a given stack recovered heat $P_{\text{recovered heat}}$ and coolant ΔT is calculated as follows:

$$\dot{V} = \frac{P_{\text{recovered heat}}}{c_p \cdot \Delta T \cdot \rho} \quad [\dot{V}] = \text{l/min}$$

where c_p is the specific heat capacity, $\Delta T = T_{\text{cool,out}} - T_{\text{cool,in}}$ and ρ the coolant density.

Table 2.2 shows the specific heat capacity c_p and density ρ of WEG at different temperatures and mixing ratios (vol%). 0% is pure water here.

This means that the required coolant volume flow for WEG (50vol%, 60°C) needs to be 12% higher compared to pure DI water.

Temp. ratio	0°C		20°C		40°C		60°C		80°C	
	c_p kJ/kg K	ρ g/cm³								
0%	4.218	0.9998	4.182	0.9982	4.179	0.9922	4.184	0.9832	4.196	0.9718
10%	4.09	1.018	4.10	1.011	4.12	1.002	4.13	0.993	4.15	0.983
30%	3.68	1053	3.72	1044	3.76	1034	3.80	1023	3.84	1010
50%	3.28	1.086	3.34	1.075	3.40	1.063	3.46	1.050	3.53	1.036

Table 2.2: Coolant properties

2.4 Fuel cell system efficiency

2.4.1 FCS electric efficiency

The overall FCS efficiency considers the fuel, electric and thermal input and electric and thermal output (see [8], 5.1.9.1):

$$\eta_{FCS} = \frac{\text{electric and thermal output}}{\text{fuel and thermal input}}$$

When the thermal output is used in the vehicle and the electric and thermal inputs are negligible, this equation simplifies to:

$$\eta_{FCS, el} = \frac{P_{\text{net output}}}{P_{\text{fuel input}}}$$

“Fuel power input” $P_{\text{fuel input}}$ is the fuel (chemical) energy content fed into the FCS (see equation 1.12). It can be expressed based on LHV or HHV; both [1] and [8] refer to LHV.

The electric net power output $P_{\text{net output}}$ is the stack gross power minus the total electric power consumption of all auxiliary FCS components (e.g. compressor or blower, pumps, valves, etc.):

$$P_{\text{net}} = P_{\text{gross}} - P_{\text{aux}} \quad P_{\text{aux}} = \sum_i P_{\text{component i}}$$

FCS efficiency can also be expressed as the product of different (system related) efficiencies (see also [1], page 718):

$$\eta_{FCS el} = \eta_{\text{stack}} \cdot \eta_{\text{fuel}} \cdot \eta_{\text{peripheral}}$$

with

$$\eta_{\text{stack}} = \frac{\text{AveCell}}{1.253 \text{ V}}, \quad \eta_{\text{fuel}} = \frac{1}{\lambda_{\text{fuel}}} \quad \text{and} \quad \eta_{\text{peripheral}} = \frac{P_{\text{net}}}{P_{\text{gross}}}$$

2.4.2 Auxiliary components

The power consumption P_{aux} of the auxiliary components inside the FCS is typically not constant; but depending on the FCS power level. Depending on the process air (cathode) pressure drop of the entire FCS, the air compression process maybe the most dominant power consumer.

The power consumption for air compression can be estimated with the following given parameters (see also chapter 6.3):

- Stack load [A] and cell count
- Cathode stoichiometry $\lambda_{\text{cathode}}(I)$ (as a function of stack load)
- Compressor pressure ratio $\Pi(I)$ as a function of stack load, inlet temperature (constant)
- Compressor efficiency $\eta_{\text{compressor}}(\Pi, \dot{m})$, as a function of pressure ratio and air mass flow (see compressor efficiency map)

$$\dot{m} = \dot{m}_{\text{air}}(I) = \frac{I \cdot N}{4F \cdot x_{\text{O}_2}} \cdot \lambda_{\text{cathode}}(I) \cdot M_{\text{air}}$$

$$P_{\text{compressor}} = \dot{m} \cdot c_{\text{p, m}} T_1 \cdot \left(\Pi(I)^{\frac{\kappa-1}{\kappa}} - 1 \right) \cdot \frac{1}{\eta_{\text{compressor}}(\Pi, \dot{m})}$$

Under the assumption that the power consumption of all other auxiliary components is constant, the total aux power consumption can be estimated.

3 Example calculations

Hydrogen flow power: A hydrogen flow transports (chemical) power. According to equation 1.12 the hydrogen flow of e.g. 1 g/sec is equivalent to:

$$1 \frac{\text{g}}{\text{sec}} \equiv 667.1 \frac{\text{l}_n}{\text{min}} \equiv 40.0 \frac{\text{m}_n^3}{\text{h}} \equiv 120.0 \text{kW}_{\text{LHV}} \equiv 141.8 \text{kW}_{\text{HHV}}$$

See chapter 1.4 for more information.

Stack efficiency calculation: A fuel cell stack produces 10 kW electric power, the hydrogen feed is 150 l_n/min, and the stack runs at 600 mV average cell voltage. Calculate the electric efficiency, the fuel efficiency and the anode stoichiometry (based on LHV).

$$\eta_{\text{el, LHV}} = \frac{\text{AveCell}}{E_{\text{LHV}}^0} = \frac{0.6 \text{ V}}{1.253 \text{ V}} = 47.9\%$$

$$\dot{n}_{\text{H}_2 \text{ feed}} = \frac{150 \frac{\text{l}_n}{\text{min}}}{22.414 \frac{\text{l}_n}{\text{mol}} \cdot 60 \frac{\text{sec}}{\text{min}}} = 0.1115 \frac{\text{mol}}{\text{sec}}$$

$$\eta_{\text{fuel, el, LHV}} = \frac{P_{\text{el}}}{\dot{n}_{\text{H}_2 \text{ feed}} \cdot \text{LHV}} = \frac{10 \frac{\text{kJ}}{\text{sec}}}{0.1115 \frac{\text{mol}}{\text{sec}} \cdot 241.82 \frac{\text{kJ}}{\text{mol}}} = 37.1\%$$

$$\lambda_{\text{anode}} = \frac{\eta_{\text{el, LHV}}}{\eta_{\text{fuel, el, LHV}}} = \frac{47.9\%}{37.1\%} = 1.29$$

Average cell voltage and hydrogen consumption: A 1 kW fuel cell stack is running at 50% electric efficiency and 40% fuel electric efficiency. What is the average cell voltage, and how much hydrogen is feed to the stack (based on LHV)?

According to equation 1.18 the electric efficiency is 50% at an average cell voltage of:

$$1.253 \text{ V} \cdot 50\% = 0.6265 \text{ V}$$

At 1 kW electric power and 40% fuel electric efficiency the hydrogen feed is equivalent to 2.5 kW (chemical power).

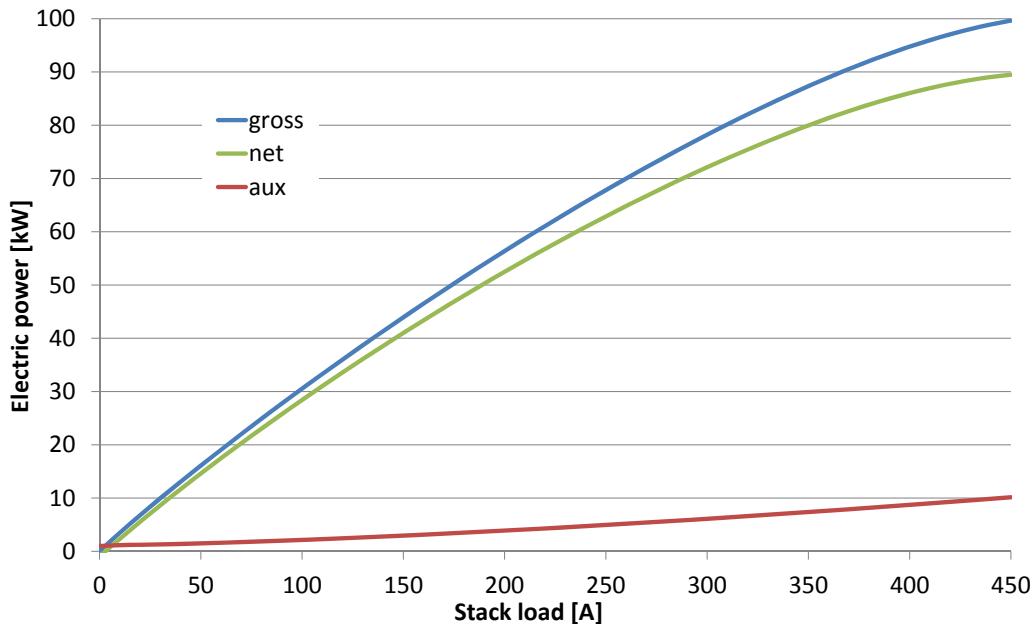


Figure 3.1: FCS power

Fuel cell system efficiency Here is an example for a FCS efficiency estimation. The auxiliary power consumption is calculated as follows:

$$P_{\text{aux}} = P_{\text{compressor}} + \sum_i P_{\text{component i}}$$

$\sum_i P_{\text{component i}}$ is the summary of all other electric consumers inside the FCS, beside the compressor. This value can be assumed to be constant, e.g. 1 kW here in this example.

In this example the compressor power $P_{\text{compressor}}$ is a function of cathode stoichiometry, cathode inlet pressure (pressure ratio II), and compressor efficiency. The cathode stoic λ_{cathode} is 5.0 to 2.0 for low load and 1.8 above 0.15 A/cm^2 . The cathode inlet pressure is linear between 130 kPa at low and 200 kPa at high load. The compressor efficiency is linear between 70% at low and 80% at high air mass flow.

Based on the polarization curve shown in chapter 1.5, and using the above parameter to calculate P_{aux} , we get the electric power showed in figure 3.1:

With an assumed net anode stoichiometry of 1.3 at low and 1.05 at higher loads above 0.15 A/cm^2 , the FCS efficiencies can be calculated as shown in figure 3.2.

The FCS peak efficiency is 55% for this example. The zero power level is called *idle point*; here the FCS net power is zero, but the FCS is still operating and consumes fuel.

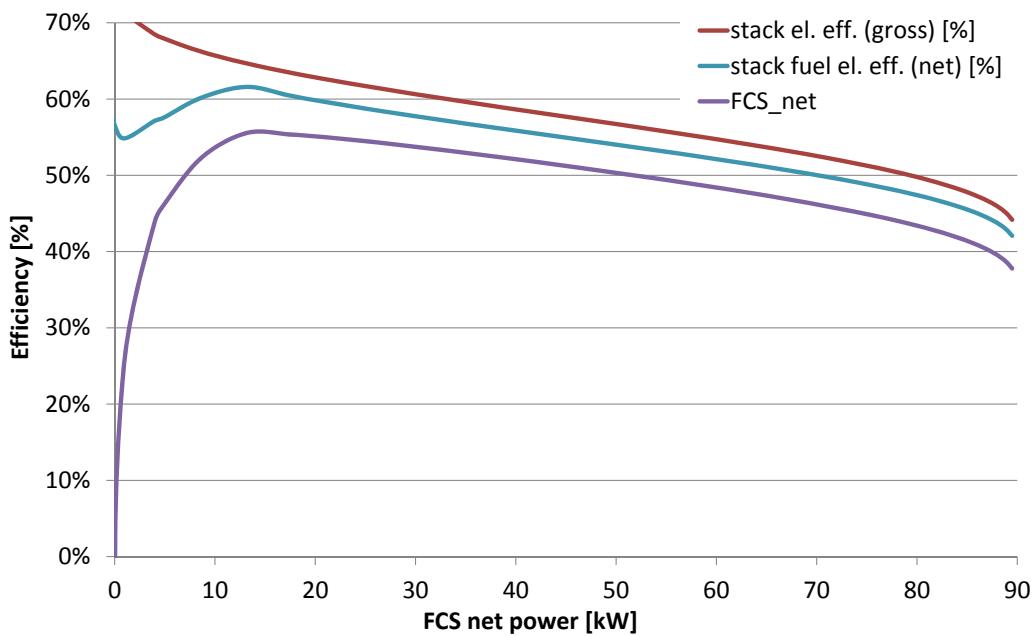


Figure 3.2: FCS efficiency

3.1 Stack operating parameters

Example H₂/air fuel cell stack with 200 cells and 300 cm² active area:

Stack electric							
Current density *	A/cm2	0.05	0.10	0.20	0.40	0.60	1.00
Ave cell voltage *	mV	839	797	756	703	661	588
Current (gross)	A	15	30	60	120	180	300
Voltage	V	168	159	151	141	132	118
Power (gross)	kW el	3	5	9	17	24	35
Stack anode							
Stoichiometry *	-	3.0	2.0	1.3	1.3	1.3	1.3
Hydrogen flow	Nl/min	62.7	83.6	108.7	217.4	326.2	543.6
Hydrogen flow	g/sec	0.09	0.13	0.16	0.33	0.49	0.81
Stack cathode in							
Stoichiometry *	-	2.2	2.0	1.8	1.8	1.8	1.8
Air flow	Nl/min	109.5	199.1	358.4	716.8	1075.2	1792.1
Air flow	g/sec	2.4	4.3	7.7	15.4	23.2	38.6
Air flow	kg/h	8.5	15.4	27.8	55.6	83.4	138.9
Stack thermal							
P therm LHV	kW	1.2	2.7	6.0	13.2	21.3	39.9
P therm HHV	kW	1.9	4.1	8.7	18.7	29.5	53.6
delta HHV - LHV	kW	0.7	1.4	2.7	5.5	8.2	13.7
Coolant inlet temp *	°C	60	60	60	60	60	60
Coolant outlet temp *	°C	61	63	66	67	68	70
Coolant delta T	K	1	3	6	7	8	10
Coolant flow LHV ²	l/min	17.9	13.1	14.3	27.1	38.3	57.4
Coolant flow HHV ²	l/min	27.7	19.7	20.8	38.3	53.1	77.0
Stack cathode out							
RH *	%	100%	100%	100%	100%	100%	100%
pws at coolant outlet temp	kPa abs	20.84	22.83	26.12	27.30	28.52	31.12
Pressure out	kPa abs	120	120	125	131	137	149
Product water out	g/sec	0.3	0.6	1.1	2.2	3.4	5.6
Consumed oxygen	g/sec	0.2	0.5	1.0	2.0	3.0	5.0
Dry cathode out	g/sec	2	4	7	13	20	34
Wet cathode out	g/sec	2	4	8	16	24	39
Enthalpy out	kJ/kg	405	445	497	499	500	503
P enthalpy out	kW	1	2	3	7	10	17
Stack power in (hydrogen)							
Hydrogen feed	mol/sec	0.05	0.06	0.08	0.16	0.24	0.40
P chem H2 LHV	kW	11	15	20	39	59	98
P chem H2 HHV	kW	13	18	23	46	69	116
Stack efficiency (LHV)							
Electric efficiency	%	67%	64%	60%	56%	53%	47%
Fuel efficiency	%	22%	32%	46%	43%	41%	36%

* given values

¹ 20°C and 50% compressor efficiency² WEG 50vol% at 60°C

Table 3.1: Example stack operating conditions

4 Appendix 1: Fundamentals

4.1 Thermodynamic fundamentals

The four thermodynamic potentials are:

Internal energy U is the total energy of an thermodynamic system and the sum of all forms of energies. In an isolated system the internal energy is constant and can not change. As one result of the first law of thermodynamics the change in the inner energy can be expressed as the heat dq supplied to the system and the work dw performed by the system: $dU = dq + dw$

Free or Helmholtz energy F (or A): is the "useful" work obtainable from a thermodynamic system at isothermal and isobaric conditions.

Enthalpy H : The enthalpy is a measure for the energy of a thermodynamic system and the sum of internal energy and the work for changing the volume: $H = U + pV$. For each chemical reaction the entropy change defines the reaction to be endothermic ($\Delta H < 0$) or exothermic ($\Delta H > 0$).

Free or Gibbs enthalpy G : The Gibbs or thermodynamic free enthalpy is the work that a thermodynamic system can perform: $G = H - TS$. For each chemical reaction ΔG defines the reaction to be exergonic ($\Delta G < 0$) or endergonic ($\Delta G > 0$).

The thermodynamic (or Guggenheim) square is a mnemonic for the relation of thermodynamic potentials with each other.

$-S$	U	V
H		A
$-p$	G	T

Table 4.1: Thermodynamic Square

How to get the total differential on a thermodynamic potential?

1. Select one thermodynamic potential in the middle of one border, e.g. U .
2. Take the two coefficients in the opposite edge, this is $-p$ and T for U . As a first step we get: $dU = -p\{ \} + T\{ \}$
3. Take now the opposite edge of both coefficients, here $-S$ is opposite to T and V is opposite to $-p$. Put those in the brackets to get the following result here: $dU = -pdV + TdS$

The following total differentials of the four thermodynamic potentials can be determined:

$$dU = -pdV + TdS \quad dH = Vdp + TdS$$

$$dA = -SdT - pdV \quad dG = Vdp - SdT$$

How to determine the Maxwell relations?

1. Select two units in the edge of one border, e.g. T and V .
2. Select the corresponding units in the opposite border, here it is $-p$ and $-S$.
3. Now the Maxwell relation is here: $\partial T/\partial V = -\partial p/\partial S$

The following four Maxwell relations can be determined:

$$(\partial T/\partial V)_S = -(\partial p/\partial S)_V$$

$$(\partial T/\partial p)_S = (\partial V/\partial S)_p$$

$$(\partial p/\partial T)_V = (\partial S/\partial V)_T$$

$$(\partial V/\partial T)_p = -(\partial S/\partial p)_T$$

And finally the following dependencies can be determined by the Guggenheim square:

$$(\partial U/\partial S)_V = T \quad \text{and} \quad (\partial U/\partial V)_S = -p$$

$$(\partial H/\partial S)_p = T \quad \text{and} \quad (\partial H/\partial p)_S = V$$

$$(\partial A/\partial V)_T = -p \quad \text{and} \quad (\partial A/\partial T)_V = -S$$

$$(\partial G/\partial p)_T = V \quad \text{and} \quad (\partial G/\partial T)_p = -S$$

4.2 Energy and relevant energy units

Energy is the product of power and time: $E = P \cdot t$

Units for energy:

$$[E] = \text{J} = \text{kg m}^2/\text{s}^2 = \text{Nm} = \text{Ws}$$

Joules and kilowatt-hour:

$$1 \text{ kWh} = 1000 \text{ Wh} \equiv 3.600.000 \text{ Ws} = 3.600.000 \text{ J} = 3.600 \text{ kJ} = 3.6 \text{ MJ}$$

4.3 Temperature dependency of thermodynamic values

Heat capacity of air $c_{p,\text{air}}$ of air as a function of temperature ($^{\circ}\text{C}$), calculated with HSC Chemistry 6.21, air with 78 Vol% N_2 , 21% O_2 and 1% Ar, is shown in table 4.2.

T	0	25	50	100	200	300	400	500	600
cp [J/molK]	29.06	29.10	29.13	29.25	29.67	30.25	30.93	31.64	32.29
cp [J/kgK]	1003.4	1004.6	1005.9	1009.9	1024.4	1044.5	1067.9	1092.3	1114.8

Table 4.2: Air heat capacity versus temperature

Molar heat capacity cp [J/molK] vs t [°C]									
Species	0	25	50	100	200	300	400	500	600
N ₂ (g)	29.12	29.13	29.14	29.19	29.47	29.95	30.57	31.26	31.92
O ₂ (g)	29.26	29.38	29.50	29.87	30.83	31.83	32.76	33.56	34.21
H ₂ (g)	28.47	29.05	28.90	28.75	28.77	28.99	29.29	29.64	30.00
CO ₂ (g)	36.04	37.12	38.31	40.39	43.81	46.61	48.97	50.97	52.62
H ₂ O(g)	33.56	33.60	33.71	34.04	34.97	36.07	37.25	38.48	39.74
Specific heat capacity cp [J/kgK] vs t [°C]									
Species	0	25	50	100	200	300	400	500	600
N ₂ (g)	1039.3	1039.7	1040.3	1042	1052	1069	1091	1116	1140
O ₂ (g)	914.4	918.2	922.0	934	963	995	1024	1049	1069
H ₂ (g)	14124	14409	14335	14260	14271	14380	14531	14703	14884
CO ₂ (g)	818.9	843.5	870.4	918	995	1059	1113	1158	1196
H ₂ O(g)	1863.1	1865.3	1871.0	1889	1941	2002	2068	2136	2206

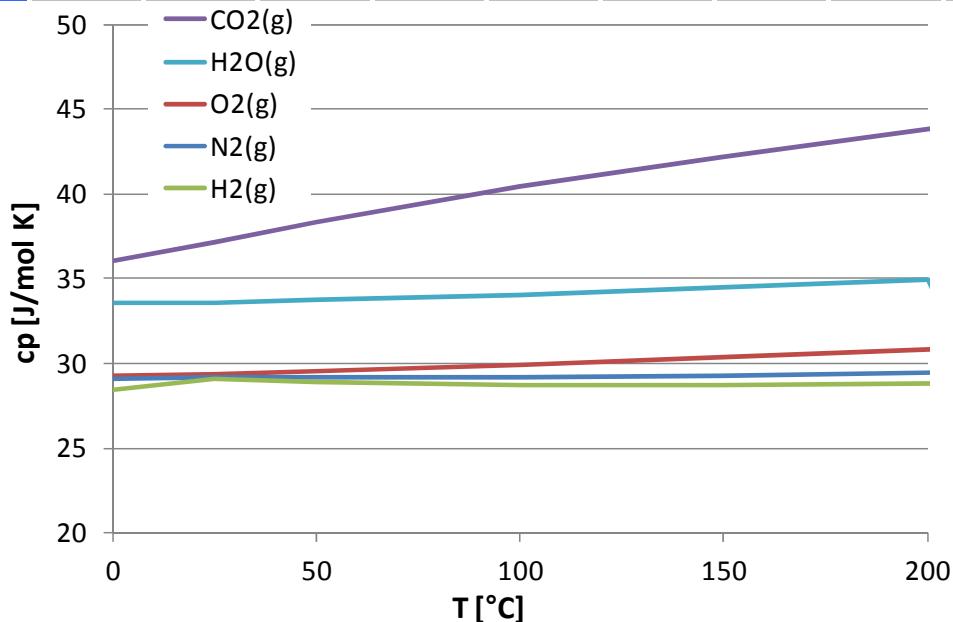


Figure 4.1: Molar and specific heat capacity of different gases

Heat capacity of other gases c_p of different gases as a function of temperature ($^{\circ}\text{C}$), calculated with HSC Chemistry 6.21, shown in table 4.1:

4.4 Standard temperature and pressure

Standard temperature and pressure (STP) is needed for many fuel cell related calculations; e.g. to calculate the volumetric reactant flow for a stack. Therefore it seems to be a simple question to ask for the correct reference temperature and pressure for STP. But the answer is not simple at all, as the following table shows [9]:

T [$^{\circ}\text{C}$] / [K]	p_{abs} [kPa]	Publishing or establishing entity
0 / 273.15	100.000	IUPAC (present)
0 / 273.15	101.325	IUPAC (former), NIST, ISO 10780
15 / 288.15	101.325	DIN IEC 62282-3-2 [10]
20 / 293.15	101.325	EPA, NIST
25 / 298.15	101.325	EPA
25 / 298.15	100.000	SATP

Thermodynamic values are defined at 25°C and 100.000 kPa. Therefore SATP (standard ambient temperature and pressure) is used to express that within this document.

Which “standard” is to choose now? To calculate a gas volume flow \dot{V} from a molar flow \dot{n} or mass flow \dot{m} , the reference temperature and pressure need to be defined, also is mass flow controllers are used!

The purpose of Mass flow controllers (MFCs) is to feed a required liquid or gas flow. From their measurement principle those components do measure a mass flow (e.g. kg/h or g/sec). But often volumetric values (e.g. l/min or m^3/h) are more common. To transfer gas mass flows into gas volumetric flows, the gas density (kg/m^3) must be known.

Since the gas density itself is dependent on temperature and pressure, a reference temperature and pressure is needed. Well known MFCs manufacturers like Brooks, Bronkhorst, Bürkert, Aera or Omega do use the following temperature and pressure as reference for standard volume flows:

$$T_0 = 273.15 \text{ K} \quad \text{and} \quad p_0 = 101.325 \text{ kPa}$$

Using such types of MFCs require using this reference temperature and pressure to ensure correct calculations like described above!

By the way The well known molar volume of an ideal gas is given at this temperature and pressure:

$$V_{0, \text{mol}} = R \cdot \frac{T_0}{p_0} = 22.414 \text{ l}_n/\text{mol}$$

4.5 HHV and LHV

The higher heating value (HHV) of any fuel can be measured within a calorimeter. The result of this measurement is the energy of the chemical (oxidation) reaction starting at 25°C and ending at 25°C; therefore product water is condensed completely. Due to that the HHV includes the latent heat of water vaporization; but the specific amount of product water produced by the fuel oxidation reaction needs to be considered.

The lower heating value (LHV) itself can not be measured directly; therefore the LHV needs to be calculated from HHV minus latent heat of water vaporization.

4.6 PolCurve parameter variation

Charts 4.2 show parameter variations for the empirical PolCurve equation 1.15. The baseline parameters are: $E_0 = 1.0$ V, $b = 0.08$ V/dec, $R = 0.1 \Omega \text{ cm}^2$, $m = 0.0003$ V, and $n = 3.30 \text{ cm}^2/\text{A}$.

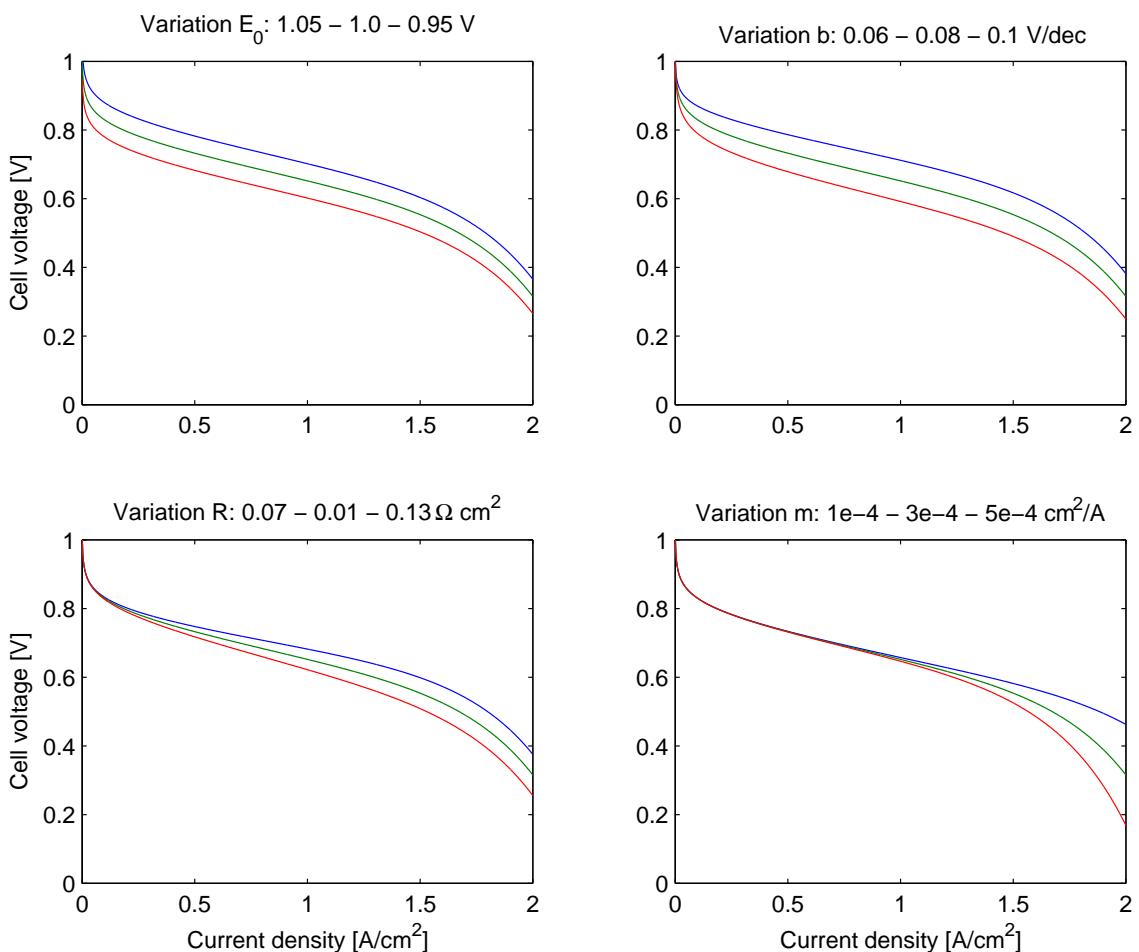


Figure 4.2: Polarization curve model parameter variation

5 Appendix 2: Constant values and abbreviations

Constant values

Faraday's constant	$F = 96\,485.3399 \frac{\text{A sec}}{\text{mol}}$ [11]
Molar gas constant	$R = 8.314472 \frac{\text{J}}{\text{K mol}}$ [11]
Magnus equation const	$C_1 = 610.780 \text{ Pa}$
	$C_2 = 17.08085$
	$C_3 = 234.175 \text{ }^\circ\text{C}$

Thermodynamics

Standard temp. and pressure (STP, see section 4.4)	$T_0 = 273.15 \text{ K}$ [12] $p_0 = 101.325 \text{ kPa}$ [12]
Molar volume of ideal gases (at STP)	$V_{0,\text{mol}} = RT_0/p_0 = 22.414 \text{ l}_\text{n}/\text{mol}$
Standard ambient T and p (SATP)	$T_c = 298.15 \text{ K}$ [13] $p_c = 100.000 \text{ kPa}$ [13]
LHV of H ₂ (at SATP)	$-\Delta H_{\text{H}_2\text{O}_{(\text{g})}} = 241.82 \frac{\text{kJ}}{\text{mol}}$ [13], [14] $\hat{=} 119.96 \text{ kJ/g}$ [15]
HHV of H ₂ (at SATP)	$-\Delta H_{\text{H}_2\text{O}_{(\text{l})}} = 285.83 \frac{\text{kJ}}{\text{mol}}$ [13], [14] $\hat{=} 141.79 \text{ kJ/g}$ [15]
Gibbs free enthalpy of H ₂ O _(g) and H ₂ O _(l) (at SATP)	$-\Delta G_{\text{H}_2\text{O}_{(\text{g})}} = 228.57 \frac{\text{kJ}}{\text{mol}}$ [13] $-\Delta G_{\text{H}_2\text{O}_{(\text{l})}} = 237.13 \frac{\text{kJ}}{\text{mol}}$ [13]

Molar weights

Molar weight water	$M_{\text{water}} = 18.0153 \text{ g/mol}$
hydrogen	$M_{\text{H}_2} = 2.01588 \text{ g/mol}$ [11]
oxygen	$M_{\text{O}_2} = 31.9988 \text{ g/mol}$ [11]
nitrogen	$M_{\text{N}_2} = 28.01348 \text{ g/mol}$ [11]
CO ₂	$M_{\text{CO}_2} = 44.0095 \text{ g/mol}$ [11]
air	$M_{\text{air}} = 28.9646431 \text{ g/mol}$ [11]
Molar fraction of O ₂ in air	$x_{\text{O}_2} = 0.21$

Other relevant constants

Individual gas constant of air	$R_{\text{air}} = R/M_{\text{air}} = 287.06 \frac{\text{J}}{\text{kg K}}$
Individual gas const. water vapor	$R_w = R/M_w = 461.52 \frac{\text{J}}{\text{kg K}}$
Density of air (at STP)	$\rho_{\text{air}} = 1.293 \text{ kg/m}^3$
Density of H ₂ (at STP)	$\rho_{\text{H}_2} = 0.0899 \text{ kg/m}^3$
Specific heat capacity of water (20°C)	$c_{p, \text{m, water}} = 4182 \frac{\text{J}}{\text{kg K}}$
Density of water (20°C)	$\rho_{\text{water}} = 998.2 \text{ kg/m}^3$
Specific heat cap. air (p = const)	$c_{p, \text{m, air}} = 1005.45 \frac{\text{J}}{\text{kg K}}$
Specific heat cap. air (V = const)	$c_{V, \text{m, air}} = c_{p, \text{m, air}} - R_{\text{air}}$ $= 718.39 \frac{\text{J}}{\text{kg K}}$
Ratio of specific heats for air	$\kappa = c_p/c_V = 1.40$ $(\kappa - 1)/\kappa = 0.285$
Specific heat capacity of water vapor	$c_{p, \text{water}} = 1858.94 \frac{\text{J}}{\text{kg K}}$
Enthalpy of water vaporization (0°C)	$h_{\text{we}} = 2500.827 \frac{\text{J}}{\text{g}}$

5.1 Relevant units based on SI units

Physical unit	Name (symbol)	SI unit	non SI units
Force F	Newton (N)	kg m/s ²	-
Pressure p	Pascal (Pa)	kg/(m s ²)	N/m ²
Energy/work E/W	Joule (J)	kg m ² /s ²	Nm, Pa · m ³
Power P	Watt (W)	kg m ² /s ³	J/s
Charge Q	Coulomb (C)	A s	-
Voltage U	Volt (V)	kg m ² /(s ³ A)	W/A, J/C
Resistance R	Ohm (Ω)	kg m ² /(s ³ A ²)	V/A

5.2 Used abbreviations

FCS	Fuel cell system
LHV	Lower heating value
HHV	Higher heating value
OCV	Open circuit voltage
EMF	Electromotive force
Nl (or l _n), Nm ³ (or m _n ³)	Norm liter or norm cubic meter (normalized to standard conditions)
RH	Relative humidity
STP	Standard temperature and pressure
SATP	Standard ambient temp. and pressure
TD	Thermodynamic
WEG	Water ethylene glycol
EMC	Electromagnetic Compatibility
EMI	Electromagnetic Interference
CAN	Controller Area Network

6 Appendix 3: Air

6.1 Moist air

6.1.1 Water vapor saturation pressure

The water vapor partial pressure at saturation $p_{ws}(t)$ is a function of temperature t [$^{\circ}\text{C}$]. Its values are listed in tables (e.g. in [16], see also table 6.1). There are several formulas to fit this table values and to calculate $p_{ws}(t)$ as a function of temperature. Maybe the most simple and therefore popular one is the Magnus equation. But other equations fit with a higher accuracy to the table values.

Magnus equation:

$$p_{ws}(t) = C_1 \cdot \exp \frac{C_2 \cdot t}{C_3 + t} \quad [p_{ws}(t)] = \text{Pa}, [t] = ^{\circ}\text{C} \quad (6.1)$$

Magnus equation converted to temperature versus water vapor saturation pressure:

$$t = \frac{C_3 \cdot \ln \frac{p_{ws}(t)}{C_1}}{C_2 - \ln \frac{p_{ws}(t)}{C_1}}$$

WMO Technical Regulations (WMO-No. 49) [17]:

$$\begin{aligned} \lg p_{ws}(T) &= 10.79574 \cdot \left(1 - \frac{T_1}{T}\right) & (6.2) \\ &\quad - 5.02800 \cdot \lg \frac{T}{T_1} \\ &\quad + 1.50475 \cdot 10^{-4} \cdot \left(1 - 10^{-8.2969 \cdot \left(\frac{T}{T_1} - 1\right)}\right) \\ &\quad + 0.42873 \cdot 10^{-3} \cdot \left(10^{4.76955 \cdot \left(1 - \frac{T_1}{T}\right)} - 1\right) \\ &\quad + 0.78614 \quad [p_{ws}(T)] = \text{hPa}, [T] = \text{K} \end{aligned}$$

T is the temperature in Kelvin and $T_1 = 273.16$ (the triple point of water).

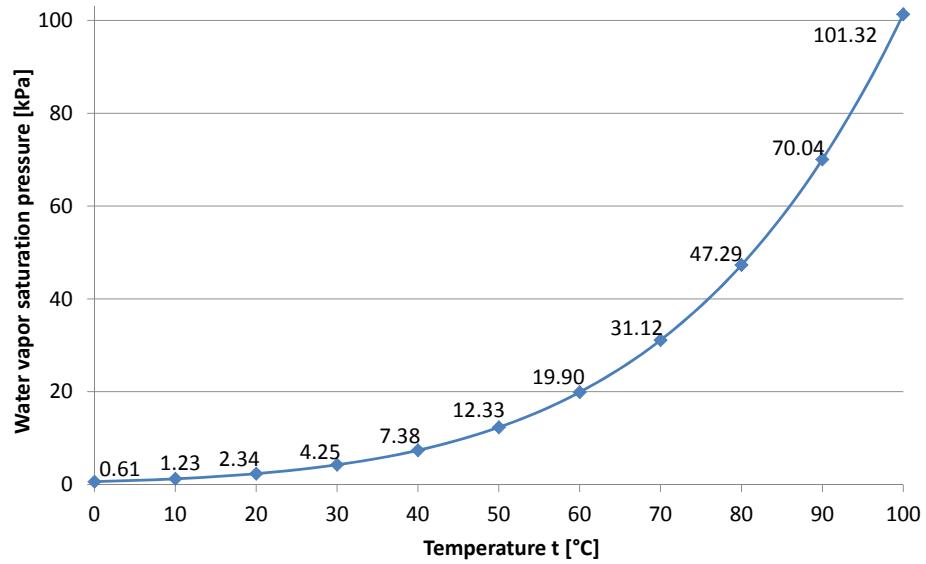


Figure 6.1: Water vapor saturation pressure (Magnus equation, 0 to 100°C)

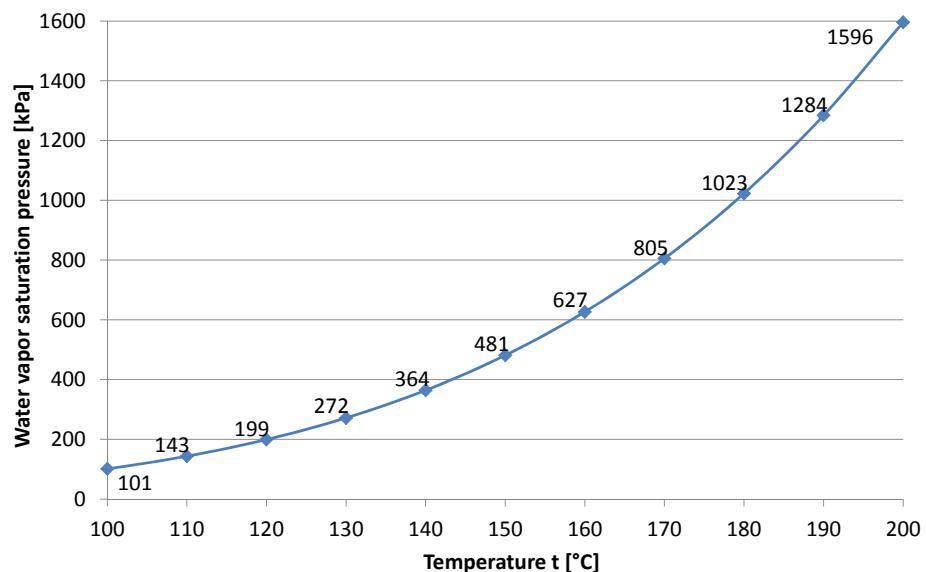


Figure 6.2: Water vapor saturation pressure (Magnus equation, 100 to 200°C)

Equation used by Vaisala (documented in old user manuals):

$$\Theta = T - \sum_{i=0}^3 C_i T^i$$

With T = temperature in K, $C_0 = 0.4931358$, $C_1 = -4.6094296 \cdot 10^{-3}$, $C_2 = -1.3746454 \cdot 10^{-5}$, and $C_3 = -1.2743214 \cdot 10^{-8}$.

$$\ln p_{ws}(T) = \sum_{i=-1}^3 b_i \Theta^i + b_4 \ln \Theta$$

With $b_{-1} = -5.8002206 \cdot 10^3$, $b_0 = 1.3914993$, $b_1 = -4.8640239 \cdot 10^{-2}$, $b_2 = 4.1764768 \cdot 10^{-5}$, $b_3 = -1.4452093 \cdot 10^{-8}$, and $b_4 = 6.5459673$.

Antoine equation:

$$\log_{10} p_{ws}(t) = A - \frac{B}{t + C}$$

With t = temperature in °C, $A = 10.20389$, $B = 1733.926$, and $C = 233.665$. Other parameters are defined depending on the temperature range.

Comparison of accuracy: Between 25 and 100°C the WMO equation has the best accuracy compared to table values 6.1. The maximum relative failure is 0.07%, followed by the Vaisala equation with 0.10%, Magnus with 0.17% and Antoine with 0.36%. Due to the simplicity of Magnus this is maybe the most preferable equation to fit the water vapor saturation pressure.

6.1.2 Other formulas to express humidity of air

Specific humidity or humidity (mixing) ratio Specific humidity Y is the ratio between the actual mass of water vapor m_w in moist air to the mass of the dry air $m_{dry\ air}$:

$$Y(p, t) = \frac{m_w}{m_{dry\ air}} = \frac{R_{air}}{R_w} \cdot \frac{p_w(t)}{p_{air} - p_w(t)} = \frac{M_w}{M_{air}} \cdot \frac{p_w(t)}{p_{air} - p_w(t)} \quad [Y] = \text{kg/kg} \quad (6.3)$$

With $R_w/R_{air} = 0.622$ and $p_w(t) = \varphi \cdot p_{ws}(t)$ (see below) we get:

$$Y(p, t, \varphi) = 0.622 \cdot \frac{\varphi p_{ws}(t)}{p_{air} - \varphi p_{ws}(t)} \quad (6.4)$$

The maximum amount of water vapor in the air is achieved when $p_w(t) = p_{ws}(t)$ the saturation pressure of water vapor at the temperature t .

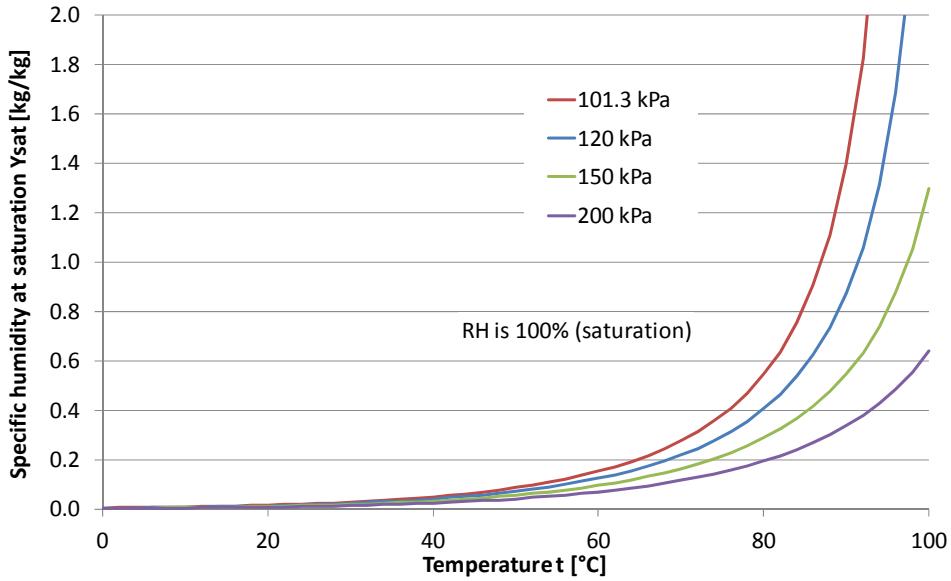


Figure 6.3: Specific humidity at saturation versus temperature

For other gases the molar weight has to be considered in the equation above. The constant value 0.622 is only valid for moist air!

Since the water vapor pressure is small regarding to the atmospheric pressure, the relation between the humidity ratio and the saturation pressure is almost linear at temperature far below 100°C.

Relative humidity RH (or φ) is the ratio of the partial pressure of water vapor $p_w(t)$ to the partial pressure of water vapor at saturation $p_{ws}(t)$:

$$\varphi = \frac{p_w(t)}{p_{ws}(t)} = \frac{a_w(t)}{a_{ws}(t)} = \frac{m_w}{m_{ws}} \quad \varphi = 0.0 - 1.0$$

RH can also be calculated with $Y(t)$:

$$\varphi = \frac{Y(t)}{\frac{M_w}{M_{air}} + Y(t)} \cdot \frac{p}{p_s(t)} = \frac{Y(t)}{0.622 + Y(t)} \cdot \frac{p}{p_s(t)} \quad (6.5)$$

Absolute humidity or water vapor density Absolute humidity $a(t)$ is the actual mass of water vapor present in the moist air and a function of t :

$$a(t) = \frac{M_w}{R} \cdot \frac{p_w(t)}{T_0 + t} = \frac{1}{R_w(t)} \cdot \frac{p_w}{T_0 + t} = 2.167 \frac{\text{g K}}{\text{J}} \cdot \frac{p_w(t)}{T_0 + t}$$

$$[a(t)] = \text{g/m}^3, [t] = {}^\circ\text{C}$$

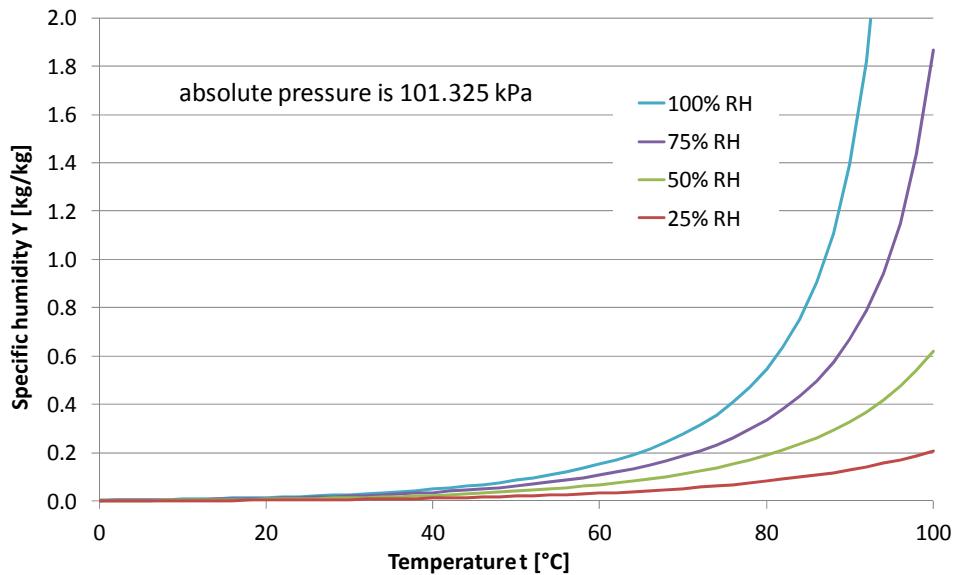


Figure 6.4: Specific humidity at constant pressure versus temperature

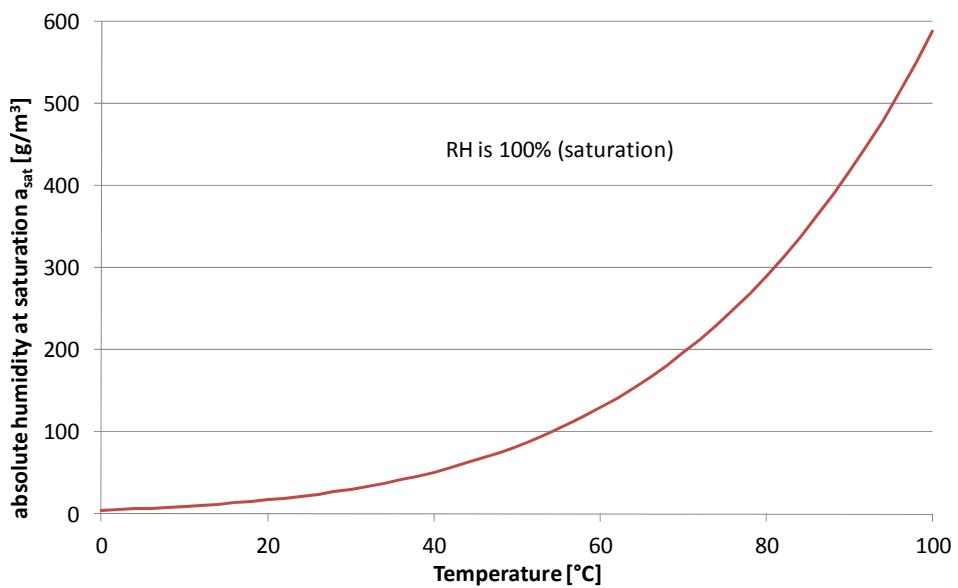


Figure 6.5: Absolute humidity

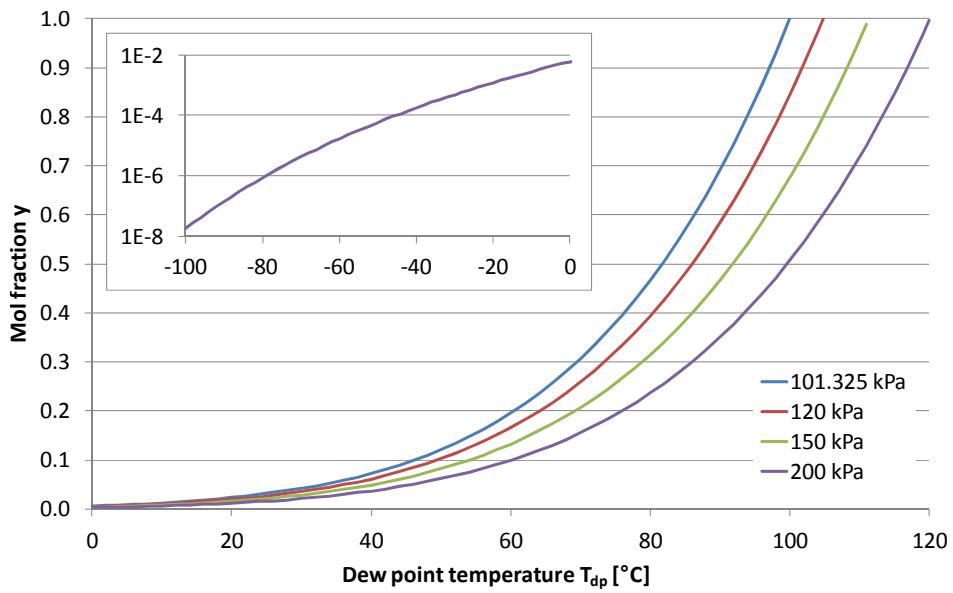


Figure 6.6: Molar fraction versus dew point temperature

Molar fraction The molar fraction $y(t)$ of water vapor is calculated as:

$$y(t) = \frac{p_w(t)}{p_a} \quad y = 0.0 - 1.0$$

At standard pressure and 100°C $y = 1$ because there is only water in vapor phase (and no air).

Dew point temperature The dew point temperature (DPT) T_{dp} is the temperature at which water vapor starts to condense out of the air, the temperature at which air becomes completely saturated. Above this temperature the moisture will stay in the air.

If the DPT is close to the air temperature, the relative humidity is high; and if the dew point is well below the air temperature, the relative humidity is low.

The following equation allows to calculate the DPT T_{dp} based on RH ($\varphi = \text{RH}/100\%$) and temperature t :

$$T_{dp} = \frac{C_3 \cdot \left(\ln \varphi + \frac{C_2 \cdot t}{C_3 + t} \right)}{C_2 - \ln \varphi - \frac{C_2 \cdot t}{C_3 + t}}$$

$$[T_{dp}] = {}^\circ\text{C}, [t] = {}^\circ\text{C}, \varphi = 0.0 - 1.0$$

To calculate RH from temperature and DPT:

$$\varphi = \frac{p_w(t)}{p_{ws}(t)} = \frac{\exp \frac{C_2 \cdot T_{dp}}{C_3 + T_{dp}}}{\exp \frac{C_2 \cdot t}{C_3 + t}}$$

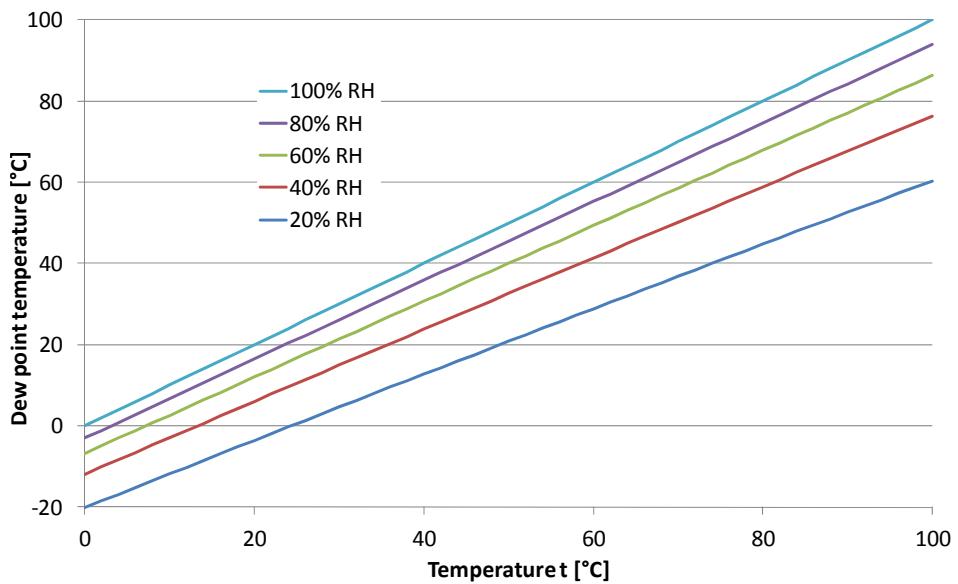


Figure 6.7: Dew point temperature versus temperature

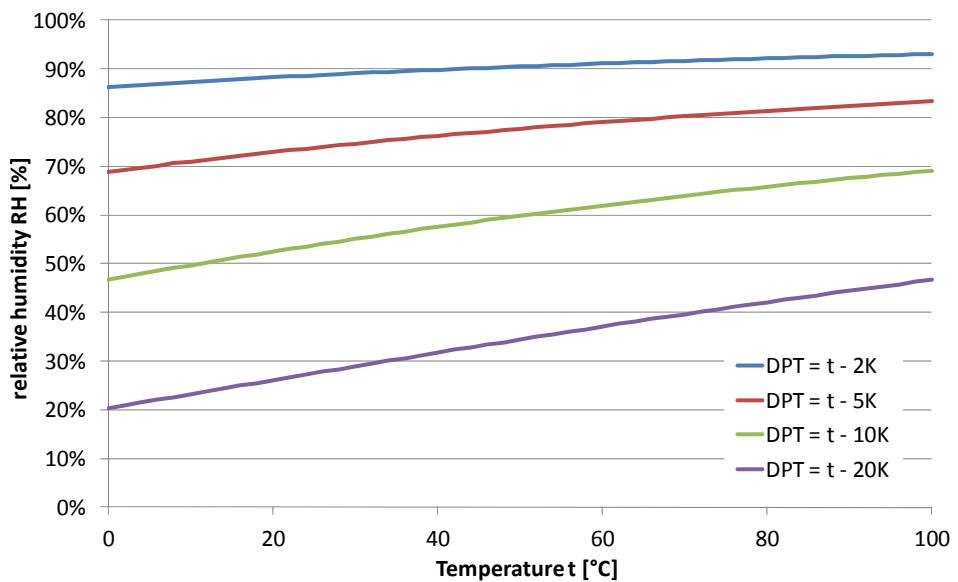


Figure 6.8: Relative humidity versus temperature

Enthalpy The air enthalpy h is needed to calculate energy and power of air. The enthalpy of moist air consists of sensible heat and latent heat. Since moist air is a mixture of dry air and water vapor, the enthalpy includes the enthalpy of the dry air (the sensible heat h_{air}) and the enthalpy of the evaporated water (the latent heat h_{water}).

Specific enthalpy h [kJ/kg] of moist air is defined as the total enthalpy of the dry air and the water vapor mixture per kg of moist air.

The enthalpy consists of three parts: a) warming up dry air from the reference temperature to the air temperature t , b) evaporating water inside the moist air and c) warming up water vapor from the reference temperature to the air temperature t :

$$h = h_{\text{air}} + Y \cdot h_{\text{water}} \quad (6.6)$$

with

$$h_{\text{air}} = c_{p, \text{air}} \cdot t \quad \text{and} \quad h_{\text{water}} = c_{p, \text{water}} \cdot t + h_{\text{we}}$$

$$h = c_{p, \text{air}} \cdot t + Y \cdot (c_{p, \text{water}} \cdot t + h_{\text{we}}) \quad [h] = \text{J/g}$$

where Y is the specific humidity of moist air, $c_{p, \text{air}}$ is the specific heat capacity of dry air, $c_{p, \text{water}}$ is the specific heat capacity of water vapor and h_{we} is the specific enthalpy of water vaporization. In case of dry air ($Y = 0$), the enthalpy is a linear function of temperature (with slope $c_{p, \text{air}}$). Heat capacities are dependent on temperature (see chapter 4.3), but between 0 and 100°C this may be neglected.

Because the enthalpy is not an absolute value; only the enthalpy difference to a reference temperature can be calculated. Depending on the unit of temperature, the reference temperature is 0°C if $[t] = ^\circ\text{C}$; or 0 K if $[t] = \text{K}$. If the temperature is given in °C, the enthalpy is 0 $\frac{\text{kJ}}{\text{kg}}$ at 0°C. If temperature is given in K, the enthalpy is 0 $\frac{\text{kJ}}{\text{kg}}$ at 0 K.

Due to the fact that only the enthalpy difference is used, it doesn't matter if temperature is given in K or °C! It's just important not to switch between both units.

The following chart show the enthalpy based on 0°C reference:

For dry air there is another empirical fit to calculate the enthalpy. This equation is used in DIN IEC 62282-3-2 [10]:

$$h(t) = (A \cdot t + B \cdot t^2 + C \cdot t^3) / M_{\text{air}} \quad [h(t)] = \text{kJ/kg}, [t] = ^\circ\text{C or K}$$

with $A = 27.434$, $B = 6.18/2000$, $C = -0.8987/3 \cdot 10^6$.

Also here the temperature t can be given in °C or K, see above. But this equation is only valid for dry air!

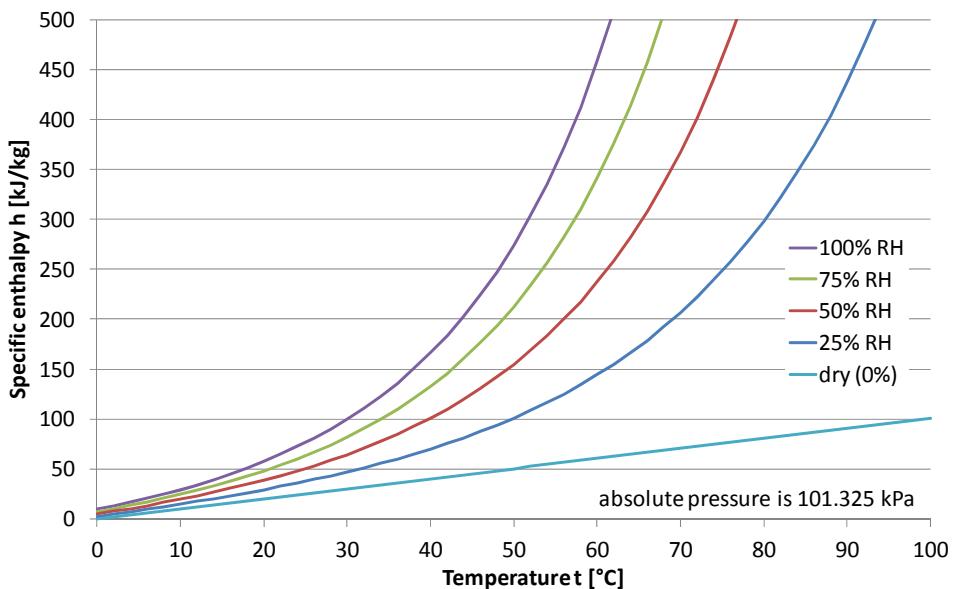


Figure 6.9: Specific enthalpy versus temperature at constant pressure

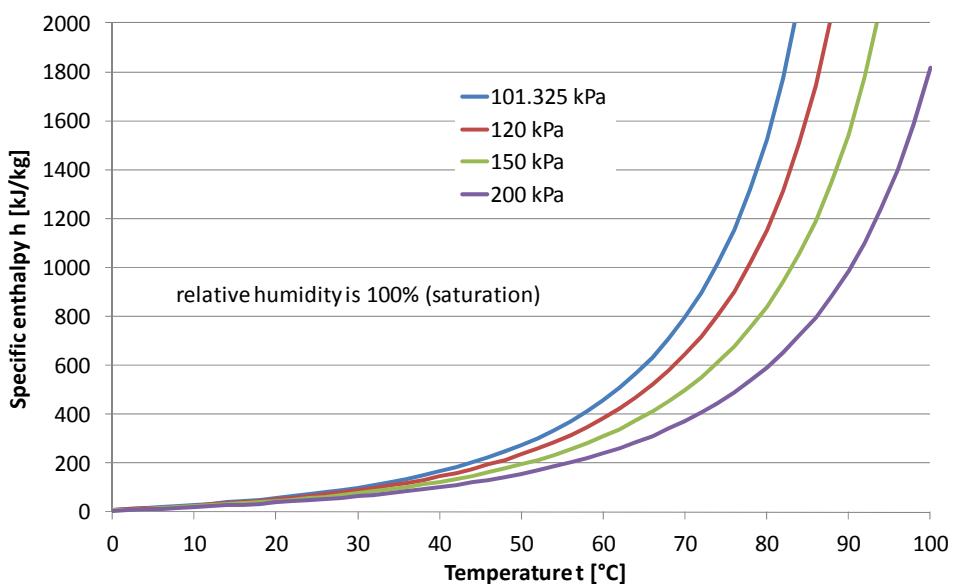


Figure 6.10: Specific enthalpy versus temperature at saturation

The following table lists the water vapor saturation pressure over liquid water (between 0 and 200 °C) according to [16].

t [°C]	p [kPa]						
0	0.61129	51	12.97	101	104.99	151	488.61
1	0.65716	52	13.623	102	108.77	152	501.78
2	0.70605	53	14.303	103	112.66	153	515.23
3	0.75813	54	15.012	104	116.67	154	528.96
4	0.81359	55	15.752	105	120.79	155	542.99
5	0.8726	56	16.522	106	125.03	156	557.32
6	0.93537	57	17.324	107	129.39	157	571.94
7	1.0021	58	18.159	108	133.88	158	586.87
8	1.073	59	19.028	109	138.5	159	602.11
9	1.1482	60	19.932	110	143.24	160	617.66
10	1.2281	61	20.873	111	148.12	161	633.53
11	1.3129	62	21.851	112	153.13	162	649.73
12	1.4027	63	22.868	113	158.29	163	666.25
13	1.4979	64	23.925	114	163.58	164	683.1
14	1.5988	65	25.022	115	169.02	165	700.29
15	1.7056	66	26.163	116	174.61	166	717.83
16	1.8185	67	27.347	117	180.34	167	735.7
17	1.938	68	28.576	118	186.23	168	753.94
18	2.0644	69	29.852	119	192.28	169	772.52
19	2.1978	70	31.176	120	198.48	170	791.47
20	2.3388	71	32.549	121	204.85	171	810.78
21	2.4877	72	33.972	122	211.38	172	830.47
22	2.6447	73	35.448	123	218.09	173	850.53
23	2.8104	74	36.978	124	224.96	174	870.98
24	2.985	75	38.563	125	232.01	175	891.8
25	3.169	76	40.205	126	239.24	176	913.03
26	3.3629	77	41.905	127	246.66	177	934.64
27	3.567	78	43.665	128	254.25	178	956.66
28	3.7818	79	45.487	129	262.04	179	979.09
29	4.0078	80	47.373	130	270.02	180	1001.9
30	4.2455	81	49.324	131	278.2	181	1025.2
31	4.4953	82	51.342	132	286.57	182	1048.9
32	4.7578	83	53.428	133	295.15	183	1073
33	5.0335	84	55.585	134	303.93	184	1097.5
34	5.3229	85	57.815	135	312.93	185	1122.5
35	5.6267	86	60.119	136	322.14	186	1147.9
36	5.9453	87	62.499	137	331.57	187	1173.8
37	6.2795	88	64.958	138	341.22	188	1200.1
38	6.6298	89	67.496	139	351.09	189	1226.9
39	6.9969	90	70.117	140	361.19	190	1254.2
40	7.3814	91	72.823	141	371.53	191	1281.9
41	7.784	92	75.614	142	382.11	192	1310.1
42	8.2054	93	78.494	143	392.92	193	1338.8
43	8.6463	94	81.465	144	403.98	194	1368
44	9.1075	95	84.529	145	415.29	195	1397.6
45	9.5898	96	87.688	146	426.85	196	1427.8
46	10.094	97	90.945	147	438.67	197	1458.5
47	10.62	98	94.301	148	450.75	198	1489.7
48	11.171	99	97.759	149	463.1	199	1521.4
49	11.745	100	101.32	150	475.72	200	1553.6
50	12.344						

Table 6.1: Water vapor saturation pressure

6.2 Energy and power of air

Energy and power of dry and wet air are important to calculate e.g. the power demand for air humidification in a fuel cell system or to calculate efficiencies. See also ASME PTC 50-2002 Fuel Cell Power Systems Performance [18] and DIN IEC 62282-3-2 Fuel cell technologies - Part 3-2: Stationary fuel cell power systems [10].

The energy of air contains the air enthalpy and the pressure:

$$E_{\text{air}} = h_{\text{air}} + E_{p, \text{air}} \quad [E_{\text{air}}] = \text{kJ/kg}$$

The air power is given as:

$$P_{\text{air}} = E_{\text{air}} \cdot \dot{m}_{\text{air}} \quad [P_{\text{air}}] = \text{kW}$$

The air enthalpy h_{air} is defined by equation 6.6. Please be aware that always enthalpy differences are calculated and not the absolute enthalpy!

The energy of compressed air is given by:

$$E_{p, \text{air}} = R_{\text{air}} \cdot T_0 \cdot \ln \frac{p}{p_0}$$

T_0 and p_0 are the reference temperature and pressure, see section 4.4.

Example 1: How much power is required to heat dry air from 20 to 60°C with a mass flow of 30 kg/hr?

$$\Delta h = h_{60^\circ\text{C}/0\%} - h_{20^\circ\text{C}/0\%} = 40.218 \text{ kJ/kg}$$

$$P = \Delta h \cdot \dot{m}_{\text{air}} = 40.218 \text{ kJ/kg} \cdot 30 \text{ kg/hr} \cdot \frac{1}{3600} \text{ hr/sec} = 335 \text{ W}$$

Example 2: How much power is required to heat and humidify air at ambient pressure from 20°C and 50% RH to 60°C and 80% RH? Air mass flow is 30 kg/hr.

$$h_{20^\circ\text{C}/50\%} = 38.56 \text{ kJ/kg}$$

$$h_{60^\circ\text{C}/80\%} = 363.18 \text{ kJ/kg}$$

$$\Delta h = 326.61 \text{ kJ/kg}$$

$$P = \Delta h \cdot \dot{m}_{\text{air}} = 326.61 \text{ kJ/kg} \cdot 30 \text{ kg/hr} \cdot \frac{1}{3600} \text{ hr/sec} = 2722 \text{ W}$$

6.3 Air compression

6.3.1 Definitions

Adiabatic Process where no heat is transferred to or from the surroundings ($dq = 0$).

Reversible Process can be reversed without loss or dissipation of energy ($dS = 0$).

Isentropic Process with equal entropy

Any reversible adiabatic process is an isentropic process ($dq = dS = 0$). But not vice versa!

6.3.2 Thermodynamics

Compression and expansion

A gas mass flow \dot{m}_1 is compressed or expanded from pressure p_1 and temperature T_1 to pressure p_2 and temperature T_2 . $p_2 > p_1$ in case of compression and $p_2 < p_1$ in case of expansion. The pressure ratio Π is defined as:

$$\Pi = \frac{p_2}{p_1}$$

For compression $\Pi > 1$ and for expansion $\Pi < 1$.

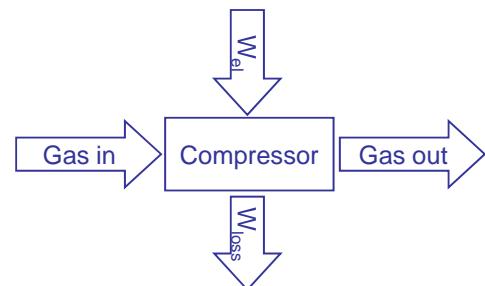


Figure 6.11: Gas compression

A compression process consumes energy or work, an expansion process produces energy or work.

To calculate the efficiency of a compression process the theoretical energy demand needs to be calculated based on an isentropic process. In a real compression process there is always heat transferred to the surrounding (or cooling), and also gas mass flow losses can occur inside the compressor.

Thermodynamic of gases

Internal energy U The first law of thermodynamics [13] defines infinitesimal changes in internal energy dU of an ideal gas as changes in added heat dq and provided work dw :

$$dU = dq + dw$$

Enthalpy H is defined as $H = U + pV$. Infinitesimal changes dH are therefore defined as:

$$dH = dU + pdV + Vdp$$

Heat capacities C describe the temperature dependencies of internal energy U and enthalpy H :

$$C_V = (\partial U / \partial T)_V \quad C_p = (\partial H / \partial T)_p$$

C_V is the heat capacity at constant volume and C_p the heat capacity at constant pressure of an ideal gas:

$$dU = C_V dT \quad \text{and} \quad dH = C_p dT \quad (6.7)$$

With $pV = nRT$ it is $dH = dU + nRdT$ and therefore:

$$C_p - C_V = nR$$

For ideal gases the specific heat capacities c_p and c_V with $[c] = \text{J/mol K}$ are independent of temperature! For ideal one atomic gases it is:

$$c_p = \frac{C_p}{n} = \frac{5}{2}R \quad c_V = \frac{C_V}{n} = \frac{3}{2}R \quad \kappa = \frac{5}{3} = 1.67$$

And for ideal two atomic gases:

$$c_p = \frac{7}{2}R \quad c_V = \frac{5}{2}R \quad \kappa = \frac{7}{5} = 1.40$$

The specific heat capacities $c_{p,m}$ and $c_{V,m}$ are given as:

$$c_{p,m} = c_p / M \quad \text{and} \quad c_{V,m} = c_V / M$$

$$[c_{p,m}] = [c_{V,m}] = \text{J/kg K}$$

Polytropic process For all thermodynamic processes of ideal gases it is in general:

$$pV^n = \text{const} \quad n = \text{polytropic index (constant)}$$

The energy or work in a volume change process is in general:

$$dw = dU = -p dV = C_V dT$$

With $pV = nRT$ it is:

$$C_V \frac{dT}{T} = -nR \frac{dV}{V}$$

The integral over start (1) and end state (2) is:

$$C_V \int_1^2 \frac{dT}{T} = -nR \int_1^2 \frac{dV}{V}$$

$$C_V \ln(T_2/T_1) = -nR \ln(V_2/V_1)$$

Isentropic process The isentropic process is a special case of a polytropic process, where the polytropic index becomes the isentropic index or heat capacity ratio κ :

$$n = \kappa = \frac{c_p}{c_v} > 1$$

With $c_p - c_v = R$, $c_v = C_V/n$ and therefore $\frac{C_V}{nR} = \frac{c_v}{c_p - c_v} = \frac{1}{\kappa-1}$ it is:

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1} \right)^{\kappa-1}$$

The following ratios are valid for an isentropic process:

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1} \right)^{\kappa-1} \quad \frac{T_1}{T_2} = \left(\frac{p_1}{p_2} \right)^{\frac{\kappa-1}{\kappa}} \quad \frac{p_1}{p_2} = \left(\frac{V_2}{V_1} \right)^{\kappa}$$

Volume work and technical work

The *volume (change) work* $w_{V,12}$ is the work that is done on a piston to reduce the start volume V_1 to the end volume V_2 . It is equivalent in the change of inner energy. The volume work for an adiabatic process ($dq = 0$) is defined as:

$$w_{V,12} = - \int_{V_1}^{V_2} p \, dV = \int_1^2 dU = C_V \int_{T_1}^{T_2} dT = C_V \Delta T$$

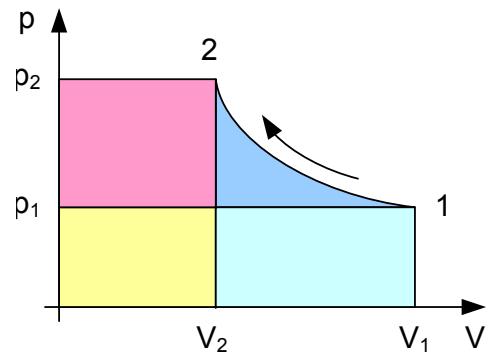
The *technical work* $w_{t,12}$ is the work that is transferred from or mass flow via a technical system (for instance a mechanical axle). The technical work is equal to the enthalpy of the kinetic and potential energy of a stationary mass flow. The technical work $w_{t,12}$ for compression is the work given to the drive shaft of the compressor; it contains the displacement work, but not the friction [19]!

The technical work for an adiabatic process ($dq = 0$) is defined as:

$$w_{t,12} = + \int_{p_1}^{p_2} V \, dp = \int_1^2 dH = C_p \Delta T$$

Each compression process (polytropic, isentropic, isothermal etc.) follows a (similar but not the same) curve the pV chart (see figure 6.12) from the start (1) to the end (2) point. Adding the different process areas shown in the pV chart gives:

$$p_2 V_2 + \int_{V_2}^{V_1} p \, dV = p_1 V_1 + \int_{p_1}^{p_2} V \, dp$$



Therefore:

Figure 6.12: pV chart

$$w_{t,12} = w_{V,12} + p_2 V_2 - p_1 V_1$$

Comment: For liquids $\Delta V \approx 0$ and therefore $w_{V,12} \approx 0$; then it is: $w_{t,12} \approx (p_2 - p_1) \cdot V$

The thermodynamic derivation (see above) defines the following ratios for the isentropic compression or expansion:

$$\Pi = \left(\frac{V_1}{V_2} \right)^\kappa \quad \text{and} \quad \frac{T_1}{T_2} = \left(\frac{V_2}{V_1} \right)^{\kappa-1} = \Pi^{\frac{\kappa-1}{\kappa}}$$

Therefore for the volume work it is:

$$w_{V,12} = c_{V,m} \cdot (T_2 - T_1) = c_{V,m} T_1 \cdot \left(\Pi^{\frac{\kappa-1}{\kappa}} - 1 \right)$$

And similar for the technical work:

$$w_{t,12} = c_{p,m} \cdot (T_2 - T_1) = c_{p,m} T_1 \cdot \left(\Pi^{\frac{\kappa-1}{\kappa}} - 1 \right)$$

$$w_{t,12} = h_2 - h_1 \quad \text{with} \quad h = c_{p,m} \cdot T$$

$$w_{t,12} = \kappa \cdot w_{V,12} \quad \text{with} \quad \kappa = c_p/c_V$$

The technical work is always more than the volume work, because $\kappa > 1$.

6.3.3 Ideal and real compressor

Ideal The ideal compression is an isentropic process. There is no (energy or air mass flow) exchange with the surroundings.

Real Due to friction the gas compression in a real compressor always dissipates energy to the surroundings or to the cooling system. This compression process is polytropic. After a polytropic compression the actual end temperature $T_{2,\text{act}}$ is always higher compared to an ideal isentropic compression $T_{2,\text{s}}$:

$$T_{2,\text{act}} > T_{2,\text{s}}$$

The isentropic efficiency η_s of a compressor is the ratio between isentropic technical work $w_{s,12}$ and actual technical work $w_{\text{act},12}$:

$$\eta_s = \frac{w_{s,12}}{w_{\text{act},12}} = \frac{T_{2,\text{s}} - T_1}{T_{2,\text{act}} - T_1} = \frac{h_{2,\text{s}} - h_1}{h_{2,\text{act}} - h_1}$$

$w_{\text{act},12}$ is $w_{s,12}$ plus specific friction work (dissipation).

To calculate the isentropic work, first of all the isentropic end temperature $T_{2,\text{s}}$ needs to be calculated:

$$T_{2,\text{s}} = T_1 \cdot \Pi^{\frac{\kappa-1}{\kappa}}$$

Now the isentropic technical work can be calculated as:

$$w_{s,12} = c_{p,m} \cdot (T_{2,\text{s}} - T_1) = c_{p,m} T_1 \cdot \left(\Pi^{\frac{\kappa-1}{\kappa}} - 1 \right)$$

6.3.4 Examples

Example 1: Isentropic efficiency

Air is compressed from 1 bara at 30°C (303.15 K) to 3 bara at 150°C (423.15 K). In the compressor there is no energy or air mass flow loss to the surroundings.

The actual technical work that is done at the air is:

$$w_{\text{act}} = c_{p,m} \cdot (T_{2,\text{act}} - T_1) = 1005 \frac{\text{J}}{\text{kg} \cdot \text{K}} \cdot 120 \text{ K} = 120.6 \frac{\text{kJ}}{\text{kg}}$$

Isentropic temperature:

$$T_{2,\text{s}} = T_1 \cdot \Pi^{\frac{\kappa-1}{\kappa}} = 303.15 \text{ K} \cdot \left(\frac{3 \text{ bara}}{1 \text{ bara}} \right)^{0.285} = 414.6 \text{ K}$$

Isentropic technical work:

$$\begin{aligned} w_s &= c_{p,m} \cdot (T_{2,\text{s}} - T_1) \\ &= 1005 \frac{\text{J}}{\text{kg} \cdot \text{K}} \cdot (414.6 \text{ K} - 303.15 \text{ K}) = 112.4 \frac{\text{kJ}}{\text{kg}} \end{aligned}$$

Isentropic efficiency:

$$\eta_s = \frac{w_s}{w_{act}} = \frac{112.4 \text{ kJ/kg}}{120.6 \text{ kJ/kg}} = 0.932 \quad \text{or} \quad 93.2\%$$

Example 2: Electric efficiency

27 kg/h air is compressed from 2.4 to 6 barabs, the electric power consumption of the compressor is 1305 W:

$\dot{m} = 27 \text{ kg/h}$, $p_1 = 2.4 \text{ barabs}$ and $T_1 = 18^\circ = 291K$

$p_2 = 6 \text{ barabs}$ and $P_{el} = 1305 \text{ W}$

Air mass flow losses due to gaps and other heat losses to the surroundings are neglected!
But of course heat is transferred to the cooling!

The isentropic technical work given to the air is:

$$\begin{aligned} w_s &= c_{p,m} T_1 \cdot \left(\Pi^{\frac{\kappa-1}{\kappa}} - 1 \right) \\ &= 1005 \frac{\text{J}}{\text{kg}\cdot\text{K}} \cdot 291 \text{ K} \cdot \left(\left(\frac{6 \text{ bar}}{2.4 \text{ bar}} \right)^{0.285} - 1 \right) = 87.6 \frac{\text{kJ}}{\text{kg}} \end{aligned}$$

Isentropic technical power:

$$P_s = \dot{m} \cdot w_s = 87.6 \frac{\text{kJ}}{\text{kg}} \cdot 27 \text{ kg/h} = 2365.2 \text{ kJ/h} = 657.0 \text{ W}$$

The electric efficiency of this compressor is:

$$\eta_{el} = \frac{P_s}{P_{el}} = \frac{657.0 \text{ W}}{1305 \text{ W}} = 0.50 \quad \text{or} \quad 50\%$$

6.3.5 Comment

The technical work equation is often given in literature with different indices. The next two equations show the relation between κ , R , c_p and c_V :

$$\frac{\kappa}{\kappa-1} \cdot R = \frac{c_p/c_V}{c_p/c_V - 1} \cdot (c_p - c_V) = \frac{c_p}{c_p - c_V} \cdot (c_p - c_V) = c_p$$

$$\frac{1}{\kappa-1} \cdot R = \frac{1}{c_p/c_V - 1} \cdot (c_p - c_V) = \frac{c_V}{c_p - c_V} \cdot (c_p - c_V) = c_V$$

7 Appendix 4: Fuel cell stack water management

7.1 Assumptions

Simple calculation of fuel cell stack water management, based on calculation of specific humidity at cathode exhaust with the following assumptions:

1. The product water is removed via cathode side; that means there is no water removal via anode side.
2. Cathode air is heated inside the stack to a specific temperature t (which does not necessarily have to be the stack coolant outlet temperature).
3. Condensation is not considered! All water exits the stack as water vapor.
4. All gases (air, hydrogen, water vapor) are treated as ideal gases.

7.2 Derivation

Stack inlet: Humidified air with specific humidity Y (calculated by equation 6.4)

$$\dot{m}_{\text{air in}} = \frac{NI}{4F} \cdot M_{\text{air}} \cdot \frac{\lambda}{x} \quad \text{see equation 1.9}$$

$$\dot{m}_{\text{water in}} = \dot{m}_{\text{air in}} \cdot Y_{\text{in}} \quad \text{see equation 6.3}$$

Stack outlet: Water inlet and product water exit the cathode

$$\dot{m}_{\text{cathode, out}} = \frac{IN}{4F} \cdot \left(\frac{\lambda_{\text{cathode}}}{x_{\text{O}_2}} \cdot M_{\text{air}} - M_{\text{O}_2} \right) \quad \text{see equation 1.10}$$

$$\dot{m}_{\text{water, out}} = \dot{m}_{\text{water, in}} + \dot{m}_{\text{water, prod}}$$

The specific humidity at cathode outlet is:

$$Y_{\text{out}} = \frac{m_{\text{water, out}}}{\dot{m}_{\text{cathode, out}}} = \frac{\dot{m}_{\text{water, in}} + \dot{m}_{\text{water, prod}}}{\frac{IN}{4F} \cdot \left(\frac{\lambda_{\text{cathode}}}{x_{O_2}} \cdot M_{\text{air}} - M_{O_2} \right)} = \frac{\frac{\lambda}{x} \cdot Y_{\text{in}} + 2 \cdot \frac{M_{\text{water}}}{M_{\text{air}}}}{\frac{\lambda}{x} - \frac{M_{O_2}}{M_{\text{air}}}}$$

Relative humidity can be calculated using equation 6.5.

8 Appendix 5: FCS controls parameters

8.1 Fuel cell stack pressure drop

The reactant pressure drops through the fuel cell stack anode and cathode are important stack parameters for system design considerations. Especially the pressure drop on the cathode side needs to be considered, because air needs to be compressed accordingly. For simplification the stack can be seen as an orifice with a specific pneumatic resistance, see figure 8.1

p_1 (p.Si.C) and p_2 (p.So.C) are gauge pressures before (upstream) and behind (downstream) the stack or orifice. For gases the mass flow \dot{m} is given by the following orifice equation:

$$\dot{m} = \alpha A \cdot \sqrt{2 \rho_1 \Delta p} \quad (8.1)$$

$\rho_1 = \rho_0 \frac{p_1 + p_0}{p_0}$ is the gas density at pressure p_1 (temperature is not considered here!), and $\Delta p = p_1 - p_2$ is the pressure drop at the orifice. αA is an orifice specific parameter containing the orifice flow coefficient α and the orifice cross-sectional area A , $[\alpha A] = m^2$. This coefficient is hardly accessible by theory, but it can easily be measured if all other parameters of equation 8.1 are known.

Example: The air flow through a single cell is $\dot{V} = 10 \text{ Nl/min}$ ($\dot{m} = 0.216 \text{ g/sec}$). Pressures are measured to be $p_1 = 15 \text{ kPa}$ and $\Delta p = 10 \text{ kPa}$ (and therefore $p_2 = 5 \text{ kPa}$), then $\alpha A = 1.251 \cdot 10^{-6} \text{ m}^2$.

This orifice equation 8.1 can be solved to Δp with the following result:

$$\Delta p = \frac{p_2 - p_0}{2} + \frac{\sqrt{(\alpha A \rho_0)^2 \cdot (p_0 + p_2)^2 + 2 \dot{m}^2 p_0 \rho_0}}{2 \alpha A \rho_0} - p_2 \quad \Delta p \propto \dot{m}^x \quad (8.2)$$

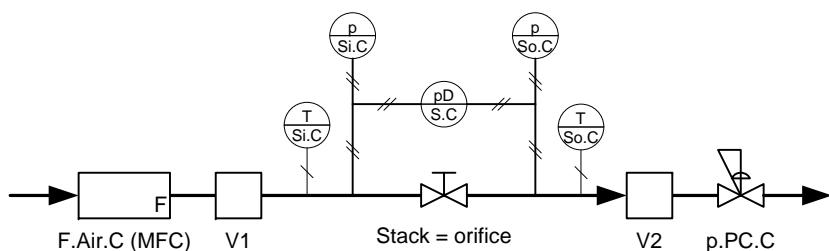


Figure 8.1: Cathode pressure drop schematic

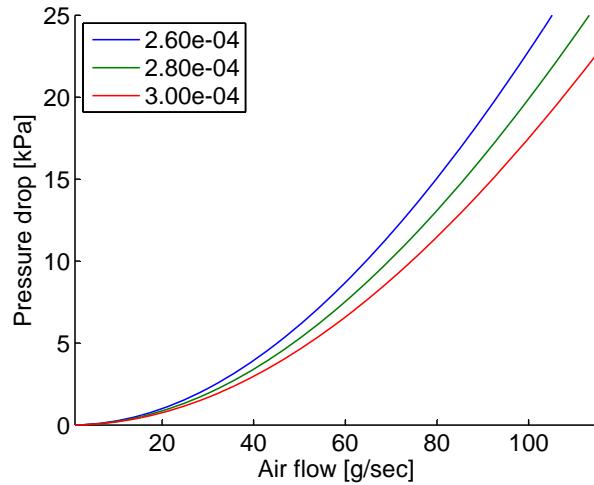


Figure 8.2: Pressure drop versus air mass flow

Figure 8.2 shows the pressure drop Δp as a function of air mass flow \dot{m} with three different values of αA . According to equation 8.1 $\alpha A = 2.9 \cdot 10^{-4} \text{ m}^2$ for a given pressure drop of 25 kPa at the air mass flow of 115 g/sec and cathode exhaust pressure of 130 kPaabs.

8.2 Cathode dynamics - UNDER CONSTRUCTION ***

The dynamic behavior of the cathode subsystem can be discussed based on the simplified schematic in figure 8.3, where the stack again is considered as a pneumatic resistor R_{Stack} . In case of steady state conditions the air mass flow into the system is equal to the air mass flow out of the system:

$$\text{during steady state: } \dot{m}_{\text{in}} \equiv \dot{m}_{\text{out}}$$

But during air mass flow transients the volume V between the air feed and the fuel cell stack needs to be considered, as described here [20]. The reason therefore is that each individual air flow corresponds to a specific pressure drop (see equation 8.2), and therefore also the pressure p_1 before the stack is a function of air flow. An increasing air flow \dot{m}_{in} also increases the pressure in the volume V , and therefore $\dot{m}_C > 0$:

$$\text{during transients: } \dot{m}_{\text{in}} = \dot{m}_C + \dot{m}_{\text{out}}$$

The volume V can be described as a pneumatic capacity C_{Vol} . During air flow up (or down) transients additional air flow \dot{m}_C goes into (or comes out of) this capacity. Corresponding to an electric RC-circuit (Δp corresponds to electric voltage, \dot{m} to electric current), the following equations are valid also for this pneumatic RC-circuit:

$$\tau = R_{\text{Stack}} C_{\text{Vol}} \quad \text{and} \quad R_{\text{Stack}} = \frac{\Delta p(\dot{m})}{\dot{m}_{\text{Stack}}} \quad (\text{non-linear})$$

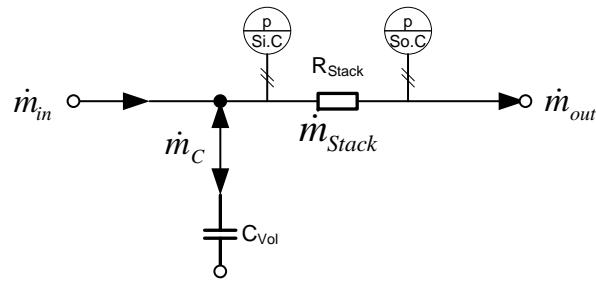


Figure 8.3: Pneumatic RC schematic

The relation between volume V and hydraulic capacity C_{Vol} is given by the individual gas constant R_{air} and the temperature T :

$$C_{Vol} = \frac{V}{R_{air}T} \quad \text{and therefore} \quad \tau \propto \frac{V \Delta p}{\dot{m}}$$

With the information on C_{Vol} and R_{Stack} the dynamic response of Δp (and therefore also air flow) transients for any cathode subsystem can be calculated as follows:

$$\Delta p(t) = \Delta p_{static} \cdot \exp\left(-\frac{t}{\tau}\right) \quad (8.3)$$

On fuel cell teststands often the air flow \dot{m} is lower and the volume V is higher than in the final FCS application. Especially there the dynamic response needs to be considered! During electric load transients it needs to be considered that the reactant flows through the stack may be significantly delayed by several seconds (depending on τ)! Anode and cathode starvation issues may occur.

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