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# Script Thermodynamics II

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## Introduction

Today's energy system is dominated by chemical energy sources, the majority of which are of fossil origin. In particular, the mitigation of climate change calls for a massive reduction of fossil  $\text{CO}_2$ , which is released into the atmosphere as a product of combustion processes. However, according to the latest estimates of the International Energy Agency (IEA), chemical energy sources will continue to play an essential role throughout the 21st century. Their great advantages lie not only in their unrivaled volumetric and gravimetric energy density compared to electrical storage, but also (relatedly) in their ability to provide "energy on demand", especially electricity. This is particularly valuable in a future where high shares of volatile power generation from renewable sources (wind, solar) pose challenges regarding grid stability. Also important will be the market share of chemical energy sources in medium- and long-haul transport (intercontinental shipping, international aviation, freight transport by heavy-duty vehicles).

However, two conditions must be met to ensure that fuels do not jeopardize the goals of the Paris Agreement (limiting global warming to no more than 2 degrees Celsius), namely:

- Increasing the efficiency of the corresponding energy converters (gas and steam turbines, internal combustion engines, fuel cells) and
- their generation by renewable (or nuclear, if necessary) primary energy. In addition to biomass,  $\text{CO}_2$ -“free” electricity via electrolysis to hydrogen could be considered, with subsequent synthesis, via a carbon source (e.g., recycling of atmospheric  $\text{CO}_2$ ), of synthetic gaseous or liquid hydrocarbons from  $\text{H}_2$  and  $\text{CO}_2$ .

Chemically bound, mechanical, and electrical energy have one hundred percent exergy content, and high-temperature heat has at least a high such content. The conversion of one form of energy into another is predominantly accomplished by thermomechanical or electromechanical processes. Examples of the former are internal combustion engines and solar chemical reactors, those of the latter fuel cells and electrolyzers.

Chemical thermodynamics deals with the description of such transformation processes and the corresponding components and systems.

Therefore, in the first part of the Thermodynamics II lecture we will deal with these aspects and learn about their fundamentals and applications.

## Content of the lecture (part 1, 7 lessons):

**Introduction:** Content and learning objectives.

**Chapter 1:** Multicomponent systems with chemical reactions - conservation of mass and stoichiometries.

**chap. 2:** 1st law of thermodynamics for chemically reacting systems - energy balance, enthalpy of reaction and (for combustion) adiabatic flame temperature

**chap. 3:** 2nd law of thermodynamics for chemically reacting systems - complete chemical equilibrium, chemical potential, equilibrium function

**chap. 4:** exergy consideration - extension to chemically reacting systems, reversible work and free enthalpy of reaction

**chap. 5:** Electrochemical conversion (especially fuel cells), further "non-combustion" processes

**chap. 6:** Molecular fundamentals (kinetic theory of gases) of transport properties (heat, mass, momentum transport)

In this first part of the lecture (7 lessons), we aim to achieve the following learning objectives:

- Calculate mass, mole, and volume flows in reactors for multicomponent systems; learn basic concepts (e.g., stoichiometry); global / elementary reactions.
- Formulate energy balance in chemically reactive systems; be able to calculate (adiabatic) flame temperature for complete combustion; understand bond energies and reaction enthalpies.
- Be able to formulate conditions for chemical equilibrium; Understand chemical potential and equilibrium function; Be able to calculate composition of multicomponent chemically reactive systems at complete equilibrium.
- Be able to identify sources of irreversibilities (entropy increase, exergy loss) in combustion processes (thermodynamic cycles).
- Be able to set up energy and mass balances, or elementary reactions for fuel cells; calculate power, exergetic efficiency, reversible and irreversible heat flows.
- Understand basic differences between *thermochemical* (Carnot-limited) and *electrochemical* (NOT Carnot-limited) energy converters.

- Understand and be able to calculate - at least qualitatively - the properties of transport variables (heat and mass diffusion, momentum exchange) based on the kinetic theory of gases.

Important:

The lessons in the first half of the Thermodynamics II lecture are based on the content of Thermodynamics I and assume the corresponding understanding. However, they extend the basic concepts and applications to chemically reacting systems. Wherever possible, the same terminology, symbols, and tables are used. In some cases, however, deviations are unavoidable.

# Chapter 1

## Multicomponent systems with chemical reactions - conservation of mass and stoichiometries

### Learning objectives:

- Learn general notation of chemical reactions; understand differences between global and elementary reactions.
- Be able to calculate and convert mass, volume, mole fractions, molecular concentrations, and partial pressures in multicomponent systems.
- Be able to calculate stoichiometric coefficients of (global) combustion and electrochemical reactions.
- Know and be able to use the terms "air ratio" and "equivalence ratio" to perform simple dimensioning of e.g. combustion chambers.

### Important

Terms and nomenclature of this chapter are valid for both combustion and electrochemical reactions. Usually, however, they are used primarily in reference to combustion processes.

Additional: In this and all subsequent chapters, we refer to gaseous mixture components. Where not explicitly mentioned otherwise, these are ideal gases.

### General notation of chemical reactions

The general notation of a chemical reaction is:

$$\sum_i \nu'_j \cdot M_j \rightleftharpoons \sum_i \nu''_j \cdot M_j \quad (1)$$

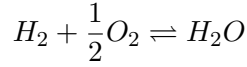
With component index  $j$ ,  $M_j$  the respective molar mass and  $\nu'_j$ ,  $\nu''_j$  the stoichiometric coefficients of the reactants and the products, respectively.

Note the arrows in both directions of the chemical reaction: in general, chemical reactions proceed in both directions, but (with the exception of chemical equilibrium) not at the same rate.

The example of hydrogen oxidation is used to show how these coefficients are calculated. Convention usually dictates that the reactants (reactants) are on the left side of the reaction and the products are on the right side (i.e., the arrow to the right dominates). In this case:

$$\begin{array}{ll} \nu'_j \neq 0, \nu''_j = 0 & \text{For Reactants} \\ \nu'_j = 0, \nu''_j \neq 0 & \text{For Products} \end{array}$$

Example:



$$\begin{aligned} \text{It holds: } \nu'_{H_2} &= 1, \nu'_{O_2} = 1/2, \nu'_{H_2O} = 0 \\ \text{and } \nu''_{H_2} &= 0, \nu''_{O_2} = 0, \nu''_{H_2O} = 1 \end{aligned}$$

The seemingly complicated notation of the above reaction is advantageous when dealing with a system of many reactions occurring simultaneously and the conservation equations for all components must be written down and solved numerically, as will be shown later.

### Definitions in multicomponent mixtures

( $i$ : Component running index)

→ Mass fraction:

$$Y_i = \frac{m_i}{m_{tot}} \quad (2)$$

→ Volume/mole fraction:

$$X_i = \frac{n_i}{n_{tot}} \quad (3)$$

→ Molar concentration:

$$c_i = \frac{n_i}{V_{tot}} \quad (4)$$

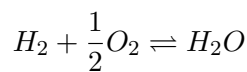
→ Partial pressure:

$$p_i = p_{tot} \cdot \frac{n_i}{n_{tot}} \quad (5)$$

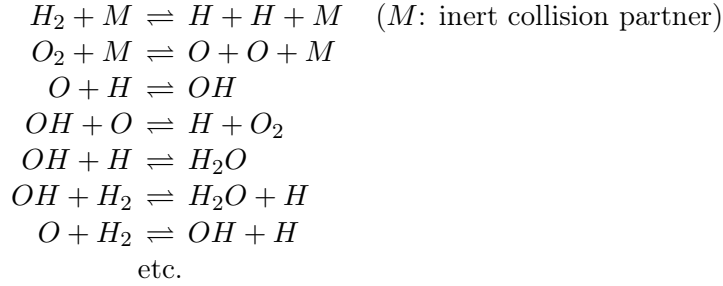
→ Conversion mole fraction to mass fraction:

$$Y_i = X_i \cdot M_i \cdot \frac{\sum_j n_j}{\sum_j n_j \cdot M_j} \quad (6)$$

When describing chemically reactive systems, it is important to distinguish between global and elementary reactions. Even one of the simplest global reactions



is in reality the result of a variety of elementary reactions that occur at the molecular level, such as (not a complete listing):



Reactants ( $H_2$ ,  $O_2$ ) are converted into products ( $H_2O$ ) via several intermediate steps that produce and consume a variety of short-lived "radicals" ( $OH$ ,  $H$ ,  $O$ , etc.). Such a global reaction usually starts with the dissociation of the reactants (with energy input from outside, as we will see later) to produce products.

The details of the elementary reactions are important for reaction kinetics (rates of the individual reactions), but not primarily for chemical equilibrium, unless one is interested in intermediate components (e.g., products of incomplete combustion).

For the oxidation of more complex fuels, however, the elementary reactions are much more important to consider. For  $CH_4$  as the simplest hydrocarbon more than 50 reactions are "known", for mixtures of higher hydrocarbons (gasoline, diesel, jet-fuel) some hundreds to some thousands.

## Stoichiometry and air ratio

Ideally, a (combustion or electrochemical) reaction proceeds at the stoichiometric, i.e., exactly proportioned, ratio of air mass to fuel mass. Less than the stoichiometric air mass leads to incomplete oxidation of the fuel, more than the stoichiometric air mass represents a certain "waste" (the air supply and exhaust costs energy and space).

air ratio (or percent excess air):

$$\lambda = \frac{m_L/m_B}{(m_L/m_B)_{st\ddot{o}ch}} \quad (7)$$

und equivalence ratio

$$\phi = \frac{1}{\lambda} \quad (8)$$

where  $\phi$  is usually used in the Anglo-Saxon literature.

Depending on the technical application,  $\lambda = 1$  or  $\lambda > 1$  can be used, in rare cases also  $\lambda < 1$  (staged combustion). In some technical systems, excess air is used specifically to ensure that no incompletely oxidized products leave the combustion chamber (or fuel cell). In other cases, however, an air ratio significantly greater than 1 is set either to reduce the flame temperature (and

thus the thermal load and nitrogen oxide emissions during combustion) or to implement power control of the internal combustion engine.

In general, the fuel mass flow rate defines the chemical (chemical-thermal in the case of combustion) power flow and the air ratio defines the air mass flow requirement, on which, among other things, the sizing of the flow velocities and cross-sections of the plant depends.

#### Examples of various combustion applications

- Stationary (small burner)  $\lambda = 1.1 - 1.2$
- Gasoline engine with 3-way catalyst  $\lambda = 1.0$  (exact!)
- Diesel engine (full load/part load)  $\lambda = 1.2/5$
- Stationary gas turbine (power plant)  $\lambda = 2 - 2.3$

### **Mass balance in the oxidation of hydrocarbons**

$$C_xH_y + \lambda \cdot \left(x + \frac{y}{4}\right) \cdot O_2 + 3.76 \cdot \lambda \cdot \left(x + \frac{y}{4}\right) \cdot N_2 =$$

$$= x \cdot CO_2 + \frac{y}{2} \cdot H_2O + (\lambda - 1) \cdot \left(x + \frac{y}{4}\right) \cdot O_2 + 3.76 \cdot \lambda \cdot \left(x + \frac{y}{4}\right) \cdot N_2 \quad (9)$$

with this, it holds:

$$\left(\frac{m_L}{m_B}\right)_{st\ddot{o}ch} = \left(x + \frac{y}{4}\right) \cdot \frac{M_{O_2} + 3.76 \cdot M_{N_2}}{x \cdot M_C + y \cdot M_H} \quad (10)$$

and

$$\left(\frac{n_L}{n_B}\right)_{st\ddot{o}ch} = 4.76 \cdot \left(x + \frac{y}{4}\right) \quad (11)$$

#### Comments / recommendations

- Calculate the stoichiometric mass and mole ratios for specific fuels (methane, iso-octane ( $C_8H_{18}$ ), hydrogen). In particular, what do the mole fractions mean for the design of the total volume flow through an open flow-through combustor? And what do the mass fractions of air and fuel mean for important thermodynamic properties of the reaction mixture, such as specific heat capacities?
- Renewable biomass fuels often contain oxygen (O) in the molecule. Calculate the stoichiometric ratios for ethanol  $CH_3CH_2OH$ . What do you learn from this?



## Concentrations of important combustion products in exhaust gas

In most applications, it is important to monitor and control, i.e., correct if necessary, the actual  $\lambda$  value during the operation of a plant. Assuming complete combustion, the actual air ratio can be determined (in addition to a costly separate and continuous measurement of air and fuel mass flow) by determining the mole fraction of oxygen and/or  $\text{CO}_2$  in the exhaust gas stream, if the appropriate measuring equipment is available. The following equations are authoritative:

$$X_{\text{O}_2} = \frac{(\lambda - 1) \cdot (x + \frac{y}{4})}{x + \frac{y}{2} + 3.76 \cdot \lambda \cdot (x + \frac{y}{4}) + (\lambda - 1) \cdot (x + \frac{y}{4})} \quad (12)$$

$$X_{\text{CO}_2} = \frac{x}{x + \frac{y}{2} + 3.76 \cdot \lambda \cdot (x + \frac{y}{4}) + (\lambda - 1) \cdot (x + \frac{y}{4})} \quad (13)$$

Fig. 1 shows the typical plot of  $X_{\text{O}_2}$  and  $X_{\text{CO}_2}$  for a given hydrocarbon.

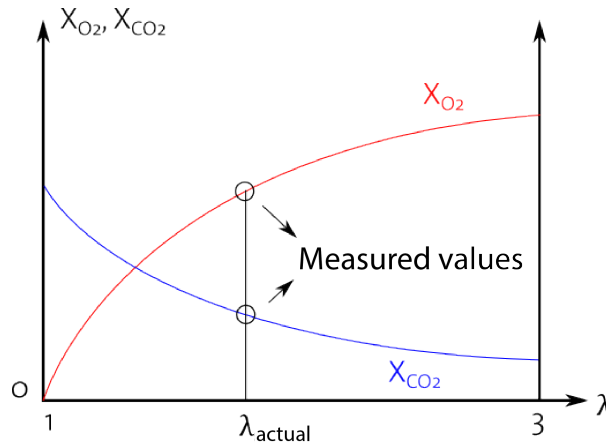


Figure 1: Molar fractions of  $\text{CO}_2$  and  $\text{O}_2$  in the combustion products as a function of the air ratio  $\lambda$  assuming complete combustion.

### Example:

Calculate the two curves once for propane ( $\text{C}_3\text{H}_8$ ) and once for dodecane ( $\text{C}_{12}\text{H}_{26}$ ). How big are the differences?

### Question/answer:

Pollutant emission regulations prescribe the mass concentration of, for example,  $\text{NO}_x$  in the exhaust gas at different  $\text{O}_2$  proportions depending on the plant (e.g., at 3%  $\text{O}_2$  for domestic burners, at 5%  $\text{O}_2$  for stationary gas engines, and at 15%  $\text{O}_2$  for gas turbines). What might a fair comparison of these values look like?

## Chapter 2

### 1st law for chemically reacting systems - energy balance of combustion - adiabatic flame temperature

#### Learning objectives:

- To learn the difference between thermal enthalpy and enthalpy of formation.
- Understand relationship between enthalpy of formation and binding energy.
- Establish 1st law / energy balance of a combustion reaction and be able to derive enthalpy of reaction and heat of reaction from it.
- Be able to calculate the adiabatic flame temperature at complete combustion (for any fuels and mixture compositions).
- Be able to identify the main parameters influencing the adiabatic flame temperature and name the reasons.

#### Bonding energy and enthalpy of formation

For chemically reacting systems, according to the 1st law of thermodynamics, for the energy balances of reactors, in addition to the thermal enthalpies and internal energies, also those must be considered which are "chemically" stored in the respective components.

In the following we illustrate this by the relation between ("chemically") enthalpies of formation (enthalpy of formation  $h_f^0$ , under reference conditions,  $T=298\text{ K}$ ,  $p=1\text{ atm}$ ) and bonding energies ( $E_b$ ) due to the structure of the corresponding molecule.

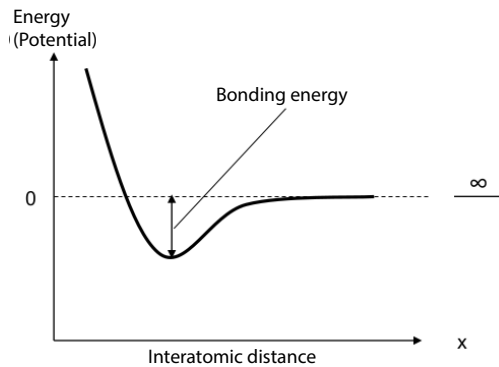


Figure 2: Bonding energy as a function of interatomic distance in a diatomic molecule.

Fig. 2 shows the course of the potential energy as a function of the interatomic distance in a diatomic molecule. There are two stable states: at the distance of the atoms from each other, where the potential energy has a minimum (stable molecule) and at the infinite distance of the atoms from each other (dissociated molecule). The *bonding energy* corresponds to the difference in potential energy between the two states.

Table 1 gives characteristic values for different bond strengths. It is important to realize that these values may vary for a concrete bond depending on where they are located in a (larger) molecule, since the potential fields of "neighboring" bonds strongly influence each other.

Mittlere Bindungsenergien bei 298 K in kJ mol <sup>-1</sup>													
Einfachbindungen													
	H	B	C	Si	N	P	O	S	F	Cl	Br	I	
H	436												
B	372	310											
C	416	352	345										
Si	323	—	306	302									
N	391	(500)	305	335	159								
P	327	—	264	—	290	205							
O	463	(540)	358	444	181	407	144						
S	361	(400)	289	226	—	(285)	—	268					
F	570	646	489	595	278	496	214	368	159				
Cl	432	444	327	398	193	328	206	272	256	243			
Br	366	369	272	329	159	264	(239)	—	280	218	193		
I	298	269	214	234	—	184	(201)	—	—	211	179	151	
Mehrfachbindungen													
C=C	615		C=N	616		C=O	708		C=S	587		N=N	419
O=O	498		S=O	420		S=S	423						
C≡C	811		C≡N	892		C≡O	1077		N≡N	945			

Die Bindungsenergie/-enthalpie  $D_{298}^\circ$  einer Bindung  $A-B$  ist hier als Reaktionsenthalpie  $\Delta H_{298}^\circ$  (also bei 298 K) der Dissoziationsreaktion  $A-B(g) \rightarrow A(g) + B(g)$  definiert. Die Spezies A und B können Atome oder Molekülfragmente sein. Die Bindungsenergie entspricht damit der Dissoziationsenergie. Bei mehratomigen Molekülen sind auch bei gleichartigen Bindungen die Dissoziationsenergien der stufenweisen Dissoziationen verschieden. So beträgt für das  $H_2O$ -Molekül die Dissoziationsenergie für die erste O—H-Bindung 497 kJ/mol, für die zweite O—H-Bindung 429 kJ/mol. Die Bindungsenergie der O—H-Bindung ist dann der Mittelwert 463 kJ/mol.

Table 1: Table with average bond energies of different bonds. Source: Allgemeine und Anorganische Chemie, Riedel und Erwin, 2010.

As the *enthalpy of formation* of a chemical component, we define the mole-specific enthalpy that must be expended (positive sign) when this component is formed from the individual *standard* chemical elements at reference conditions.

As shown in Fig. 3, the enthalpy of formation of standard elements (i.e., equiatomic molecules in their stable form and corresponding state of aggregation) is zero at reference conditions by definition. The reason for this convention is that one needs a common base as *reference*, since such elements (molecules such as  $N_2$ ,  $H_2$ ,  $O_2$ ) cannot be transformed into each other by chemical reactions.

Table 2 shows values of mole-specific enthalpies of formation for various components that occur frequently in combustion reactions. Whether the respective enthalpy of formation has positive or negative values has no meaning, because this also depends on the chosen reference value for the standard elements (just zero). It is much more important to understand which method can be used to

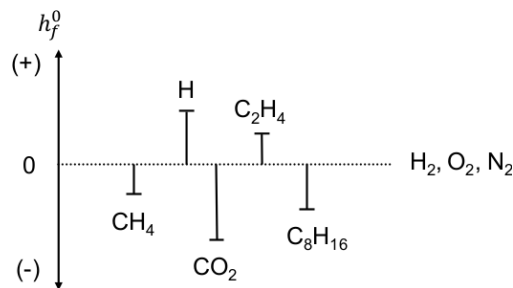


Figure 3: Schematic representation of the standard enthalpies of formation of various compounds. Enthalpies of formation of molecules of the same atom in their stable form (e.g.  $H_2$ ,  $N_2$ ,  $O_2$ ) are zero by definition.

calculate the enthalpy of formation from the relevant bond energies.

			Glassman	NIST-JANAF
C	Kohlenstoff	dampförmig	$5.29 \cdot 10^5$	$7.17 \cdot 10^5$ (gasförmig)
N	Stickstoff	gasförmig	$4.72 \cdot 10^5$	$4.73 \cdot 10^5$
O	Sauerstoffatom	gasförmig	$2.48 \cdot 10^5$	$2.49 \cdot 10^5$
$C_2H_2$	Acetylen	gasförmig	$2.27 \cdot 10^5$	$2.27 \cdot 10^5$
H	Wasserstoffatom	gasförmig	$2.18 \cdot 10^5$	$2.18 \cdot 10^5$
$O_3$	Ozon	gasförmig	$1.42 \cdot 10^5$	$1.43 \cdot 10^5$
NO	Stickstoffmonoxid	gasförmig	$9.04 \cdot 10^4$	$9.03 \cdot 10^4$
$C_6H_6$	Benzol	gasförmig	$8.3 \cdot 10^5$	$8.3 \cdot 10^5$
$C_6H_6$	Benzol	flüssig	$4.9 \cdot 10^4$	$4.9 \cdot 10^4$
$C_2H_4$	Ethen	gasförmig	$5.23 \cdot 10^4$	$5.25 \cdot 10^4$
OH	Hydroxylradikal	gasförmig	$4.21 \cdot 10^4$	$3.90 \cdot 10^4$
$O_2$	Sauerstoff	gasförmig	0	0
$N_2$	Stickstoff	gasförmig	0	0
$H_2$	Wasserstoff	gasförmig	0	0
C	Kohlenstoff	fest	0	0
$CH_4$	Methan	gasförmig	$-7.49 \cdot 10^4$	$-7.49 \cdot 10^4$
$C_2H_6$	Ethan	gasförmig	$-8.47 \cdot 10^4$	$-8.47 \cdot 10^4$
CO	Kohlenmonoxid	gasförmig	$-1.11 \cdot 10^5$	$-1.11 \cdot 10^5$
$CO_2$	Kohlendioxid	gasförmig	$-3.94 \cdot 10^5$	$-3.94 \cdot 10^5$
$SO_2$	Sulfurdioxid	gasförmig	$-2.97 \cdot 10^5$	$-2.97 \cdot 10^5$
$H_2O$	Wasser	gasförmig	$-2.42 \cdot 10^5$	$-2.42 \cdot 10^5$
$H_2O$	Wasser	flüssig	$-2.86 \cdot 10^5$	$-2.86 \cdot 10^5$
$C_8H_{18}$	Oktan	flüssig	$-2.5 \cdot 10^5$	$-2.5 \cdot 10^5$

Table 2: Table showing standard enthalpies of formation ( $T=298$  K,  $p=1$  atm) of various substances. Sources: I. Glassman, Combustion, Academic Press / <http://kinetics.nist.gov/janaf>.

In general:

The enthalpy of formation is the difference between the *energy to be expended* for breaking the chemical bonds of the required standard elements (this initially creates single atoms) and the *energy retained (gained)* when these atoms form new bonds to "assemble" the molecule of the component under consideration.

For this purpose, the example of the calculation of the enthalpy of formation

of gaseous water from the standard elements  $H_2$  and  $O_2$ , with the help of table 1, is shown below.

$$h_{f,H_2O}^0 = \underbrace{E_{b,H-H} + 0.5 \cdot E_{b,O=O}}_{\text{invested}} - \underbrace{2 \cdot E_{b,O-H}}_{\text{received back}}$$

$$= 436 \frac{kJ}{mol} + 0.5 \cdot 498 \frac{kJ}{mol} - 2 \cdot 463 \frac{kJ}{mol} = -241 \frac{kJ}{mol} = -2.41 \cdot 10^5 \frac{kJ}{kmol}$$

Comparison with value from Table 2:  $h_{f,H_2O}^0 = -2.42 \cdot 10^5 \frac{kJ}{kmol}$

The comparison of the value of the enthalpy of formation of  $H_2O$  obtained in this way with that from Table 2 is very good. However, this is conditionally true for other molecules, since the binding energies represent rough averages that can vary greatly depending on the initial standard element.

### Energy balance of a combustion reaction

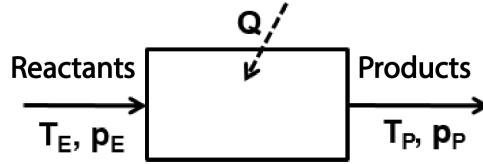


Figure 4: Schematic representation of an open, flow-through reactor.

To set up the *energy balance* of a combustion reaction, we first consider a reactor (combustion chamber), which is described as an open, flowed-through system at  $p = \text{const}$ , neglecting kinetic and potential energy, and thus without delivery to or supply of work from the outside (Fig. 4). Thus, the 1st law for this system reduces to equating the enthalpy change with the heat exchange with the environment. However, it is important to realize that according to Eq. 14, the *total enthalpy* of each component consists of the enthalpy of formation at reference conditions and the temperature-induced enthalpy difference between the reference and the respective present temperature. As a reminder from the lecture Thermodynamics I, this thermal (English term "sensible enthalpy") part of the total enthalpy of a component is due to the fact that the different degrees of freedom of a molecule are more excited with increasing temperature, making the heat capacities  $c_p$  and  $c_v$  (slightly) temperature dependent (for the ideal gases considered).

Thus, it holds:

$$h_i = h_{f,i}^0 + \Delta h_i(T_i) = h_{f,i}^0 + h_i(T_i) - h_i(T_{ref}) \quad (14)$$

for the  $i$ -th mixture component.

From the 1st law for the open, flow-through reactor applies

$$\Delta H = Q - W \quad (15)$$

and since no work is done from/to the outside at  $p = \text{const}$ , we get  $\Delta H = Q$  and from this with  $\Delta H = H_P - H_E$  (P=products, E= reactants / educts)

$$\begin{aligned} \Delta H = H_P - H_E = n_B \cdot \sum_j \nu''_j \cdot [h_{f,j}^0 + h_j(T_P) - h_j(T_{ref})] \\ - n_B \cdot \sum_j \nu'_j \cdot [h_{f,j}^0 + h_j(T_E) - h_j(T_{ref})] = Q \end{aligned} \quad (16)$$

If, in addition, the reactor is *adiabatic*, i.e. if there is no heat exchange of the system with the environment,  $\Delta H = Q = 0$ , thus  $H_P = H_E$  and, therefore

$$\begin{aligned} \Delta H_{R|T_{ref}} = n_B \cdot \sum_j (\nu''_j - \nu'_j) \cdot h_{f,j}^0 = \\ = - \left( n_B \cdot \sum_j \nu''_j \cdot [h_j(T_P) - h_j(T_{ref})] - n_B \cdot \sum_j \nu'_j \cdot [h_j(T_E) - h_j(T_{ref})] \right) = \\ = -\Delta Q_R \end{aligned} \quad (17)$$

with

$$\Delta Q_R = n_B \cdot \sum_j \nu''_j \cdot [h_j(T_P) - h_j(T_{ref})] - n_B \cdot \sum_j \nu'_j \cdot [h_j(T_E) - h_j(T_{ref})] \quad (18)$$

In a *exothermic* reaction (as combustion is), the enthalpy of formation of the products is smaller than that of the reactants, therefore the reduction of the enthalpy of formation after combustion appears in the form of released heat, namely the heat of reaction  $\Delta Q_R$ .

By the way, the enthalpy of reaction at a different temperature of the reactants ( $T_E$ ) than the reference temperature can be calculated as follows:

$$\Delta H_{R|T_E \neq T_{ref}} = \Delta H_{R|T_{ref}} + \sum_j [(\nu''_j - \nu'_j) \cdot (h_{j,T_E} - h_{j,T_{ref}})] \quad (19)$$

The enthalpy of reaction is thus slightly temperature-dependent!

The *heat of reaction*, in turn, is equivalent to the - better known - *heating value* of a fuel. Here we distinguish between *lower* heating value ( $H_u$ ), when the combustion product water is *gaseous* at the end of the process (exit from the reactor) and *upper* heating value, when the water is *liquid* at the exit from the system. The difference corresponds to the *heat of condensation* of the corresponding amount of water per unit mass of fuel. Therefore, the greater the ratio of H to C atoms in the fuel molecule, the greater the difference between *lower* and *upper* heating value (see also stoichiometric equations (eq. 9) in chapter 1).

## Adiabatic flame temperature

Based on the energy balance, e.g., over an open, flow-through system in which an exothermic (combustion) reaction occurs, assuming  $p = \text{const}$ , adiabatic system boundaries, and no changes in kinetic and potential energy, the *adiabatic flame temperature* can be determined as follows:

$$\begin{aligned} n_B \cdot \sum_j \int_{T_E}^{T_{f,ad}} \nu_j'' \cdot c_{p,j} \cdot dT &= n_B \cdot \sum_j \nu_j'' \cdot [h_j(T_{f,ad}) - h_j(T_E)] = -\Delta H_{R|T_E} = \\ &= -\Delta H_{R|T_{ref}} - n_B \cdot \sum_j (\nu_j'' - \nu_j') \cdot [h_j(T_E) - h_j(T_{ref})] \quad (20) \end{aligned}$$

Because of the temperature dependence of the relevant enthalpy terms (thermal part of the total enthalpy), Eq. 20 has to be solved iteratively, but this is not a problem.

The calculation of the adiabatic flame temperature assumes that the composition of the reaction products is known, in particular that the combustion reaction is complete, which is justified if  $\lambda > 1$  and the temperatures of the products are not too high ( $< 2'000\text{K}$ ). In general, however, consideration of complete chemical equilibrium is required for coupled calculation of the adiabatic flame temperature and the composition of the products, as we will see in Chapter 3.

The adiabatic flame temperature typically has a variation over the air ratio with a maximum usually in the region of  $\lambda = 0.8 - 0.9$ . For fuel-lean mixtures, the adiabatic flame temperature decreases very rapidly as the excess air increases because at higher  $\lambda$ , much more air must be heated for the same fuel energy. Below  $\lambda = 1$ , however (i.e., for fuel-rich mixtures), there are two effects with opposite effects as the air shortage increases, namely: on the one hand, the amount of air to be heated decreases as  $\lambda$  decreases, and on the other hand, the oxidation of the fuel cannot take place completely because of the insufficient amount of  $\text{O}_2$ , which is why the heat of reaction released becomes smaller. Fig.5 represents the mentioned course of the adiabatic flame temperature over the air ratio qualitatively.

As Fig. 6 shows, the adiabatic flame temperature additionally depends on whether the combustion takes place at constant volume or constant pressure. In the first case, the achievable adiabatic flame temperature at the same air ratio is higher because the *heat of reaction* leads to the increase of the *internal energy* of the products (and not the *enthalpy*). It is known from Thermodynamics I that for a given amount of heat supplied, the temperature increase at constant volume is greater than the case at constant pressure because of the smaller value of the corresponding heat capacity.

The adiabatic flame temperature is an important design parameter for the combustion plant. Since it is the maximum achievable temperature of the process, it has a significant influence on the thermal load of the combustion chamber components (or the first stage of a downstream expansion machine such as a gas turbine). In addition, emissions such as nitrogen oxides depend very strongly

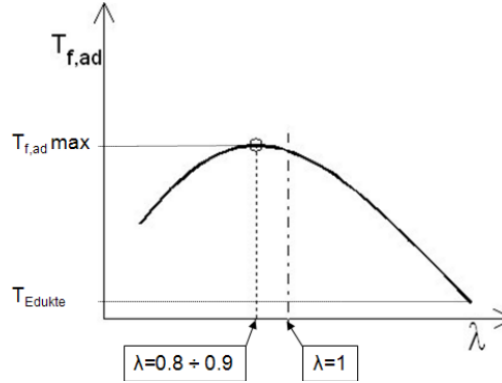


Figure 5: Adiabatic flame temperature as a function of the air ratio  $\lambda$ .

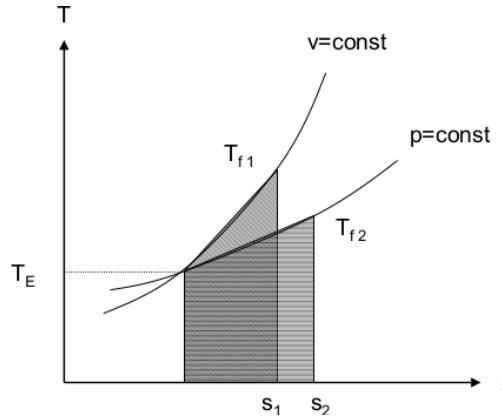


Figure 6: T-s diagram. The figure illustrates the different resulting temperature for the supply of a given amount of heat, once at constant volume ( $v=\text{const}$ ) and once at constant pressure ( $p=\text{const}$ ).

on the maximum process temperature, which is why the flame temperature is limited upward in many applications. On the other hand, a high adiabatic flame temperature is beneficial for the thermodynamic efficiency of an internal combustion engine, due to the Carnot efficiency. From all these considerations, it is clear that the optimal level of adiabatic flame temperature depends on the particular application and represents a compromise to mitigate various conflicting objectives.

Numerical values of adiabatic flame temperature at constant pressure and reference temperature of reactants are shown in table 3, once with air and once with pure oxygen as oxidant. Interestingly, the adiabatic flame temperature for most of the common fuels and air as oxidant is about 2,400K (+/- 200K) for stoichiometric mixture composition. The effect of  $\text{O}_2$  over air as oxidant can be explained simply by the absence of large amounts of  $\text{N}_2$  and, accordingly, the greatly reduced heat capacity of the combustion products. The influence of pressure on the adiabatic flame temperature can be explained by different extents of dissociation of products. However, for a solid justification, knowledge concerning conditions of chemical equilibrium is required, see Chapter 3.



Brennstoff	Oxidant	Druck(bar)	$T_{f,ad}(K)$
Acetylen ( $C_2H_2$ )	Luft	1	2600
Acetylen( $C_2H_2$ )	$O_2$	1	3410
CO	Luft	1	2400
CO	$O_2$	1	3220
$C_7H_{16}$	Luft	1	2290
$C_7H_{16}$	$O_2$	1	3100
$H_2$	Luft	1	2400
$H_2$	$O_2$	1	3080
$CH_4$	Luft	1	2210
$CH_4$	Luft	20	2270
$CH_4$	$O_2$	1	3030
$CH_4$	$O_2$	20	3460

[Quelle: Glassmann, I., 1996, Combustion, 3rd Ed., Academic Press.]

Table 3: Listing of adiabatic flame temperature of some fuels for combustion with air and with pure oxygen.

Finally, it must be emphasized that the conduct of combustion in many incinerators is not adiabatic. Mechanisms described in the second part of the Thermodynamics II lecture (heat transfer from product gas to the combustion chamber walls, heat conduction through them and cooling of the outer wall of the burner) lead to heat losses, which is why the achievable flame temperature can be lower than the adiabatic flame temperature.

## Chapter 3

### 2nd law and chemical equilibrium

#### Learning objectives:

- Be able to formulate the 2nd law of thermodynamics for chemically reactive systems.
- To know terms "chemical potential" and "free enthalpy" and their meaning.
- Be able to derive the condition for complete thermodynamic equilibrium in a system with multiple components that react with each other.
- Be able to use the "equilibrium constant" to determine the concentrations of reactants (reactants) and products of a chemical reaction.
- Under conditions of complete thermodynamic equilibrium, be able to calculate the adiabatic flame temperature and the composition of the products of a combustion reaction.

#### Extension of the 2nd law and formulation of chemical equilibrium

The 2nd law of thermodynamics for a system of multiple chemical components that can react with each other must be formulated in an extended sense so that not only the enthalpies of formation (as in the 1st law), but also the corresponding entropies of the reactants (reactants) and products are considered.

The equilibrium condition for a system of chemically reacting components is to maximize the total entropy (when the system is isolated from the environment), which means minimizing the chemical potential or free enthalpy (see below for the corresponding definitions).

In the state of complete thermodynamic equilibrium for a system of chemically reacting components, each individual elementary reaction is in equilibrium. However, this is an *dynamic* equilibrium, i.e., the rates of the forward and backward reactions are equal to each other.

The combination of 1st and 2nd main theorem at the example of a closed system is described by

$$dU = T \cdot dS - p \cdot dV + \sum_i \mu_i \cdot dn_i, \quad (21)$$

this time with the additional term representing the sum of the changed chemical potentials  $\mu_i$  of all components.  $dn_i$  corresponds to the change in the number of moles of the i-th component. The formulation for an open system corresponds to Eq. 22 and from the definition of the *free enthalpy*  $G$  follows the formulation given by Eq. 23.

$$dH = T \cdot dS + V \cdot dp + \sum_i \mu_i \cdot dn_i \quad (22)$$

$$dG = -S \cdot dT + V \cdot dp + \sum_i \mu_i \cdot dn_i \quad (23)$$

With the help of equations 21, 22, and 23, one can see the physical meaning of the chemical potential of the  $i$ -th component according to Eq. 24:

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,p,n_j(j \neq i)} = \left( \frac{\partial U}{\partial n_i} \right)_{S,V,n_j(j \neq i)} = \left( \frac{\partial H}{\partial n_i} \right)_{S,p,n_j(j \neq i)} \quad (24)$$

Thus, this chemical potential corresponds to the change in one energetic quantity ( $U$ ,  $H$ ,  $G$ ) per change in the number of moles  $n_i$  of this component, for each two constant thermodynamic state variables and for a constant number of moles of all other components ( $j \neq i$ ).

The equilibrium condition of maximizing entropy, both for a closed system at  $u, v = \text{const}$ , and for an open system at  $p, T = \text{const}$ , leads to minimization of the total chemical potential or free enthalpy of the system (for  $p, T = \text{const}$  with respect to the free enthalpy), as can be seen from Eq. 25 and 26:

From the equilibrium condition at  $u, v = \text{const}$  with  $T \cdot dS = 0$  it follows:

$$\sum_i \mu_i \cdot dn_i = 0 \quad (25)$$

The equilibrium condition at  $p, T = \text{const}$  means  $\sum_i \mu_i \cdot dn_i = 0$  and it follows from Eq. 23:

$$dG = 0 \quad (26)$$

In contrast to the enthalpy, which is only temperature dependent (Eq. 27), however, the free enthalpy  $G$  is also pressure dependent, because the entropy is pressure dependent according to Eq. 28 is pressure dependent. This equation is obtained from the 1st and 2nd laws at constant temperature and variable pressure versus a reference pressure  $p_0 = 1 \text{ atm}$ . Using Eq. 27 and 27 b, as well as Eq. 28, finally Eq. 29.

$$G(p, T) = H(T) - T \cdot S(p, T) \quad (27)$$

$$G_0(p_0, T) = H_0(T) - T \cdot S(p_0, T) \quad (27 \text{ b})$$

$$S(p, T) = S(p_0, T) - R \cdot \ln \left( \frac{p}{p_0} \right) \quad (28)$$

$$G(p, T) = G_0(T) + R \cdot T \cdot \ln \left( \frac{p}{p_0} \right) \quad (29)$$

The pressure dependence of entropy leads to the pressure dependence of the free enthalpy not only of the total system, but also of that of each chemical

component whose partial pressure is proportional to the corresponding number of moles of that component (Eq. 30).

$$g_i(p, T) = g_{f,i}^0(T) + R \cdot T \cdot \ln \left( \frac{p_i}{p_0} \right) \quad (30)$$

Setting the free enthalpy of the system equal to the sum of those of all components (Eq. 31) and using the minimization of the free enthalpy as an equilibrium condition according to Eq. 32, after some simple manipulations one obtains Eq. 33, which can be used to write a chemical reaction with the appropriate stoichiometric coefficients in terms of Eq. 34 where  $\Delta g_0$  denotes the change in free enthalpy at reference pressure  $p_0$  and at constant temperature  $T$ .

$$G(T, p) = \sum_j n_j \cdot \left[ g_{f,j}^0(T) + R \cdot T \cdot \ln \left( \frac{p_j}{p_0} \right) \right] \quad (31)$$

$$\sum_j g_{f,j}^0 \cdot dn_j + R \cdot T \cdot \sum_j (dn_j) \cdot \ln \left( \frac{p_j}{p_0} \right) + R \cdot T \cdot \sum_j n_j \cdot \left( \frac{dp_j}{p_j} \right) = 0 \quad (32)$$

$$\ln \prod_j \left[ \frac{p_j}{p_0} \right]^{dn_j} = -\frac{\Delta g_0}{R \cdot T} = \ln K_p(T) \quad (33)$$

$$\ln \prod_j \left[ \frac{p_j}{p_0} \right]^{\nu_j'' - \nu_j'} = \ln K_p(T) = \frac{-\sum_j (\nu_j'' - \nu_j') \cdot g_{f,j}^0}{R \cdot T} \quad (34)$$

Equation 34 is extremely important because it connects, for the state of chemical equilibrium of a reaction, the *free enthalpy of reaction* at reference pressure on the one hand and the *partial pressures* of reactants and products related to a reference pressure on the other hand. The function  $K_p$  in Eq. 34 is usually referred to in textbooks as *equilibrium constant*, which is contradictory, because  $K_p$  is a temperature- (but not pressure-) dependent function! According to Eq. 34, the equilibrium constant  $K_p$  is dimensionless.

Eq. 30 shows that equilibrium functions can be defined not only with reference to partial pressures, but also to number of moles or mole concentrations. With respect to molar concentrations  $c_j$  of the individual components,  $K_c$  is given by Eq. 35.

$$\ln K_c = \ln \prod_j [c_j]^{\nu_j'' - \nu_j'} \quad (35)$$

Logarithmic values of the equilibrium function for  $K_p$  are plotted as a function of temperature (at reference pressure) and for several important elementary reactions in Table 4 (corresponds to excerpt from Table A 27 in Moran and Shapiro; origin: JANAF Thermodynamic Tables). Note: These tables do not use natural logarithms, but those with base 10.

Temp. K	H <sub>2</sub> ↔ 2H	O <sub>2</sub> ↔ 2O	N <sub>2</sub> ↔ 2N	$\frac{1}{2}$ O <sub>2</sub> + $\frac{1}{2}$ N <sub>2</sub> ↔ NO	H <sub>2</sub> O ↔ H <sub>2</sub> + $\frac{1}{2}$ O <sub>2</sub>	H <sub>2</sub> O ↔ OH+ $\frac{1}{2}$ H <sub>2</sub>	CO <sub>2</sub> ↔ CO+ $\frac{1}{2}$ O <sub>2</sub>	CO <sub>2</sub> +H <sub>2</sub> ↔ CO+H <sub>2</sub> O	Temp °R
298	-71.224	-81.208	-159.600	-15.171	-40.048	-46.054	-45.066	-5.018	537
500	-40.316	-45.880	-92.672	-8.783	-22.886	-26.130	-25.025	-2.139	900
1000	-17.292	-19.614	-43.056	-4.062	-10.062	-11.280	-10.221	-0.159	1800
1200	-13.414	-15.208	-34.754	-3.275	-7.899	-8.811	-7.764	0.135	2160
1400	-10.630	-12.054	-28.812	-2.712	-6.347	-7.021	-6.014	0.333	2520
1600	-8.532	-9.684	-24.350	-2.290	-5.180	-5.677	-4.706	0.474	2880
1700	-7.666	-8.706	-22.512	-2.116	-4.699	-5.124	-4.169	0.530	3060
1800	-6.896	-7.836	-20.874	-1.962	-4.270	-4.613	-3.693	0.577	3240
1900	-6.204	-7.058	-19.410	-1.823	-3.886	-4.190	-3.267	0.619	3420
2000	-5.580	-6.356	-18.092	-1.699	-3.540	-3.776	-2.884	0.656	3600
2100	-5.016	-5.720	-16.898	-1.586	-3.227	-3.434	-2.539	0.688	3780
2200	-4.502	-5.142	-15.810	-1.484	-2.942	-3.091	-2.226	0.716	3960
2300	-4.032	-4.614	-14.818	-1.391	-2.682	-2.809	-1.940	0.742	4140
2400	-3.600	-4.130	-13.908	-1.305	-2.443	-2.520	-1.679	0.764	4320
2500	-3.202	-3.684	-13.070	-1.227	-2.224	-2.270	-1.440	0.784	4500
2600	-2.836	-3.272	-12.298	-1.154	-2.021	-2.038	-1.219	0.802	4680
2700	-2.494	-2.892	-11.580	-1.087	-1.833	-1.823	-1.015	0.818	4860
2800	-2.178	-2.536	-10.914	-1.025	-1.658	-1.624	-0.825	0.833	5040
2900	-1.882	-2.206	-10.294	-0.967	-1.495	-1.438	-0.649	0.846	5220
3000	-1.606	-1.898	-9.716	-0.913	-1.343	-1.265	-0.485	0.858	5400

Based on data from the JANAF Thermochemical Tables, NSRDS-NBS-37, 1971.

Table 4: Logarithm to base 10 of equilibrium constant  $K_p$  for selected reactions. Caution:  $\log_{10}(K_p)$  is tabulated.

Based on this table, several interesting observations can be made: All the reactions listed have equilibrium functions which increase with increasing temperature. In the following we will see that such reactions are *endothermic*, including the most important dissociation reactions. And according to eq. 34, it can be shown that higher values of the equilibrium function  $K_p$  mean that the partial pressures of the products increase at the expense of those of the reactants. For example, it is evident that in dissociation reactions higher temperatures tend to produce more atoms at the equilibrium state at the expense of the molecules of a certain element (examples:  $H_2 = 2H$ ,  $O_2 = 2O$ ,  $N_2 = 2N$ ).

## Van't-Hoff equation

The relationship between endothermicity and exothermicity of a chemical reaction and the temperature dependence of the corresponding equilibrium function is obtained as follows:

By differentiating the equilibrium condition as in Eq. 36 and manipulating it, with the aid of the combined 1st and 2nd laws of thermodynamics according to Eq. 37, 38, and 39 via 40, the very important Van't-Hoff equation (Eq. 41) is finally obtained. The index 0 of the free enthalpy is obtained from Eq. 37 is omitted since we assume the pressure to be constant. The Van't Hoff equation states that the equilibrium function of endothermic reactions increases with increasing temperature; conversely, exothermic reactions exhibit a decreasing equilibrium function with increasing temperature. Figure 7. illustrates this fact graphically.

$$\frac{d}{dT}(\ln K_p) = -\frac{1}{R} \cdot \frac{d}{dT} \left( \frac{\Delta g_0}{T} \right) \quad (36)$$

$$\frac{d}{dT} \left( \frac{g}{T} \right) = -\frac{1}{T^2} \cdot g + \frac{1}{T} \cdot \frac{dg}{dT} = \frac{T \cdot \left( \frac{dg}{dT} \right) - g}{T^2} \quad (37)$$

$$\frac{dg}{dT} = \frac{dh}{dT} - T \cdot \frac{ds}{dT} - s = \frac{du}{dT} + p \cdot \frac{dV}{dT} + \underbrace{V \cdot \frac{dp}{dT}}_{=0, \text{ da } p=\text{const}} - s - \underbrace{T \cdot \frac{ds}{dT}}_{=\frac{du}{dT} + p \cdot \frac{dV}{dT}} \implies \frac{dg}{dT} = -s \quad (38)$$

$$T \cdot \frac{ds}{dT} = \frac{du}{dT} + p \cdot \frac{dv}{dT} \quad (39)$$

$$\frac{d}{dT} \left( \frac{g}{T} \right) = \frac{-g - T \cdot s}{T^2} = -\frac{h}{T^2} \quad (40)$$

$$d(\ln K_p) = -\frac{\Delta h_R}{R} \cdot d \left( \frac{1}{T} \right) \quad (41)$$

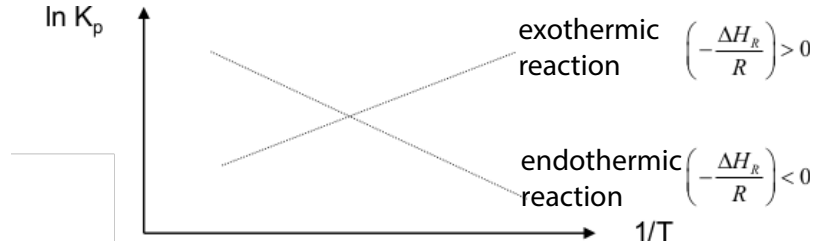


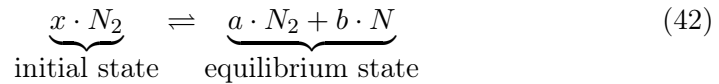
Figure 7: Relationship between endo- / exothermicity of a reaction and the change of  $K_p$  with temperature.

Interestingly, this finding means that in a global exothermic reaction, such as combustion, at very high temperatures, complete conversion to the products becomes more difficult.

### Elemental dissociation reactions at equilibrium: fraction of molecules vs. atoms

Starting from a condition in which nitrogen is found entirely in molecular form, according to Eq. 42, the proportions of molecular ( $N_2$ ) and atomic ( $N$ ) nitrogen in the equilibrium state are sought.

Eq. 43 represents the notation of the dissociation reaction (from left to right / forward) and the recombination reaction (from right to left / backward).



$$\underbrace{N_2 \xrightleftharpoons{p_{eq}, T_{eq}} 2 \cdot N}_{\text{decisive equilibrium reaction}} \quad (43)$$

For such questions it is advisable first to establish a mass balance of the element nitrogen, i.e. the conservation equation for the number of nitrogen atoms (or of all atoms involved in more complex reactions). Eq. 44 thus provides a first equation for determining the unknown number of molecules  $a$  and atoms  $b$  of nitrogen from the original  $x$  molecules  $N_2$ .

To determine the two unknowns  $a$  and  $b$ , one needs an additional equation. This yields the equilibrium function Eq. 45 with its value at the temperature assumed to be known at equilibrium. Also assumed to be known here is the total pressure  $p_{tot}$  at equilibrium.

$$2x = 2a + b \quad (44)$$

$$K_p(T_{eq}) = \frac{\left(\frac{p_N}{p_0}\right)^2}{\left(\frac{p_{N_2}}{p_0}\right)^1} = \frac{p_N^2}{p_{N_2} \cdot p_0} = \frac{\left(\frac{n_N}{n_{tot}} \cdot p_{tot}\right)^2}{\left(\frac{n_{N_2}}{n_{tot}} \cdot p_{tot}\right)^1} \cdot \frac{1}{p_0} = \frac{n_N^2}{n_{N_2} \cdot n_{tot}} \cdot \frac{p_{tot}}{p_0} = f(T_{eq}) \quad (45)$$

Even without solving the system from Eq. 44 and Eq. 45, one can understand the influence of the thermodynamic state ( $T_{eq}$  and  $p_{tot}$ ) on the composition at equilibrium. Namely, one can use Eq. 45 rewritten as follows:

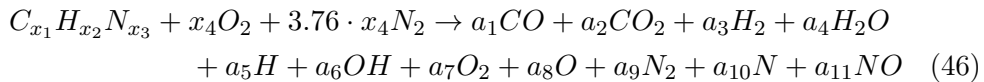
$$\frac{b^2}{a(a+b)} \cdot \frac{p_{tot}}{p_0} = f(T_{eq}) \Rightarrow \frac{a}{b} \left( \frac{a}{b} + 1 \right) = \frac{p_{tot}}{p_0} \cdot \frac{1}{f(T_{eq})} \quad (45 \text{ a})$$

From this we see that the higher the total pressure and the lower the temperature, the higher the nitrogen fraction as a molecule,  $a$ , and thus the smaller the dissociation (since for this endothermic dissociation reaction the equilibrium function increases monotonically with temperature).

The following observation is also interesting: although the equilibrium function is temperature-dependent but not pressure-dependent, the partial pressures of a reaction at equilibrium can also be pressure-dependent. This is the case when - as in the present dissociation reaction - the sum of the stoichiometric coefficients on the reactant and on the product side is not equal.

### Calculation of adiabatic flame temperature in a global combustion reaction at equilibrium

Equation 46 shows the global combustion reaction of an oxygenated hydrocarbon to illustrate the complexity of real combustion.



If the initial conditions are known, both the chemical composition and the adiabatic flame temperature must be calculated at equilibrium (here assuming an open, flow-through, lossless system at constant pressure).

In contrast to the discussion in Chapter 2, this means that at equilibrium the composition of the mixture cannot be assumed a priori. As eq. 46 shows, the products of incomplete fuel oxidation as well as the byproducts (such as nitrogen oxides) and finally components in the form of radicals can occur. The 11 components on the product side (i.e., at equilibrium) of this global reaction do not represent an exhaustive list.

The challenge to calculate the equilibrium state is that on the one hand the adiabatic flame temperature depends on the - in principle still unknown - composition of the final products (coefficients  $\nu_j''$ ) according to Eq. 47 and on the other hand this composition in turn is determined by the temperature dependence of the equilibrium function Eq. 34 cannot be assumed.

$$n_B \cdot \sum_j \int_T^{T_{f,ad}} \nu_j'' \cdot c_{p,j} \cdot dT = -\Delta H_{R|T_{ref}} - n_B \cdot \sum_j \left[ (\nu_j'' - \nu_j') \cdot (h_j(T_{f,ad}) - h_j(T_{ref})) \right] \quad (47)$$

To stay with the example of the global reaction eq. 46, this means that we need the same number of equations to calculate the number of moles of the 11 chemical components in the equilibrium state. As usual, four linear equations are obtained from the mass balances of the atomic species involved, C, N, O, and H. Thus, seven equations are still missing. These can be calculated from the equilibrium function of seven partial reactions (yet to be found), which are linearly independent of each other and contain only chemical components that are present on the product side of the global oxidation reaction according to eq. 46. As long as these conditions are met, it does not matter which partial reactions are used at equilibrium.

Finally, the procedure for calculating the adiabatic flame temperature and the chemical composition at equilibrium is a iterative procedure, namely:

- First, a value for the adiabatic flame temperature is assumed according to experience-based estimation.
- Using the mass balances of the atoms and the equilibrium functions of the partial reactions, the number of moles of each component is calculated.
- Substituted into Eq. 47, the adiabatic flame temperature is calculated. This is calculated using the assumed value of the estimate as above.
- If a deviation is found, the iterative procedure is repeated with a new estimate (e.g., by interpolation between assumed and calculated adiabatic flame temperature) until a convergence criterion is met.

Note that after this convergence, it is possible to investigate whether additional components can occur in the equilibrium state in appreciable concentrations by checking "a posteriori" values of the equilibrium functions of additional suitable partial reactions (e.g.,  $OH + O \rightleftharpoons HO_2$  for the additional component  $HO_2$ ).



Nowadays, public domain or commercial software is available for the calculation of the full thermodynamic equilibrium of complex systems with chemical reactions, because the numerical effort for the solution in the case of a nonlinear system with very many unknowns is extremely high. However, when using such software, it is important to understand exactly the methodology of finding the solution.

## Chapter 4

### Chemical exergy and workability of reactive systems

#### Learning objectives:

- Recall (repetition) the concept of exergy and ability to do work of a system interacting with the environment (without chemical reactions).
- Understand extension of exergy concept to chemically reacting systems: Be able to formulate exergy balance and work capacity of a system outside of chemical equilibrium with the environment.
- Understand relationship between Gibbs free energy of the reaction and work capacity.
- Be able to calculate the exergy of a fuel.
- Understand total exergy as the sum of thermomechanical and chemical exergy.

#### Repetition exergy

In this chapter we want to extend the concept of exergy, known from the lecture Thermodynamics I, to chemically reactive systems and show that such systems, even if they are in thermomechanical equilibrium with the environment, can do additional work when carrying out a reaction, due to the exergy content of the fuel. The maximum (reversible, i.e., in the absence of any losses) work that can be gained then corresponds to the exergy difference between products and reactants, which is equivalent to the *free* enthalpy of reaction, as we will show below.

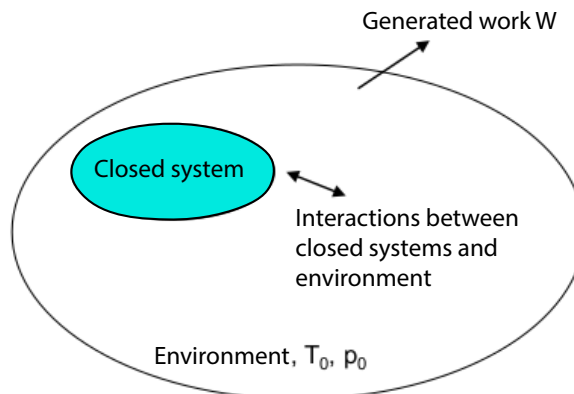


Figure 8: Conceptual representation of the interaction of a closed system with the environment.

We start from the *thermomechanical* exergy of a system in disequilibrium with the environment, according to Fig. 8. For a closed system, its exergy, due to the differences in internal energy, volume, and entropy with respect to the environment, can be calculated using Eq. 48. In general form, the exergy also includes the kinetic and potential energy of a system, but these will be neglected for our considerations below. As is well known, the exergy corresponds to the maximum work that can be gained after interaction with the environment. In reality, there are "always" losses that lead to an irreversible increase in entropy, so that the effectively gained work according to Eq. 49, compared to the reversible such, becomes smaller by the amount  $T_0 \cdot \Delta S_{irrev}$ .

$$Ex = (U - U_0) + p_0 \cdot (V - V_0) - T_0 \cdot (S - S_0) \quad (48)$$

$$W \nearrow = \underbrace{(U - U_0) + p_0 \cdot (V - V_0) - T_0 \cdot (S - S_0)}_{Ex} - \underbrace{T_0 \cdot \Delta S_{irrev}}_{\text{Losses}} \quad (49)$$

However, in the ideal case ( $\Delta S_{irrev} = 0$ ), Eq. 50 for the recoverable work in transferring the original system to the equilibrium state with the environment. The *minimal* work required, in transferring a system from equilibrium with the environment to a non-equilibrium state, can be given by Eq. 51. In reality, the required supplied work here is larger by the term  $T_0 \cdot \Delta S_{irrev}$  (due to the irreversible entropy increase that usually occurs), as eq. 52 shows.

$$W_{max} \nearrow = (U - U_0) + p_0 \cdot (V - V_0) - T_0 \cdot (S - S_0) = Ex_{\text{system vs. environment}} \quad (50)$$

$$W_{min} \swarrow = Ex_{\text{system vs. environment}} \quad (51)$$

$$W \swarrow = Ex_{\text{system vs. environment}} + T_0 \cdot \Delta S_{irrev} \quad (52)$$

Examples for partially irreversible changes of state - here exemplary for a closed system - are the expansion or compression process in an internal combustion engine, with the corresponding consequences for the effectively recoverable or expendable work according to eq. 53, resp. eq. 54. The irreversible increase in entropy corresponds in each case to the heat generated from internal (flow field) or external (bearings, piston rings) friction.

$$W \nearrow = \int_1^2 p \cdot dV|_{is} - T_0 \cdot \Delta S_{irrev \ 1 \rightarrow 2} \quad (53)$$

$$W \swarrow = (- \int_2^1 p \cdot dV)|_{is} + T_0 \cdot \Delta S_{irrev \ 2 \rightarrow 1} \quad (54)$$

It should be noted that in Eqs. 53 and 54  $W \nearrow$  corresponds to the work obtained from the system during the change of state (hence the arrow  $\nearrow$ ), whereas  $W \swarrow$  corresponds to the work that must be expended from the outside for the change of state (arrow  $\swarrow$ ).

Further entropy increases and thus exergy losses occur, for example, whenever an originally existing temperature difference between two states is not optimally used for work production by a thermodynamic cycle, but is used in a heat exchanger, as exemplified in Fig. 9, is used (see eq. 55).

$$Ex_{loss} = T_U \cdot \Delta S_{irrev} \quad (55)$$

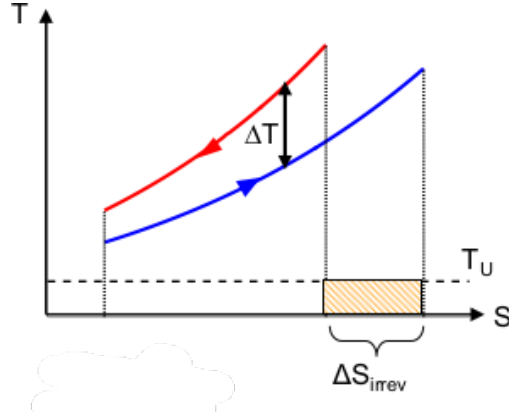


Figure 9: Visualization of exergy loss (entropy generation) during heat transfer between two temperature levels in a heat exchanger.

Fig. 10 shows different types of entropy increase and associated exergy loss, using the example of a thermodynamic cycle typical of gas turbines. As a simplification, we consider the working medium as pure air and the combustion as heat input from outside.

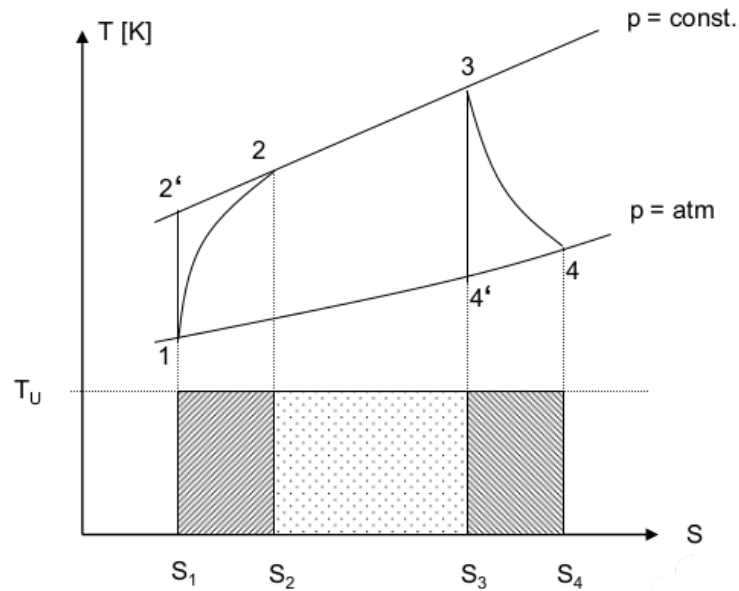


Figure 10: Various exergy losses (entropy generations) in a thermodynamic cycle, here using the example of a gas turbine.

Due to friction, irreversible entropy increases and thus exergy losses occur first in the compression and expansion of the working medium. In addition, heat addition (change of state between points 2 and 3 in the T-s diagram) generates an irreversible entropy increase ( $s_3 - s_2$ ) insofar as this heat addition occurs at a finite temperature ( $\bar{T}_{2,3}$ ). Of course, the higher this temperature, the smaller the entropy increase for a given amount of heat.

One last - shown in fig. 10 not shown for the moment - entropy increase (and thus an exergy loss) arises from the fact that the amount of heat drawn by the trapezoid  $4 \rightarrow 1 \rightarrow T_u, s1 \rightarrow T_u, s4 \rightarrow 4$  is transferred - without work output - to the environment and thus, in the sense of a basically existing work capability, wasted. In larger plants, however, it is worthwhile to utilize this "low-temperature heat" through a conversion process (e.g., via a steam turbine cycle). In modern gas-fired combined cycle power plants, for example, the original efficiency of a simple gas turbine process of about 40% can be increased to about 60% by a downstream steam process.

## Extension of the exergy term to chemically reactive systems

We subsequently generalize the exergy term to chemically reactive systems using the *thought experiment*, as shown in Fig. 11. When such a system interacts with the environment, until the equilibrium state is reached, the exergy of the system consists of two components: first, the difference of the pure *thermomechanical* state with respect to the environment, and second, the *differential chemical composition* of the system with respect to the environment. The total exergy can then be calculated for a closed system by Eq. 48 a and for an open system by Eq. 48 b.

$$ex_{\text{tot}} = (u - u_0) + p_0 \cdot (v - v_0) - T_0 \cdot (s - s_0) + ex_{ch} \quad (48 \text{ a})$$

$$ex_{\text{tot}} = (h - h_0) - T_0 \cdot (s - s_0) + ex_{ch} \quad (48 \text{ b})$$

The additional term of *chemical exergy* of system comes from the fact that at a different chemical composition between system and environment there is a possibility to generate additional work by carrying out a suitable reaction. This corresponds to the exergy difference between the state *before* and that *after* the execution of the chemical reaction (the latter state corresponds to the complete state of equilibrium with the environment). However, in order to calculate exergy differences between products and reactants, one must have available data on the exergy of each chemical component involved.

Table 5 shows values of the so-called *standard* chemical exergy of various components at *reference* conditions of  $T = 298K$  and  $p_0 = 1atm$ . These values are given according to two different calculation models (Model  $I^a$  and Model  $II^b$ ), and the discrepancies between the two are usually very small.

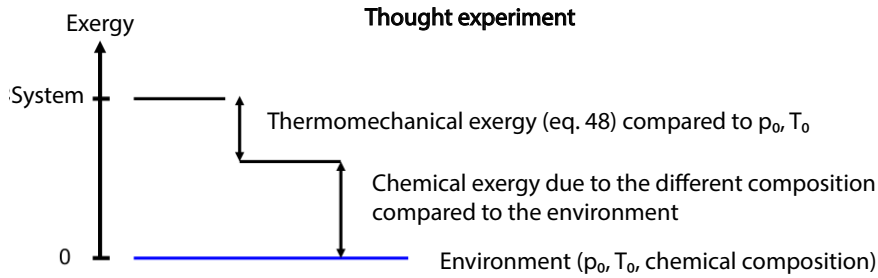


Figure 11: Distinction between thermomechanical and chemical exergy.

**TABLE A-26** Standard Molar Chemical Exergy,  $\bar{e}^{\text{ch}}$  (kJ/kmol), of Selected Substances at 298 K and  $p_0$

Substance	Formula	Model I <sup>a</sup>	Model II <sup>b</sup>
Nitrogen	N <sub>2</sub> (g)	640	720
Oxygen	O <sub>2</sub> (g)	3,950	3,970
Carbon dioxide	CO <sub>2</sub> (g)	14,175	19,870
Water	H <sub>2</sub> O(g)	8,635	9,500
Water	H <sub>2</sub> O(l)	45	900
Carbon (graphite)	C(s)	404,590	410,260
Hydrogen	H <sub>2</sub> (g)	235,250	236,100
Sulfur	S(s)	598,160	609,600
Carbon monoxide	CO(g)	269,410	275,100
Sulfur dioxide	SO <sub>2</sub> (g)	301,940	313,400
Nitrogen monoxide	NO(g)	88,850	88,900
Nitrogen dioxide	NO <sub>2</sub> (g)	55,565	55,600
Hydrogen sulfide	H <sub>2</sub> S(g)	799,890	812,000
Ammonia	NH <sub>3</sub> (g)	336,685	337,900
Methane	CH <sub>4</sub> (g)	824,350	831,650
Ethane	C <sub>2</sub> H <sub>6</sub> (g)	1,482,035	1,495,840
Methyl alcohol	CH <sub>3</sub> OH(g)	715,070	722,300
Methyl alcohol	CH <sub>3</sub> OH(l)	710,745	718,000
Ethyl alcohol	C <sub>2</sub> H <sub>5</sub> OH(g)	1,348,330	1,363,900
Ethyl alcohol	C <sub>2</sub> H <sub>5</sub> OH(l)	1,342,085	1,357,700

Aus Moran & Shapiro, Fundamentals of Engineering Thermodynamics, 5th edition

Table 5: Standard chemical exergy values of some substances with reference to two different models of the reference environment.

### Why are there different calculation models?

The estimation of the standard chemical exergy of a chemical component presupposes that one knows completely the equilibrium state of the entire system "Earth", i.e. our thermodynamic environment, including all occurring compounds (in solid, liquid and gaseous state). Only then, by adding the chemical component in question, can one even define the possible chemical reactions to create the new chemical equilibrium. In the practical sense the task is not

solvable, therefore one helps oneself with different strong simplifications in the description of the chemical composition of the system "earth" ( $\cong$  "environment"), e.g. even with model  $I^a$ , and/or model  $II^b$ .

In any case, an important finding from the study of the 5 table is that, with the exception of *fuels*, most of the other occurring chemical components have comparatively very low exergy values. It is the compounds known to us as *fuels* that have exergy values several orders of magnitude higher. We will see that the reason for this is that these - originally still out of equilibrium with the environment - bring about a chemical reaction with oxidation partners and thus bring out a high enthalpy of reaction, which causes a corresponding work capacity (more precisely corresponding to the *free* enthalpy of reaction). This working capacity corresponds precisely to the *reaction exergy* which transfers the original chemical composition of the system into that of the state of equilibrium with the environment.

Important: When calculating the fuel exergy, we assume that only the fuel is at the reference pressure, while all other reactants have their equilibrium partial pressure (or mole fraction) as they occur in the environment (this applies to oxidation partners and reaction products). Typical values of such mole fractions can be found, for example, in table 6:

Component	Molar fraction $X_i$ (%)
$N_2$	75.67
$O_2$	20.35
$H_2O$ (gaseuos)	3.12
$CO_2$	0.03
others	0.83

Table 6: Typical composition of the reference environment. Source: Moran & Shapiro, Fundamentals of Engineering Thermodynamics, 5th edition.

Eq. 56 expresses the - by definition - fact that the maximum work that can be gained or the minimum work that has to be expended exclusively by the reaction performance corresponds to the exergy difference between products and reactants.

$$W_{rev} \nearrow = -[n_B \cdot \sum_j (\nu_j'' - \nu_j') \cdot ex_j] \quad (56)$$

From the combined 1st and 2nd law of thermodynamics, taking into account the additional irreversible entropy increase that often occurs in the process and thus the corresponding exergy loss, we obtain Eq. 57.

$$W \nearrow = - \underbrace{[n_B \cdot \sum_j (\nu_j'' - \nu_j') \cdot h_{f,j}^0] + [n_B \cdot \sum_j (\nu_j'' - \nu_j') \cdot s_j] \cdot T_U}_{-\Delta G_{R,U}} - \underbrace{T_U \cdot \Delta S_{irrev}}_{\text{irreversible heat}} \quad (57)$$

For a reversible (lossless) reaction performance, it follows from the combination of Eq. 56 and 57 then Eq. 58.

$$\begin{aligned} -\Delta Ex_{Reaction|U} &= -[n_B \cdot \sum_j (\nu_j'' - \nu_j') \cdot ex_{j,U}] = W_{rev} \nearrow = \\ &= -n_B \cdot \sum_j (\nu_j'' - \nu_j') \cdot h_{f,j,U}^0 + n_B \cdot \sum_j (\nu_j'' - \nu_j') \cdot s_{j,U} \cdot T_U = \\ &= - \underbrace{\Delta H_{R,U}}_{\text{reaction enthalpy}} + \underbrace{\Delta S_{R,U} \cdot T_U}_{\text{reaction entropy}} = -\Delta G_{R,U} \quad (58) \end{aligned}$$

From this it can be seen that in this case the *reaction exergy* is equal to the *free reaction enthalpy* and this, in turn, is equal to the maximum work that can be gained or the minimum work that can be expended, during the interaction of the system with the environment. This allows the reversible work in carrying out a chemical reaction to be derived directly from the difference in the free enthalpies of the products and reactants. These in turn are tabulated for very many chemical components for reference conditions of pressure and temperature.

### Calculation of the chemical exergy of a fuel

In addition, one can analogously calculate (based on Eq. 58) the exergy of a fuel from the free enthalpies of the products and reactants participating in an appropriate reaction to establish complete equilibrium with the environment. This calculation is given by Eq. 59, which describes the conversion process of any hydrocarbon  $C_xH_y$  by oxidation in an electrochemical device (fuel cell, i.e., without the detour of a combustion-induced heat of reaction) according to Fig. 12. It should be emphasized here, on the one hand, that - as mentioned before - the fuel has the reference pressure  $p_0$  when entering the system, while all other components have their equilibrium partial pressure in the environment, and, on the other hand, that the term with the logarithm of the partial pressures on the right-hand side of Eq. 59 takes into account the difference between the *standard entropy* of this component and the entropy at the respective - from the reference pressure deviating - partial pressure.

$$\begin{aligned} ex_B &= [h_{C_xH_y} + (x + \frac{y}{4}) \cdot h_{O_2} - x \cdot h_{CO_2} - \frac{y}{2} \cdot h_{H_2O}]_{(T_0, p_0)} \\ -T_0 \cdot [s_{C_xH_y} + (x + \frac{y}{4}) \cdot s_{O_2} - x \cdot s_{CO_2} - \frac{y}{2} \cdot s_{H_2O}]_{(T_0, p_0)} &+ R \cdot T_0 \cdot \ln \left[ \frac{X_{O_2}^{x+\frac{y}{4}} \cdot 1}{X_{CO_2}^x \cdot X_{H_2O}^{\frac{y}{2}}} \right] \quad (59) \end{aligned}$$



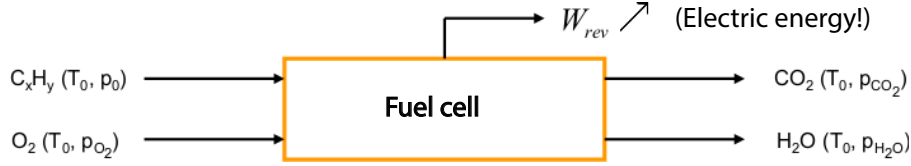


Figure 12: Schematic representation of a lossless (reversible process control) fuel cell at  $T = T_0$  and  $p = p_0$  (open, flow-through system).

In compact form, the exergy of the fuel is given by Eq. 60:

$$ex_B = \underbrace{-\Delta h_R + T_0 \cdot \Delta s_{R,0}}_{-\Delta g_{R,0}} - R \cdot T_0 \cdot \ln \left[ \frac{X_{CO_2}^x \cdot X_{H_2O}^{\frac{y}{2}}}{X_{O_2}^{x+\frac{y}{4}} \cdot 1} \right] \quad (60)$$

Subsequently, it can be shown that after the reaction has been carried out (at which point the fuel has its equilibrium partial pressure), there is no more exergy and the system is in complete equilibrium with the environment, as described by Eq. 60 b.

$$-\frac{\Delta g_{R,0}}{R \cdot T_0} = \ln \left[ \frac{(X_{CO_2}^e)^x \cdot (X_{H_2O}^e)^{\frac{y}{2}}}{(X_{O_2}^e)^{x+\frac{y}{4}} \cdot X_{C_xH_y}^e} \right] \quad (60 \text{ b})$$

Table 7 shows values for the upper or lower heating value, the *reversible work* in carrying out the corresponding oxidation reaction and the exergy of the fuel for various fuels. It is striking that - with a few exceptions (sulfur-containing fuels) - both the reversible work and the (*upper*) *heating value* of a fuel differ from its exergy (and also from each other) by only very few percentage points. This is due to the fact (as commented in slide 12 of chap. 4) that in eq. 60

- The logarithm of the partial pressures is almost negligible with respect to the Gibbs free energy of the reaction and
- In the case of the Gibbs free energy of the reaction itself, the term of the entropy of reaction at reference temperature is significantly smaller than the enthalpy of reaction.

**Tabelle 10.13.** Molarer Heizwert  $H_{\text{um}}$ , molarer Brennwert  $H_{\text{om}}$ , reversible Reaktionsarbeit  $W_{\text{tm}}^{\text{rev}}$  und molare chemische Exergie  $E_{\text{B}}$  chemisch einheitlicher Brennstoffe in kJ/mol für  $t = 25^\circ\text{C}$ ,  $p = 100\text{ kPa}$ .  $E_{\text{B}}$  wurde nach dem Umgebungsmodell von Abschnitt 5.5.6 berechnet

Brennstoff	$H_{\text{um}}$	$H_{\text{om}}$	$-W_{\text{tm}}^{\text{rev}}$	$E_{\text{B}}$	$E_{\text{B}}/H_{\text{om}}$	$E_{\text{B}}/(-W_{\text{tm}}^{\text{rev}})$
Feste und gasförmige Brennstoffe						
C	393,51	393,51	394,37	405,55	1,0306	1,0283
S	296,8	296,8	300,1	531,5	1,791	1,772
H <sub>2</sub>	241,83	285,84	237,15	234,68	0,8210	0,9896
H <sub>2</sub> S	518,0	562,0	503,8	732,8	1,304	1,455
COS	551,9	551,9	620,6	865,6	1,568	1,395
CO	282,98	282,98	257,21	270,88	0,9572	1,0535
CH <sub>4</sub>	802,30	890,32	817,90	824,16	0,9257	1,0077
C <sub>2</sub> H <sub>6</sub>	1427,8	1559,8	1467,3	1482,3	0,9503	1,0102
C <sub>3</sub> H <sub>8</sub>	2044,0	2220,0	2108,3	2132,0	0,9604	1,0112
C <sub>4</sub> H <sub>10</sub>	2658,5	2878,5	2747,7	2780,1	0,9658	1,0118
C <sub>2</sub> H <sub>2</sub>	1255,6	1299,6	1235,1	1255,0	0,9657	1,0161
C <sub>2</sub> H <sub>4</sub>	1323,2	1411,2	1331,5	1348,9	0,9559	1,0131
Flüssige Brennstoffe						
C <sub>5</sub> H <sub>12</sub>	3245	3509	3386	3427	0,9766	1,0121
C <sub>6</sub> H <sub>14</sub>	3855	4163	4023	4073	0,9784	1,0124
C <sub>7</sub> H <sub>16</sub>	4465	4817	4659	4718	0,9794	1,0127
C <sub>8</sub> H <sub>18</sub>	5075	5471	5296	5363	0,9803	1,0127
C <sub>6</sub> H <sub>6</sub>	3135,6	3267,6	3202,7	3262,4	0,9984	1,0186
CH <sub>3</sub> OH	637,7	725,7	701,7	710,4	0,9789	1,0124
C <sub>2</sub> H <sub>5</sub> OH	1235,5	1367,6	1326,6	1343,6	0,9825	1,0132

[Quelle: Baehr, Thermodynamik 12. Auflage, Springer Verlag, 2005]

Table 7: Upper and lower heating values, maximum recoverable (reversible) work and chemical exergy of selected fuels.

## Chapter 5

### Electrochemical conversion - fuel cells

#### Learning objectives:

- Be able to calculate maximum (reversible) work done by conversion on a fuel cell using the free enthalpy of the reaction.
- Know types of fuel cells, suitable energy sources, and operating temperature ranges.
- Be able to describe the chemical reactions at the anode, cathode, and global reaction of common types of fuel cells.
- Understand characteristic curve  $U = f(I)$  of a fuel cell and be able to calculate from it efficiency, power, exergy loss and required mass flow of the fuel.
- Understand the influence of the operating temperature on the maximum work to be done and the maximum work to be delivered by an electrolyzer and a fuel cell, respectively.

In this chapter we will study characteristic features of electrochemical energy conversion using fuel cells as an example. In contrast to *thermomechanical* cycles, which are based on heat supply at high temperatures by the exothermic combustion reaction (*thermochemical* conversion), a fuel cell generates electricity directly from the chemically bound energy in the fuel, without the detour via the high-temperature reaction heat. This is a *electrochemical* energy conversion and the thermodynamic efficiency of this process is not subject to the Carnot upper bound. This is a major reason why - at least in principle - fuel cells have a higher conversion efficiency than internal combustion engines. However, since the former are subject to further loss mechanisms, their efficiency advantages apply predominantly to smaller plants, whereas for those in the range of several MW<sub>el</sub> there is virtually parity between the two types of conversion.

Using the example of the simple oxidation reaction  $H_2 + 0.5O_2 \rightleftharpoons H_2O$  (and its inversion), one can demonstrate the difference between the two processes:

During combustion, the enthalpy of reaction is converted into heat of reaction and this leads to a high (maximum adiabatic) flame temperature. The reaction products then generate mechanical work - by expansion in a gas turbine or in an internal combustion engine - which is converted to electricity via a generator if required.

In the fuel cell, the same oxidation reaction occurs, ideally at constant pressure and near isothermal. The maximum recoverable work in the form of electricity corresponds to the free enthalpy of reaction  $\Delta G_R$ . If required, the electricity

can then be converted to mechanical work via an electric motor, for example to power a vehicle.

The reverse process is called electrolysis. Through this, electricity can be used to split water (vapor) to produce hydrogen (as a chemical energy carrier) and oxygen.  $H_2$  can also be produced from  $H_2O$  by thermochemical means, as we will see at the end of this chapter. This, however, requires an external heat supply at such high temperatures that materials for corresponding reactors are hard to find.

In electrochemical conversion, for historical reasons, one still sometimes uses the term "electrochemical efficiency"  $\eta_{cell}$ , which is the ratio of the *free* reaction enthalpy  $\Delta G_R$  governing the work obtained to the reaction enthalpy  $\Delta H_R$ , Eq. 62. It should be noted, however, that this is not a thermodynamic efficiency in the true sense, because it says nothing about the ratio of the work achievable, in the reality of execution, to a theoretical/ideal maximum value.

$$\Delta G_R = \Delta H_R - T \cdot \Delta S_R \quad (61)$$

$$\eta_{Cell} = \frac{\Delta G_R}{\Delta H_R} = 1 - T \cdot \frac{\Delta S_R}{\Delta H_R} \quad (62)$$

By the example of the oxidation reaction of  $H_2$  one can see that this "efficiency" is smaller than one, which is due to the fact that all three quantities  $\Delta G_R$ ,  $\Delta H_R$  and  $\Delta S_R$  are negative. However, as table 8 shows, there are fuels for which electrochemical oxidation this "efficiency" can be greater than one (e.g., liquid methanol, because in this case the *reaction enthalpy*  $\Delta S_R$  is positive).

Fuel ( $H_2O$ gaseous) at $T = T_{\text{environment}}$	Max. electrochemical efficiency at $T = 298 \text{ K}$
$H_2O$ (Helium)	0.94
$CH_4$ (Methane)	0.92
$C_3H_8$ (Propane)	0.95
$CH_3OH$ (liquid methanol)	1.07

Table 8: Maximum electrochemical "efficiency" (at  $T = 298K$ ) of a fuel cell for operation with typical fuels.

## Types of fuel cells

In Table 9 different types of fuel cells are listed. They differ primarily in the operating temperature, then also in the materials used for the anode, cathode and electrolyte, and finally - quite significantly - in the different fuels that can be used.

The main types of fuel cells considered today are the proton-conducting membrane fuel cell (PEMFC: Proton Exchange Membrane Fuel Cell), which operates at temperatures lower than  $100^\circ C$ , and the solid oxide fuel cell (SOFC: Solid Oxide Fuel Cell), which operates at very high temperatures ( $> 800^\circ C$ ). Due to the high temperature range, SO fuel cells are used in stationary applications because transient operation, with rapidly changing power, leads to high thermal stresses and reduced lifetime. Hydrocarbons, especially methane, can

Bezeichnung	Abkürzung	Englische Bezeichnung	Elektrolyt	Betriebs-temperatur
Alkalische Brennstoffzelle	AFC	<b>Alkaline Fuel Cell</b>	KOH-Lösung	60–80 °C
Protonenleitende Membran-BZ	PEMFC	<b>Proton Exchange Membrane Fuel Cell</b>	Spezielle Kunststoffmembran	80–90 °C
Phosphorsaure Brennstoffzelle	PAFC	<b>Phosphoric Acid Fuel Cell</b>	Konzentrierte Phosphorsäure	160–220 °C
Schmelzkarbonat-Brennstoffzelle	MCFC	<b>Molten Carbonate Fuel Cell</b>	Kalium- und Lithium-Karbonat	600–650 °C
Festoxid-Brennstoffzelle	SOFC	<b>Solid Oxide Fuel Cell</b>	Zirkondioxid	950–1000 °C

[Quelle: Baehr, Thermodynamik 12. Auflage, Springer Verlag, 2005]

Table 9: Different types of fuel cells. First and foremost, the differences lie in the operating temperature of the fuel cell and, associated with this, what material the electrolyte is made of.

be readily processed in SO fuel cells after an initial reforming step to synthesis gas ( $\text{CO} + \text{H}_2$ ). For PEM fuel cells, on the other hand, practically only hydrogen can be considered as fuel, because carbon-containing components, especially CO, lead to "poisoning" of the platinum-containing catalyst located at the anode. On the other hand, rapid power changes can be realized with a PEM fuel cell, because no thermal stress occurs due to the low operating temperature and the materials used. Accordingly, PEM-type fuel cells are particularly suitable for powering vehicles whose operation is highly transient.

Fuel cell	Anode reaction	Cathode reaction
AFC	$\text{H}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2e^-$	$\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^-$
PAFC and PEMFC	$\text{H}_2 \rightarrow 2\text{H}^+ + 2e^-$	$\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}$
MCFC	$\text{H}_2 + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2e^-$	$\frac{1}{2}\text{O}_2 + \text{CO}_2 + 2e^- \rightarrow \text{CO}_3^{2-}$
SOFC	$\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2e^-$	$\frac{1}{2}\text{O}_2 + 2e^- \rightarrow \text{O}^{2-}$
	$\text{CO} + \text{O}^{2-} \rightarrow \text{CO}_2 + 2e^-$	$\frac{1}{2}\text{O}_2 + 2e^- \rightarrow \text{O}^{2-}$

Source: Baehr, Thermodynamik 12. Auflage, Springer Verlag, 2005

Table 10: Anode and cathode reactions of different fuel cell types. The charge carriers of the electrolytes are highlighted in bold print.

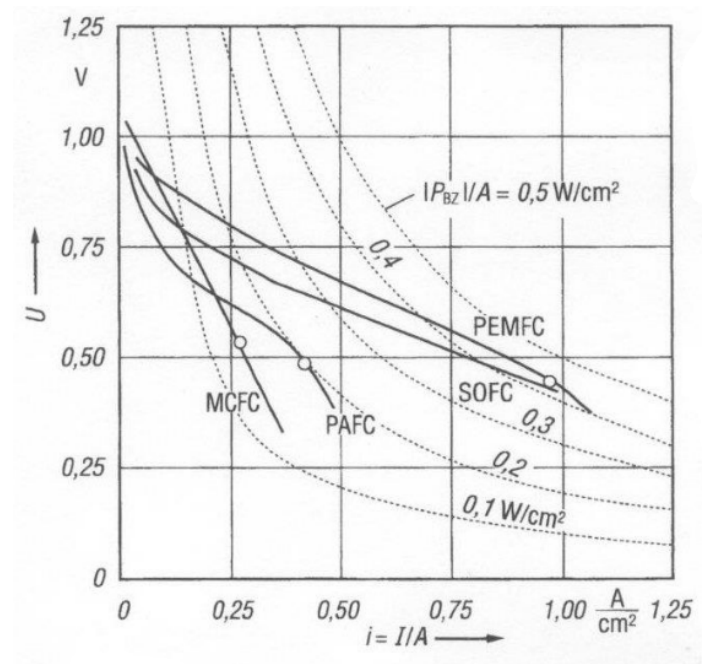
Table 10 shows the chemical reactions that take place at the two electrodes (anode and cathode) for the fuel cell types mentioned. Common to all is:

- At the anode, the respective fuel undergoes an initial reaction in which electrons are released.
- These electrons arrive via an external circuit (electrical load) in the cathode, where they participate in a reaction with the oxidant (here  $\text{O}_2$ ).

- Essential for the occurrence of the global reaction is the flow of a charged chemical component through the electrolyte: in the case of the PEM and PA fuel cell, the flow of positively charged H atoms from the anode to the cathode, and for the other fuel cell types, the flow of a negatively charged chemical component from the cathode to the anode.
- products can either be produced on the cathode side (as in the PEM and PA fuel cells) or on the anode side (as in the other fuel cell types listed in Tab. 10 fuel cell types listed).

#### Small task:

For all fuel cell types listed in Figure 10, write the global reaction as the "sum" of the partial chemical reactions at the two electrodes.



[Quelle: Baehr, Thermodynamik 12. Auflage, Springer Verlag, 2005]

Figure 13: Typical current-voltage characteristics, as well as curves of constant power density  $\frac{|P_{FC}|}{A} = U \cdot i$ , for different types of fuel cells. The current  $I$  is usually related to the electrode area  $A$ . The circles denote the states of maximum power density.

### Thermodynamic analysis of a fuel cell

Fig. 13 shows the characteristic curves of different types of fuel cells in the commonly used voltage-current ( $U - I$ ) diagram. In this particular diagram, the  $x$  axis shows the current flowing through the outer circuit related to the surface area of the electrodes, while the  $y$  axis plots the electric voltage between

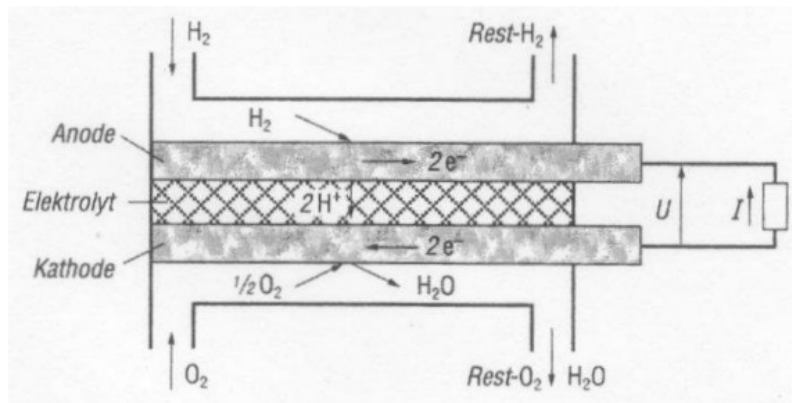
the anode and cathode measured for each current value. Also shown in this diagram are the electrical powers resulting for each fuel cell type as the product of current and voltage. Noticeable in this figure is that:

- The measured voltage - starting from a quiescent value (at  $I/A \sim 0$ ) - decreases continuously (although to different degrees depending on the fuel cell type) on the order of about 1 volt with increasing current.
- The surface specific current is at most  $1A/cm^2$  until the maximum fuel cell power is reached.
- Finally, this maximum achievable fuel cell power is a few tenths of  $W/cm^2$ .

The decrease of the electric voltage with increasing current has to do with various kinds of (ohmic, diffusion/transport) losses and leads to an irreversible entropy increase or to a corresponding exergy loss.

Since the generated voltage (and thus the surface related electrical power) at a single cell is too small to drive e.g. an electric motor for a vehicle application, single cells are combined in a fuel cell stack to realize a total voltage in the order of 100 V and more. Another way to increase the power density of a fuel cell is to pressurize it (i.e., "supercharge" the fuel and oxygen supply), which makes all diffusion processes of chemical components faster.

In the following, we will focus on the PEM fuel cell with  $H_2$  as fuel as an example.

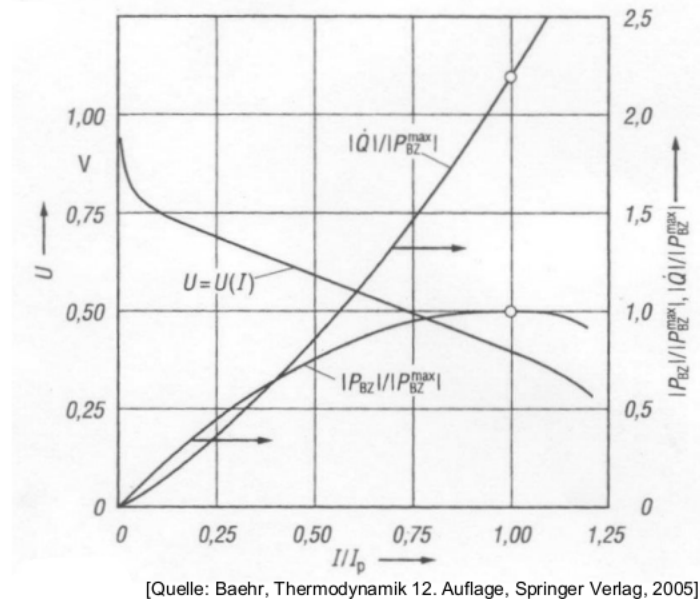


[Quelle: Baehr, Thermodynamik 12. Auflage, Springer Verlag, 2005]

Figure 14: Simplified schematic of a  $H_2$ - $O_2$  fuel cell with proton-conducting electrolyte (PEM fuel cell).

Fig. 14 shows schematically/conceptually the geometrical arrangement of such an electrochemical cell. It can be seen from this that, in addition to the two electrodes, the electrolyte and the connected electrical load, the reactants must be supplied and the products of the global reaction must be removed. Since, as a rule, the hydrogen cannot be completely converted at the anode (diffusion to the anode is often the limiting conversion step given the prevailing short

residence times), the remaining (unreacted)  $H_2$  must be recycled (i.e., returned to the inlet). The movement of these fluids through the fuel cell, as well as the required cooling (and coolant pump) to remove the generated heat, results in non-negligible power requirements for the corresponding auxiliary equipment.



[Quelle: Baehr, Thermodynamik 12. Auflage, Springer Verlag, 2005]

Figure 15: Ratio  $|P_{FC}|/|P_{FC}^{max}|$  as a function of  $I/I_P$ , calculated from the characteristic  $U = U(I)$  of a PEM fuel cell.  $I_P$  denotes the current at the maximum power density condition.

In fig. 15, the  $U - I$ -diagram shows the curves of the resulting thermal power, which is related to the maximum electrical power, and the electrical power itself. The rapid increase in the heat power to be dissipated with increasing current is due to the irreversible increase in entropy ( $\rightarrow$  loss of exergy due to the decrease in electrical voltage with increasing current).

According to Eq. 63 and Eq. 64, the electric current is proportional to the number of electrons flowing across the outer circuit and thus moles of  $H_2$  converted per unit time, the proportionality factor being related to the Faraday number ( $F = 96,485.3 \frac{A \cdot s}{mol}$ ), as the product of the Avogadro number and the electric charge of an electron. From Eq. 65 then gives the cell power obtained.

$$I = \dot{n}_e \cdot e \cdot N_A = \dot{n}_e \cdot F \quad (63)$$

$$I = \dot{n}_e \cdot F = 2 \cdot F \cdot \dot{n}_{H_2} \quad (64)$$

$$P_{FC} = -U \cdot I \quad (65)$$

From the combination of the 1st and 2nd laws of thermodynamics and Eqs. 64 and eq. 65, and the knowledge that the maximum reversible electric power is proportional to the free enthalpy of reaction of the oxidation reaction per unit



time, Eq. 67 the reversible voltage  $U_{rev} = f(T, p)$  as the maximum possible value that can be measured on a fuel cell operating with hydrogen. Analogously, by Eq. 66 to define a so-called caloric voltage  $U_H = f(T)$ , which is related to the value of the reaction enthalpy  $\Delta h_R$ .

$$U_H(T) = \frac{h_U(T)}{2F} = \frac{-\Delta h_R(T)}{2F} \quad (66)$$

$$U_{rev}(T, p) = \frac{-\Delta g_R(T, p)}{2F} = \frac{-P_{FC}^{rev}}{I} \quad (67)$$

T [°C]	25	100	200	300	600	700	900	1000
$U_H$ [V]	1.2533	1.2574	1.2621	1.2662	1.2771	1.2803	1.2863	1.2891
$U_{rev}$ [V]	1.1847	1.1668	1.1420	1.1162	1.0352	1.0073	0.9507	0.9219

[Quelle: Baeher, Thermodynamik 12. Auflage, Springer Verlag, 2005]

Table 11: Characteristic voltages  $U_H$  and  $U_{rev}$  of a PEM fuel cell operated with  $H_2$  at  $p=1$ atm, as a function of temperature (in °C), calculated with the molar enthalpies and Gibbs functions.

As Table 11 shows,  $U_H$  is very weakly dependent on the operating temperature, with  $U_{rev}$  decreasing quite sharply as the temperature of the cell increases. Interestingly, one takes from Table 12 the finding that the reversible (and thus maximum recoverable) voltage across a fuel cell also exhibits similar values in the range of slightly more than 1 volt at reference conditions when other fuels are oxidized.

<b>Examples of other fuels at <math>p_0=100</math> kPa, <math>T=298</math> K</b>	$U_{rev}$ (V)	1.06	1.09	1.18
	<b>Fuel</b>	$CH_4 (+2 O_2)$	$C_3H_8 (+5 O_2)$	$CH_3OH (+1.5 O_2)$

Table 12: Reversible cell voltage of a PEM fuel cell operated with different fuels ( $T=298$ K,  $p=1$  atm).

With reference to fig. 15, it is important to realize that the ratio of the actual electrical voltage generated at an operating condition (i.e., at a given current) of a fuel cell to the reversible voltage at the operating pressure and temperature gives the thermodynamic efficiency of the fuel cell!

Eq. 68 gives the 1st law for the open system "fuel cell", where Eq. 69, the incident (reversible and irreversible) heat flux is expressed in terms of the electrical quantities  $U_H$ ,  $U(I)$  and  $I$ . The effective electrical power gained can be calculated from Eq. 70. Finally, the distinction between reversible and irreversible heat flow is given by Eq. 71 and 72.

$$\dot{Q} + P_{FC} = -\dot{n}_{H_2} \cdot h_U(T) \quad (68)$$

$$\dot{Q} = -\frac{h_U}{2F} \cdot I - P_{FC} = -[U_H - U(I)] \cdot I \quad (69)$$

$$\begin{aligned}
0 \leq -P_{FC} &= -P_{FC}^{rev} - T \cdot \dot{S}_{irrev} = \\
&= U_{rev} \cdot I - T \cdot \dot{S}_{irrev} = \dot{n}_{H_2} \cdot [-\Delta g_R(T, p)] - T \cdot \dot{S}_{irrev} \quad (70)
\end{aligned}$$

$$\dot{Q}_{rev} = -[U_H - U_{rev}] \cdot I \quad (71)$$

$$\dot{Q}_{irrev} = -[U_{rev} - U(I)] \cdot I \quad (72)$$

Fig. 16 represents qualitatively the "gross" voltage as a function of the electric current (solid line) - as also shown in Fig. 13 and fig. 15 - and additionally the "net" voltage (dashed line), which can be effectively generated if the "parasitic" electrical demand of the required auxiliaries (blowers or compressors, pumps) is taken into account. Since these auxiliary units have a very low efficiency at very low mass flows (i.e., also at low electric current), the "net" voltage (and thus the effective thermodynamic efficiency of the fuel cell) reaches the maximum value in the low to medium power range (partial load).

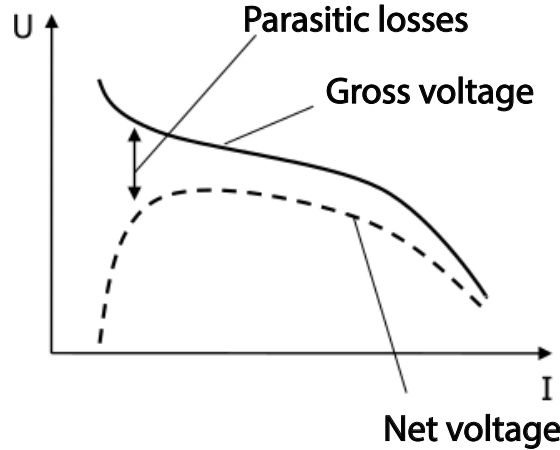
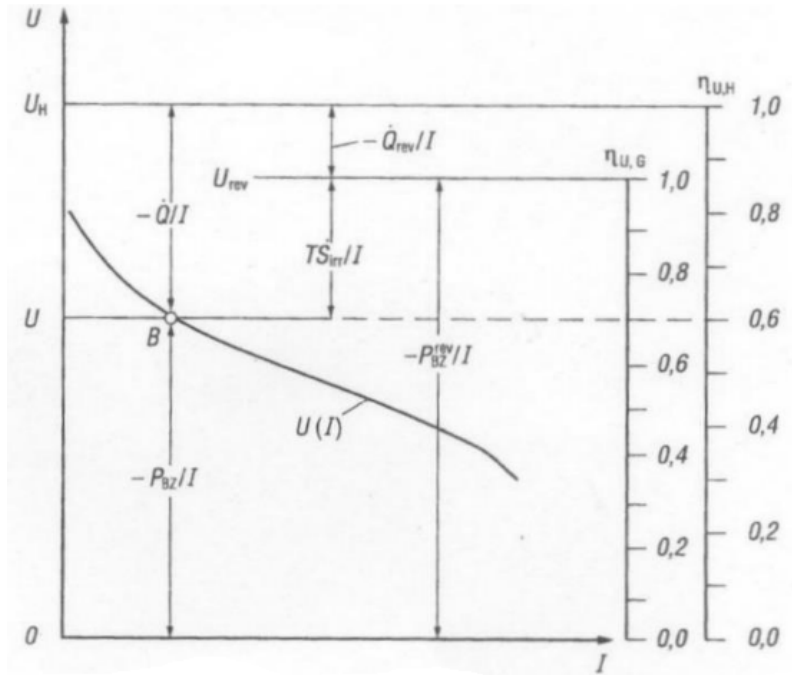


Figure 16: Qualitative representation of the effective voltage obtained from the fuel cell (net voltage), the voltage loss due to parasitic losses and the gross voltage as a function of current.

In fig. 17, by the way, the power as well as reversible and irreversible heat flows are shown according to Eqs. 68 - 72 are shown.

### Electrolysis of water

The reverse process of the fuel cell is realized by an electrolyzer. In this case, the reaction enthalpy, reaction entropy (see Slide 4 in lecture notes for Chapter 5), and free reaction enthalpy are all positive. Fig. 18 shows the values of these three quantities as a function of the temperature at which electrolysis takes place and at the reference pressure of  $1 \text{ atm}$ . From this it can be seen that if the enthalpy of reaction is nearly constant over temperature, the electrical work required



[Quelle: Baehr, Thermodynamik 12. Auflage, Springer Verlag, 2005]

Figure 17: Current-voltage characteristic curve of a fuel cell with illustration of the different terms from 1st and 2nd law. The voltage efficiencies  $\eta_{U,G} = U/U_{rev}$  and  $\eta_{U,H} = U/U_H$  can be calculated from this.

(in terms of free enthalpy of reaction) decreases significantly with increasing temperature, with the demand for heat ( $T \cdot \Delta s_R$ ) increasing. This means that high-temperature heat (e.g., from concentrated solar energy) at temperatures slightly higher than 4,000K could (ideally) cause the "fission" of  $H_2O$  without any electrical energy input. However, there are hardly any materials available that can "withstand" these high temperatures in appropriate reactors. As shown in Fig. 18, for example, at 1,500K already about 33% of the required energy can be supplied as heat and only the remaining 67% in the form of electrical energy, which in practice brings economic advantages.

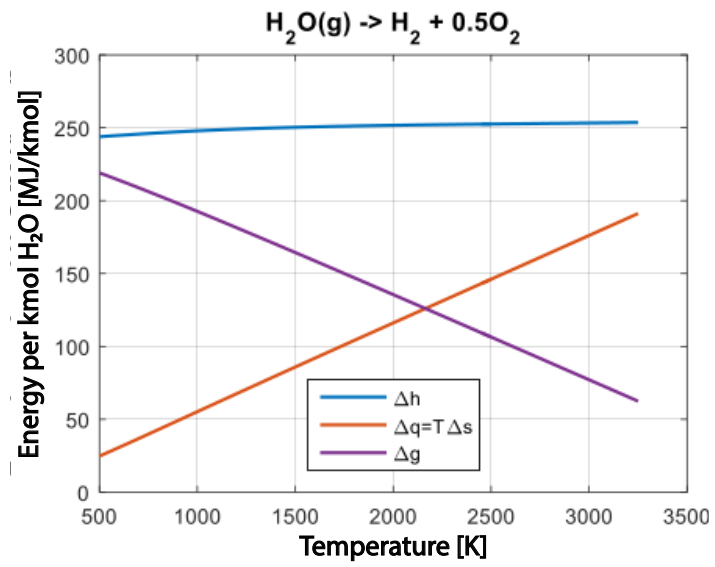


Figure 18: Energy required for the electrolysis of water to hydrogen and oxygen.  $\Delta h$  represents the total reaction enthalpy required per kmol of  $\text{H}_2\text{O}$ ,  $T \cdot \Delta s$  represents the heat required per kmol of  $\text{H}_2\text{O}$ , and  $\Delta g$  represents the electrical energy required per kmol of  $\text{H}_2\text{O}$ .

## Chapter 6

### Kinetic theory of gases

#### Learning objectives:

- Understand the molecular mechanism for the transport of momentum, heat, and components of matter in ideal gases.
- Be able to derive / estimate corresponding macroscopic transport properties as a function of temperature, pressure and molecular size.
- Be able to understand the influence of temperature, pressure, and path length on the time required to diffuse a "disorder" in an ideal gas.

An ideal gas is described by a number of molecules per volume, which interact with each other only by collisions. In these collisions, momentum and kinetic energy are exchanged. The kinetic energy of the individual molecules is different and their statistical distribution for a gas consisting of monatomic molecules is described by Maxwell's function (see Thermodynamics I).

Because only translational degrees of freedom exist in this case, the internal energy of such a gas per kmol can be given by Eq. 73.

$$\frac{3}{2} \cdot R \cdot T = \sum_i^N \frac{m \cdot c_i^2}{2} = N \cdot \frac{m \cdot \overline{c^2}}{2} \quad (73)$$

As already known, the thermodynamic temperature according to Eq. 73 is a measure for the mean kinetic energy of all molecules in the considered gas volume, as can be seen from Eq. 74 is also evident.

$$\overline{c^2} = \frac{3 \cdot R \cdot T}{M} = 3 \cdot R_m \cdot T, \text{ where } R_m: \text{ specific gas constant} \quad (74)$$

From the relation for calculating the speed of sound  $\alpha$  in an ideal gas.

$$\alpha = \sqrt{\kappa \cdot R_m \cdot T}$$

and the definition of a characteristic molecular velocity  $\tilde{c} = \sqrt{\overline{c^2}}$  corresponding to the mean kinetic energy, we obtain the ratio of both velocities

$$\alpha = \tilde{c} \cdot \sqrt{\frac{\kappa}{3}}, \text{ with } \kappa = \frac{c_p}{c_v} = 1 + \frac{R}{c_v} = 1 + \frac{2}{f}$$

where  $f$  corresponds to the number of excited degrees of freedom.

Besides the characteristic molecular velocity  $c$ , we are interested here in the notion of mean free path length  $l_f$ .

If there are  $n$  molecules per unit volume and one molecule has a diameter of  $d_M$ , as well as if all the molecules except one are at rest and the latter is moving at a velocity  $c$ , then the mean free path  $l_f$  can be calculated as the average

distance that can be travelled until the first collision with another molecule. Accordingly,  $V = N \cdot \pi \cdot d_M^2 \cdot l_f$ .

In reality, all molecules move simultaneously and it can be shown that this necessitates a correction factor  $\sqrt{2}$ , which finally gives the mean free path length given by Eq. 75, where  $n = \frac{N}{V}$ .

$$l_f = \frac{1}{\sqrt{2} \cdot \pi \cdot d_M^2 \cdot n} \quad (75)$$

For common gases (except, e.g., vapors of macromolecular compounds), the molecular diameter is typically 2 to 6 angstroms (1 angstrom  $\text{\AA} = 0.1\text{nm}$ ).

At  $T = 273\text{ K}$  and  $p = 100$ , the equation of state for ideal gases allows the number of molecules per unit volume to be calculated as  $2.7 \cdot 10^{25}\text{m}^{-3}$ . For a gas with a molecular diameter of, say,  $3\text{\AA}$ , this gives a mean free path length on the order of  $10^{-7}\text{m}$  (about 100 nm), which is a good two orders of magnitude larger than the typical molecular diameter.

Using the equation of state mentioned above, we see that the mean free path is proportional to the temperature and inversely proportional to the pressure ( $l_f \sim T \cdot p^{-1}$ ).

We now consider first the momentum exchange over a balance surface A (as in Fig. 19) in a gas with a velocity gradient perpendicular to the flow direction. The resulting momentum transport arises due to the velocity difference on both sides of the balance surface over a distance of  $2 \cdot l_f$  and can be calculated by Eq. 76.

$$dI = \frac{1}{6} \cdot A \cdot \tilde{c} \cdot dt \cdot n \cdot m \cdot (v_{x2} - v_{x1}) \quad (76)$$

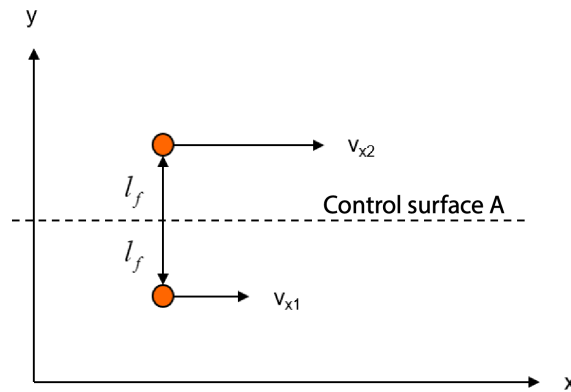


Figure 19: Model situation for deriving momentum transport: flow of a gas with a velocity gradient perpendicular to the direction of flow.

We make use of the assumption that on the microscopic plane  $1/6$  of all molecules move in positive or negative direction along the three Cartesian coor-

dinates. Because the change in momentum over time corresponds to the force, we can express the shear stress as an area-specific force by Eq. 77.

$$\tau = \frac{F}{A} = \frac{(dI/dt)}{A} = \frac{1}{6} \cdot \tilde{c} \cdot n \cdot m \cdot (v_{x2} - v_{x1}) \quad (77)$$

The velocities  $v_{x1}$  and  $v_{x2}$  are determined from the velocity gradients transverse to the control surface and the mean free path length, because molecules can pass through the control surface without collisions if they are at most at a distance  $l_f$  from it. It is valid

$$v_{x2} = v_{x0} + \frac{dv_x}{dy} \cdot l_f, \quad v_{x1} = v_{x0} - \frac{dv_x}{dy} \cdot l_f$$

which gives the shear stress according to Eq. 78.

$$\tau = \frac{1}{3} \cdot \tilde{c} \cdot n \cdot m \cdot l_f \cdot \frac{dv_x}{dy} = \mu \cdot \frac{dv_x}{dy} = \nu \cdot \rho \cdot \frac{dv_x}{dy} \quad (78)$$

The dynamic viscosity  $\mu$  and the kinematic viscosity  $\nu$  can then be defined by Eq. 79:

$$\mu = \frac{\tilde{c} \cdot n \cdot m \cdot l_f}{3} \text{ and } \nu = \frac{\tilde{c} \cdot l_f}{3}, \text{ da } \rho = n \cdot m \quad (79)$$

In the same way as for momentum transport, one can estimate the heat transport across the balance surface. The net molecular flux through the balance surface with the corresponding specific heat capacity makes it possible to calculate this surface-specific heat transport according to Eq. 80 to calculate.

$$\dot{q} = -\frac{\tilde{c} \cdot n \cdot m \cdot l_f}{3} \cdot c_v \cdot \frac{dT}{dy} = -\lambda \cdot \frac{dT}{dy} \quad (80)$$

The thermal conductivity  $\lambda$  is obtained as a function of the molecule-specific quantities  $c, n, m, l_f$  and  $c_v$ . The thermal diffusivity can be defined as  $a = \frac{\lambda}{\rho \cdot c_p} = \frac{\nu}{\kappa}$ .

Finally, by analogy, the mass transport of a gas transverse to the balance surface within a mixture of two components due to a concentration gradient can be calculated by Eq. 81 calculate

$$\frac{\dot{m}_{G1}}{A} = -\rho \cdot D \cdot \frac{dc_1}{dy} \quad (81)$$

with the diffusion coefficient  $D$ , the density of the total mixture  $\rho$ , the fraction of the mass of gas 1 relative to the mass of the mixture  $c_1 = \rho_1/\rho$ , and the area-specific mass flow of gas 1 relative to the center of mass of the mixture  $\dot{m}_{G1}/A$ .

Thus, the corresponding diffusion coefficient is given by Eq. 82

$$D = \frac{\mu}{\rho} = \frac{\tilde{c} \cdot l_f}{3} = \nu \quad (82)$$

proportional to the characteristic molecular velocity and mean free path, and in this simplified view, equal to the kinematic viscosity.

From the three specific transport quantities  $\nu = \frac{\mu}{\rho}$ ,  $a = \frac{\lambda}{\rho \cdot c_p}$  and  $D$ , the following dimensionless similarity numbers can be defined:

$$\underbrace{Pr = \frac{\nu}{a}}_{\text{Prandtl number}}, \quad \underbrace{Sc = \frac{D}{\nu}}_{\text{Schmidt number}}, \quad \underbrace{Le = \frac{D}{a}}_{\text{Lewis number}} = Pr \cdot Sc$$

For most gases,  $Pr$ ,  $Sc$  and  $Le$  have values very close to 1, which allows the formulation of analogies between momentum, heat and mass transfer.

In any case, it is very important that all molecule-specific transport quantities  $\nu$ ,  $a$ , and  $D$  have dimension  $\mathbf{m}^2/\mathbf{s}$ , because molecular transport is determined by the product of the characteristic molecular velocity  $\mathbf{c}$  [ $\mathbf{m}/\mathbf{s}$ ] and the mean free path length  $\mathbf{l}_f$  [ $\mathbf{m}$ ]!

Also important is the pressure and temperature dependence of the transport quantities, as given in Eq. 83.

$$\mu \sim T^{0.5}, \nu \sim T^{1.5} \cdot p^{-1}, D \sim T^{1.5} \cdot p^{-1} \text{ and } a \sim T^{1.5} \cdot p^{-1} \quad (83)$$

In practice, for most gases the exponent -1 is indeed obtained for the pressure, but for the temperature rather values around 1.6 - 1.7.

### Example of an application:

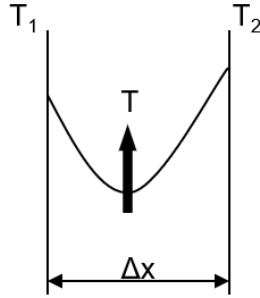


Figure 20: One-dimensional heat conduction in a gas layer of thickness  $\Delta x$ .

In the second part of Thermodynamics II, for one-dimensional unsteady heat conduction in a gas layer of thickness  $\Delta x$  (without energy exchange with the environment), it is shown that

$$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho \cdot c_p} \cdot \frac{\partial^2 T}{\partial x^2}, \text{ where } \left[ \frac{\lambda}{\rho \cdot c_p} \right] = [\nu] = [D] = \frac{\mathbf{m}^2}{\mathbf{s}}$$

Notes:



- The time to reach a steady-state temperature field of dimension  $\delta x$  can be estimated as  $\Delta t = \frac{(\delta x)^2}{\lambda/(\rho \cdot c_p)}$  if  $\frac{\lambda}{\rho \cdot c_p}$  is known.  $\rightarrow$  The diffusion time scales with the square of the distance.
- Discuss the influence of pressure on exchange processes of momentum, heat, and mass diffusion.