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EXERGY IN CHEMICAL REACTIONS OF COMBUSTION AND GASIFICATION
PART 2: SOME NUMERICAL EXAMPLES
EXERGIE V CHEMICKÝCH REAKCÍCH SPALOVÁNÍ A ZPLYŇOVÁNÍ
ČÁST 2: NĚKOLIK NUMERICKÝCH PŘÍKLADŮ

Abstract

The exergy concept applied to chemical reactions of combustion and gasification has been presented and discussed in detail. All the essential cases will be taken into account, namely the equimolar and non–equimolar — homogeneous and heterogeneous — stoichiometric processes, but also the non–stoichiometric ones. The numerical examples show the expected correctness of the theoretical approach which means, the method can be applied to the complex system analysis containing combustion and gasification processes. The analysis makes it clear that the method can be also used for all the chemical conversion processes in the chemical and process engineering.

Abstrakt

Exergetická koncepce byla aplikována na chemické reakce spalování a zplyňování a byla předložena a projednána detailně. Všechny základní případy budou brány v úvahu, a sice equimolární a ne-equimolární , homogenní a heterogenní stechiometrické procesy, ale také i ne-stechiometrické procesy. Numerické příklady ukazují na očekávanou správnost teoretického přístupu, což znamená, že metodu lze použít na komplexní systémové analýzy, které obsahují spalovací a zplyňovací procesy. Z analýz je zřejmé, že metoda může být také použita pro všechny chemické konverzní procesy v chemickém a procesním inženýrství.

1 INTRODUCTION

The problem of exergy rating of chemical reactions can be presented in a form of numerical examples of some special cases of combustion and gasification processes. It should be made an essential partition into two groups: the =type and the →type chemical reactions. The first group are the so–called equilibrium chemical reactions, in which all the reactants are represented in a resulting reactive mixture. They are mostly the gasification ones (but even explosive combustion processes can be described using chemical equilibrium principles). The second group, however, are reactions that occur very fast and practically the equilibrium lies at the side of the reaction products. They are presented usually in the elder thermodynamics text–books as a combustion calculation problem. The simplification is in fact justified.

For the following numerical examples, which can be used as tests for the further computation procedures, the equation derived in [01] is essential. With its help, the concentration exergy change inversion point of a specie (or reactant) r can be determined, the point K [01], i.e. the appropriate chemical reaction advancement does result from the solution of the non–linear equation

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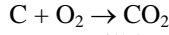
$$v_r \cdot \ln\left(\frac{1}{x_{r,0}} \cdot \frac{n_{r,1} + \xi_{r,extr} v_r}{n_1 + \xi_{r,extr} \sum\limits_r v_r}\right) + v_r - \frac{n_{r,1} + \xi_{r,extr} v_r}{n_1 + \xi_{r,extr} \sum\limits_r v_r} \cdot \sum_r v_r = 0 \qquad (01)$$

The thermodynamic analysis of the non–stoichiometric chemical reaction will be presented in the last Chapter.

2 EQUIMOLAR CHEMICAL REACTIONS OF COMBUSTION
2.1 C–Combustion in Pure Oxygen

The heterogeneous (reactants in solid and gaseous state) stoichiometric chemical reaction

$$C + O_2 \rightarrow CO_2$$

will be analyzed. This reaction is equimolar in the gaseous phase, which significantly simplifies calculations.

The real molar fraction of the element carbon C (as a coal substitute) changes from 0.5 to 0, of the oxygen O_2 from 0.5 to 0 and of the carbon dioxide CO_2 from 0 to 1. Appropriate molar fractions $x_{j,extr}$ equal to:

- oxygen $\qquad\qquad$ O_2 $\qquad\qquad$ $x_{O2,0} = 0.2095$ $\qquad$ $x_{O2,extr} = 0.0771$
- carbon dioxide $\qquad$ CO_2 $\qquad\quad$ $x_{CO2,0} = 0.0003$ $\qquad$ $x_{CO2,extr} = 0.0001$

which means, that both, O_2 and CO_2, can invert the concentration exergy change in a process. In the gaseous phase the molar fractions of the analyzed reactive mixture change as follows:

$$x_{O2,1} = 1 \qquad \rightarrow \qquad x_{O2,extr} = 0.0771 \qquad \rightarrow \qquad x_{O2,2} = 0$$
$$x_{CO2,1} = 0 \qquad \rightarrow \qquad x_{CO2,extr} = 0.0001 \qquad \rightarrow \qquad x_{CO2,2} = 1$$

First, the total amounts of a reactive mixture in a gaseous phase should be determined, for which the values of $x_{j,extr}$ are reached (for there are calculated only chemical concentration exergy changes in this phase).

- carbon (graphite) C — condensed phase (solid state):

The element coal occurs only in the condensed phase and in the reactive mixture its presence diminishes to zero, the zero exergy change will be taken into account, namely

$$\nabla\left(n\bar{e}^0_{\mu,C}\right) = (0-1) \cdot 409.9462 = -409.9462 \text{ kJ}$$

- oxygen O_2 and carbon dioxide CO_2 — gaseous phase:

The amount of oxygen in the reactive mixture changes in the following way

$$n_{O2} = n_{O2,1} + v_{O2}\xi = 1 - \xi$$

and of the carbon dioxide

$$n_{CO2} = n_{CO2,1} + v_{CO2}\xi = \xi$$

because

$$n_{O2,1} = 1 \text{ mol} \qquad n_{CO2,1} = 0 \qquad v_{O2} = -1 \qquad \text{and} \qquad v_{CO2} = 1$$

The amount of the element carbon changes just like the amount of oxygen, but it won't be taken into account by calculations of the chemical concentration exergy changes. The total amount of the gaseous phase in a process is a sum of oxygen and carbon dioxide amounts, i.e.

$$n^{gas} = n_{O2} + n_{CO2} = n_{O2,1} + n_{CO2,1} + v_{O2}\xi + v_{CO2}\xi = 1 \text{ mol}$$

which means, during the whole process the total amount of the gaseous phase does not change at all (the zero volume contraction). However, the molar fractions of oxygen and of carbon dioxide will change, namely

$$x_{O2} = \frac{n_{O2,1} + v_{O2}\xi}{n^{gas}} = \frac{1-\xi}{1} = 1 - \xi \quad \text{and} \quad x_{CO2} = \frac{n_{CO2,1} + v_{O2}\xi}{n^{gas}} = \frac{\xi}{1} = \xi$$

The both extreme values of these molar fractions $x_{O2,extr}$ and $x_{CO2,extr}$ are achieved by the same total reactive mixture amount, i.e. by 1 mol. Because of

$$x_{O2,1} = 1 \qquad \rightarrow \qquad x_{O2,extr} = 0.0771 \qquad \rightarrow \qquad x_{O2,2} = 0$$

$$x_{CO2,1}= 0 \quad \rightarrow \quad x_{CO2,extr}= 0.0001 \quad \rightarrow \quad x_{CO2,2}= 1$$

and $n^{gas}=1$ mol there is either

$$n_{O2,1} = 1 \text{ mol} \quad \rightarrow \quad n_{O2,extr} = x_{O2,extr} \cdot n^{gas} = 0.0771 \text{ mol} \quad \rightarrow \quad n_{O2,2} = 0$$

$$n_{CO2,1} = 0 \quad \rightarrow \quad n_{CO2,extr} = x_{CO2,extr} \cdot n^{gas} = 0.0001 \text{ mol} \quad \rightarrow \quad n_{CO2,2} = 1 \text{ mol}$$

Taking additionally into account, that

$$n_1^{gas} = n_2^{gas} = n^{gas} = 1 \text{ mol}$$

one becomes:

$$\nabla\left(n\bar{e}_\mu^x\right)_{O2}^> = -\left(n_{O2,extr} + n_1 x_{O2,1} \ln\frac{x_{O2,1}}{x_{O2,0}}\right)\bar{R}T_0 = -\left(0.0771 + 1\cdot1\cdot\ln\frac{1}{0.2095}\right)\bar{R}T_0 = -1.6401\,\bar{R}T_0$$

and

$$\Delta\left(n\bar{e}_\mu^x\right)_{O2}^< = \left(n_2 x_{O2,2} \ln\frac{x_{O2,2}}{x_{O2,0}} + n_{O2,extr}\right)\bar{R}T_0 = (0 + 0.0771)\bar{R}T_0 = 0.0771\,\bar{R}T_0$$

or

$$\nabla\left(n\bar{e}_\mu^x\right)_{CO2}^< = -\left(n_{CO2,extr} + n_1 x_{CO2,1} \ln\frac{x_{CO2,1}}{x_{CO2,0}}\right)\bar{R}T_0 = -(0.0001 + 0)\bar{R}T_0 = -0.0001\,\bar{R}T_0$$

and

$$\Delta\left(n\bar{e}_\mu^x\right)_{CO2}^> = \left(n_2 x_{CO2,2} \ln\frac{x_{CO2,2}}{x_{CO2,0}} + n_{CO2,extr}\right)\bar{R}T_0 = \left(1\cdot1\cdot\ln\frac{1}{0.0003} + 0.0001\right)\bar{R}T_0 = 8.1118\,\bar{R}T_0$$

Assuming $T_0 = 283.15$ K and $\bar{R} = 0.0083143\ \frac{kJ}{mol\,K}$ it will be $\bar{R}T_0 = 2.3542\ \frac{kJ}{mol}$, and hence

$$\nabla\left(n\bar{e}_\mu^x\right)_{O2}^> = -1.6401\,\bar{R}T_0 = -3.8611 \text{ kJ} \quad \Delta\left(n\bar{e}_\mu^x\right)_{O2}^< = 0.0771\,\bar{R}T_0 = 0.1814 \text{ kJ}$$

$$\nabla\left(n\bar{e}_\mu^x\right)_{CO2}^< = -0.0001\,\bar{R}T_0 = -0.0003 \text{ kJ} \quad \Delta\left(n\bar{e}_\mu^x\right)_{CO2}^> = 8.1118\,\bar{R}T_0 = 19.0968 \text{ kJ}$$

In the case of zero exergy changethe total amount of disappearing oxygen and created carbon dioxide should be taken into account. The appropriate values will be to

$$\nabla\left(n\bar{e}_\mu^0\right)_{O2} = (0-1)\cdot 3.6798 = -3.6798 \text{ kJ} \quad \text{and} \quad \Delta\left(n\bar{e}_\mu^0\right)_{CO2} = (1-0)\cdot 19.0974 = 19.0974 \text{ kJ}$$

The reaction heat is up to the process temperature. In the following table there is additionally the reaction heat exergy for T_0=283.15 K (the mixing heat is negligible).

T [K]	$Q_{rea}^{\rightarrow}$ [kJ]	$E_{Q,rea}^{\rightarrow}$ [kJ]
298.15	−393.70	−19.8071
300	−393.71	−22.1131
400	−394.21	−115.1580
500	−394.84	−171.2440
600	−395.45	−208.8282
700	−395.96	−235.7964
800	−396.39	−256.0946
900	−396.74	−271.9236
1000	−397.03	−284.6123
1100	−397.27	−295.0130
1200	−397.49	−303.6991
1300	−397.69	−311.0706
1400	−397.89	−317.4144
1500	−398.09	−322.9412

For the exothermic reaction ($Q_{rea}^{\rightarrow} < 0$) the following temperature range is valid: 298–1500 K (because for C: 298–2300 K, for O_2: 298–1500 K, and for CO_2: 273–1860 K). The coefficients of the reaction heat temperature dependence

$$\Delta i_{298} = -393700$$

$$\Delta a = -31.09 \quad \Delta b = 0.05468 \qquad \Delta c' = 1310000 \qquad \Delta c = -0.000035$$

$$\Delta d = 0.00000000747$$

have been applied in calculations, [02].

The thermodynamic effectivity quotient can be calculated with the above determined concentration exergy changes. Generally

$$\varepsilon = \frac{\left|\Delta\left(n\bar{e}_\mu^x\right)_{O2}^<\right| + \left|\Delta\left(n\bar{e}_\mu^x\right)_{CO2}^>\right| + \left|\Delta\left(n\bar{e}_\mu^0\right)_{CO2}\right| + \left|E_{Q,rea}^{\rightarrow}\right|}{\left|\nabla\left(n\bar{e}_\mu^x\right)_{O2}^>\right| + \left|\nabla\left(n\bar{e}_\mu^x\right)_{CO2}^<\right| + \left|\nabla\left(n\bar{e}_\mu^0\right)_C\right| + \left|\nabla\left(n\bar{e}_\mu^0\right)_{O2}\right|}$$

or

$$\varepsilon = \frac{0.1814 + 19.0968 + 19.0974 + \left|E_{Q,rea}^{\rightarrow}\right|}{3.8611 + 0.0003 + 3.6798 + 409.9462} = \frac{38.3757 + \left|E_{Q,rea}^{\rightarrow}\right|}{417.4875}$$

Putting the chemical reaction heat exergy aside, the numerical value of the process thermodynamic effectivity is very low. The problem here is very similar to the problem described in an Example 4.2, [03], pp. 216–220, where the air and the carbon dioxide were compressed. In the first case the working agent losses to the surroundings due to leakages caused an increase of the process thermodynamic effectivity, and in the second case its decrease. An oxidation of carbon, which is not present in the natural environment and has been produced from atmospheric CO_2, is very clearly wasting of the basic effect. Any advantage of this process can be only obtaining of the pure carbon dioxide (in the assumed natural environment its molar fraction is $x_{CO2,0} = 0.0003$).

In the whole temperature range the analyzed chemical reaction was exothermic: the reaction heat exergy $E_{Q,rea}^{\rightarrow}$ is carried away as energy advantages and should be added to the nominator of the process thermodynamic effectivity quotient.

process thermodynamic effectivity		process exergy efficiency		
T [K]	ε	T [K]	η_{ex}'	η_{ex}
298.15	0.1394	298.15	0.0479	0.0946
300	0.1449	300	0.0535	0.0996
400	0.3678	400	0.2784	0.3246
500	0.5021	500	0.4140	0.4602
600	0.5921	600	0.5049	0.5510
700	0.6567	700	0.5701	0.6162
800	0.7053	800	0.6191	0.6653
900	0.7433	900	0.6574	0.7036
1000	0.7736	1000	0.6881	0.7343
1100	0.7986	1100	0.7132	0.7594
1200	0.8194	1200	0.7342	0.7804
1300	0.8370	1300	0.7521	0.7982
1400	0.8522	1400	0.7674	0.8136
1500	0.8655	1500	0.7808	0.8269

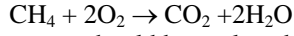The exergy process efficiency quotient can be chosen from many possible arrangements, e.g.

$$\eta_{ex} = \frac{\left|\Delta\left(n\bar{e}_\mu^0\right)_{CO2}\right| + \left|E_{Q,reac}^{\rightarrow}\right|}{\left|\nabla\left(n\bar{e}_\mu^0\right)_C\right| + \left|\nabla\left(n\bar{e}_\mu^0\right)_{O2}\right|} = \frac{19.0974 + \left|E_{Q,rea}^{\rightarrow}\right|}{3.6798 + 409.9462}$$

or

$$\eta_{ex}^{'} = \frac{\left|E_{Q,rea}^{->}\right|}{\left|\nabla\left(n\bar{e}_\mu^0\right)_C\right| + \left|\nabla\left(n\bar{e}_\mu^0\right)_{O2}\right|} = \frac{\left|E_{Q,rea}^{->}\right|}{3.6798 + 409.9462}$$

2.2 CH₄–Combustion in Pure Oxygen

The stoichiometric gaseous phase equimolar chemical reaction

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

should be analyzed. The real molar fraction of methane changes from 1/3 to 0, of oxygen from 2/3 to 0, of carbon dioxide from 0 to 1/3 and of water steam from 0 to 2/3. Appropriate $x_{j,extr}$ values equal to

– methane	CH_4	$x_{CH4,0} = 1.0$ ("apparent")	$x_{CH4,extr} = 1/e = 0.3679$
– oxygen	O_2	$x_{O2,0} = 0.2095$	$x_{O2,extr} = 0.0771$
– coal dioxide	CO_2	$x_{CO2,0} = 0.0003$	$x_{CO2,extr} = 0.0001$
– water steam	H_2O	$x_{H2O,0} = 1.0$ ("apparent")	$x_{H2O,extr} = 1/e = 0.3679$

which means, that oxygen O_2, the carbon dioxide CO_2 and water steam H_2O can show the inversion point of the concentration chemical exergy change in the process, i.e. $x_{O2,extr}=0.0771$, $x_{CO2,extr}=0.0001$ and $x_{H2O,extr}=1/e=0.3679$. The molar fractions in a reactive mixture change in the following way:

$$x_{CH4,1} = 1/3 \quad \rightarrow \quad x_{CH4,2} = 0$$
$$x_{O2,1} = 2/3 \quad \rightarrow \quad x_{O2,extr} = 0.0771 \quad \rightarrow \quad x_{O2,2} = 0$$
$$x_{CO2,1} = 0 \quad \rightarrow \quad x_{CO2,extr} = 0.0001 \quad \rightarrow \quad x_{CO2,2} = 1/3$$
$$x_{H2O,1} = 0 \quad \rightarrow \quad x_{H2O,extr} = 1/e = 0.3679 \quad \rightarrow \quad x_{H2O,2} = 2/3$$

The analyzed chemical reaction is equimolar gaseous phase process, so in this phase its total amount is the same, namely $n_1=n_2=n=3$ mol. For such a case calculations simplify significantly.

– methane CH_4

Its molar fraction does not excess the $x_{j,extr}$ point and the appropriate concentration chemical exergy change consists only of the arising one below the inversion point, i.e.

$$\Delta\left(n\bar{e}_\mu^x\right)_{CH4}^< = n\left(x_{CH4,2}\ln\frac{x_{CH4,2}}{x_{CH4,0}} - x_{CH4,1}\ln\frac{x_{CH4,1}}{x_{CH4,0}}\right)\bar{R}T_0 = 3\left(0 - \frac{1}{3}\cdot\ln\frac{1}{3}\right)\bar{R}T_0 = 1.0986\,\bar{R}T_0 = 2.5863\,kJ$$

The whole methane amount in the reactive mixture diminishes, so

$$\nabla\left(n\bar{e}_\mu^0\right)_{CH4} = (0-1)\cdot 833.7776 = -833.7776\,kJ$$

– oxygen O_2

$$\nabla\left(n\bar{e}_\mu^x\right)_{O2}^> = n\left(x_{O2,extr} + x_{O2,1}\ln\frac{x_{O2,1}}{x_{O2,0}}\right)\bar{R}T_0 = -3\cdot\left(0.0771 + \frac{2}{3}\cdot\ln\frac{2}{3\cdot0.2095}\right)\bar{R}T_0 =$$
$$= -2.5463\,\bar{R}T_0 = -5.9946\,kJ$$

and

$$\Delta\left(n\bar{e}_\mu^x\right)_{O2}^< = n\left(x_{O2,2}\ln\frac{x_{O2,2}}{x_{O2,0}} + x_{O2,extr}\right)\bar{R}T_0 = 3\cdot(0+0.0771)\bar{R}T_0 = 0.2312\,\bar{R}T_0 = 0.5443\,kJ$$

The oxygen amount in the reactive mixture diminishes in the process, and

$$\nabla\left(n\bar{e}_\mu^0\right)_{O2} = (0-2)\cdot 3.6798 = -7.3597\,kJ$$

– carbon dioxide CO_2

$$\nabla\left(n\bar{e}_\mu^x\right)_{CO2}^< = -n\left(x_{CO2,extr} + x_{CO2,1}\ln\frac{x_{CO2,1}}{x_{CO2,0}}\right)\bar{R}T_0 = -3\cdot(0.0001+0)\bar{R}T_0 = -0.0003\,\bar{R}T_0 = -0.0008\,kJ$$

and

$$\Delta\left(n\bar{e}_\mu^x\right)_{CO2}^> = n\left(x_{CO2,2}\ln\frac{x_{CO2,2}}{x_{CO2,0}} + x_{CO2,extr}\right)\bar{R}T_0 = 3\cdot\left(\frac{1}{3}\cdot\ln\frac{1}{3\cdot0.0003} + 0.0001\right)\bar{R}T_0 =$$

$$= 7.0134\,\bar{R}T_0 = 16.5110\text{ kJ}$$

the carbon dioxide will be formed in the analyzed process, and the zero chemical exergy change will equal to

$$\Delta\left(n\bar{e}_\mu^0\right)_{CO2} = (1-0)\cdot19.0974 = 19.0974\text{ kJ}$$

  − water steam H_2O

$$\nabla\left(n\bar{e}_\mu^x\right)_{H2O}^< = -n\left(x_{H2O,extr} + x_{H2O,1}\ln\frac{x_{H2O,1}}{x_{H2O,0}}\right)\bar{R}T_0 = -3\cdot\left(\frac{1}{e} + 0\right)\bar{R}T_0 = -1.1036\,\bar{R}T_0 = -2.5982\text{ kJ}$$

  and

$$\Delta\left(n\bar{e}_\mu^x\right)_{H2O}^> = n\left(x_{H2O,2}\ln\frac{x_{H2O,2}}{x_{H2O,0}} + x_{H2O,extr}\right)\bar{R}T_0 = 3\cdot\left(\frac{2}{3}\cdot\ln\frac{2}{3} + \frac{1}{e}\right)\bar{R}T_0 = 0.2927\,\bar{R}T_0 = 0.6891\text{ kJ}$$

The water steam will be created in the amount of 2 moles, so the zero chemical exergy change will equal to

$$\Delta\left(n\bar{e}_\mu^0\right)_{H2O} = (2-0)\cdot10.3865 = 20.7729\text{ kJ}$$

  − heat effect of the reaction at various temperatures (the heat exergy for T_0=283.15 K)

The mixing heat will be assumed equal to zero. The following numerical values of the reaction heat and its exergy for the temperatures between 298.15 K and 1500 K will be obtained:

T [K]	$Q_{rea}^{\rightarrow}$ [kJ]	$E_{Q,rea}^{\rightarrow}$ [kJ]	T [K]	$Q_{rea}^{\rightarrow}$ [kJ]	$E_{Q,rea}^{\rightarrow}$ [kJ]
298.15	−802.72	−40.3850	900	−804.29	−551.2485
300	−802.71	−45.8553	1000	−805.06	−577.1073
400	−802.41	−234.4049	1100	−805.93	−598.4738
500	−802.44	−348.0201	1200	−806.86	−616.4772
600	−802.68	−423.8833	1300	−807.84	−631.8879
700	−803.08	−478.2355	1400	−808.83	−645.2435
800	−803.62	−519.1897	1500	−809.78	−656.9245

The reaction heat values mean, the process is exothermic ($Q_{rea}^{\rightarrow} < 0$), the temperature range: 298–1500 K (because there are — CH_4: 273–1500 K, O_2: 298–1500 K, H_2O: 273–1800 K, CO_2: 273–1860 K) and the coefficients of the reaction heat (enthalpy, [02]):

$\Delta i_{298} = -802720$ $\Delta a = -5.53$ $\Delta b = 0.01171$ $\Delta c' = 862000$

$\Delta c = -0.00002658$ $\Delta d = 0.0000000113$

  − thermodynamic effectivity quotient

With quantities determined above it will be generally

$$\varepsilon = \frac{\left|\Delta\left(n\bar{e}_\mu^x\right)_{CH4}^<\right| + \left|\Delta\left(n\bar{e}_\mu^x\right)_{O2}^<\right| + \left|\Delta\left(n\bar{e}_\mu^x\right)_{CO2}^>\right| + \left|\Delta\left(n\bar{e}_\mu^x\right)_{H2O}^>\right| + \left|\Delta\left(n\bar{e}_\mu^0\right)_{CO2}\right| + \left|\Delta\left(n\bar{e}_\mu^0\right)_{H2O}\right| + \left|E_{Q,rea}^{\rightarrow}\right|}{\left|\nabla\left(n\bar{e}_\mu^x\right)_{O2}^>\right| + \left|\nabla\left(n\bar{e}_\mu^x\right)_{CO2}^<\right| + \left|\nabla\left(n\bar{e}_\mu^x\right)_{H2O}^<\right| + \left|\nabla\left(n\bar{e}_\mu^0\right)_{CH4}\right| + \left|\nabla\left(n\bar{e}_\mu^0\right)_{O2}\right|}$$

  or

$$\varepsilon = \frac{2.5863 + 0.5443 + 16.5110 + 0.6891 + 19.0974 + 20.7729 + \left|E_{Q,reac}^{\rightarrow}\right|}{5.9946 + 0.0008 + 2.5982 + 833.7776 + 7.3597} = \frac{60.2012 + \left|E_{Q,rea}^{\rightarrow}\right|}{849.7308}$$

  − exergy efficiency

The appropriate exergy efficiency quotients can be formulated as

$$\eta_{ex} = \frac{\left|\Delta\left(n\bar{e}_\mu^0\right)_{CO2}\right| + \left|\Delta\left(n\bar{e}_\mu^0\right)_{H2O}\right| + \left|E_{Q,rea}^{\rightarrow}\right|}{\left|\nabla\left(n\bar{e}_\mu^0\right)_{CH4}\right| + \left|\nabla\left(n\bar{e}_\mu^0\right)_{O2}\right|} = \frac{19.0974 + 20.7729 + \left|E_{Q,rea}^{\rightarrow}\right|}{833.7776 + 7.3597}$$

For the combustion rating the quotient

$$\eta_{ex}^{'} = \frac{\left|E_{Q,rea}^{\rightarrow}\right|}{\left|\nabla\left(n\bar{e}_\mu^0\right)_{CH4}\right| + \left|\nabla\left(n\bar{e}_\mu^0\right)_{O2}\right|} = \frac{\left|E_{Q,rea}^{\rightarrow}\right|}{833.7776 + 7.3597}$$

can be of interest.

Following numerical values for the three types of an exergy rating quotient could be calculated:

thermodynamic effectivity		exergy efficiency		
T [K]	ε	T [K]	η_{ex}	η_{ex}'
298.15	0.1184	298.15	0.0954	0.0480
300	0.1239	300	0.1010	0.0536
400	0.3467	400	0.3261	0.2787
500	0.4804	500	0.4611	0.4137
600	0.5697	600	0.5513	0.5039
700	0.6337	700	0.6160	0.5686
800	0.6818	800	0.6646	0.6172
900	0.7196	900	0.7028	0.6554
1000	0.7500	1000	0.7335	0.6861
1100	0.7752	1100	0.7589	0.7115
1200	0.7963	1200	0.7803	0.7329
1300	0.8145	1300	0.7986	0.7512
1400	0.8302	1400	0.8145	0.7671
1500	0.8439	1500	0.8284	0.7810

3 NON–EQUIMOLAR CHEMICAL REACTION OF H_2–COMBUSTION

3.1 H_2–Combustion in Pure Oxygen

The stoichiometric non–equimolar gas phase chemical reaction

$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$
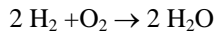
will be analyzed. The molar fraction of hydrogen H_2 changes from 2/3 to 0, of oxygen O_2 from 1/3 to 0 and of water H_2O (or water steam) from 0 to 1. Appropriate molar fractions $x_{j,extr}$ equal to:

- hydrogen H_2 $x_{H2,0} = 1.0$ (,,apparent'') $x_{H2,extr} = 1/e = 0.3679$
- oxygen O_2 $x_{O2,0} = 0.2095$ $x_{O2,extr} = 0.0771$
- water steam H_2O $x_{H2O,0} = 1.0$ (,,apparent'') $x_{H2O,extr} = 1/e = 0.3679$

Start (input) amounts are

$$n_{1,H2} = 2\,\text{mol} \qquad n_{1,O2} = 1\,\text{mol} \qquad n_1 = 3\,\text{mol} \qquad n_{1,H2O} = 0$$

and at the end (output)

$$n_{2,H2} = 0 \qquad n_{2,O2} = 0 \qquad n_2 = 2\,\text{mol} \qquad n_{2,H2O} = 2\,\text{mol}$$

Determination of the inversion point $\boldsymbol{K}$:

- <u>hydrogen ($j \equiv H_2$)</u>

$$\nu_j = -2 \qquad n_{j,1} = 2 \qquad n_1 = 3 \qquad \sum_j \nu_j = -1 \qquad x_{j,0} = 1.0 \;(,,apparent'')$$

The appropriate equation will be then to

$$-2 \cdot \ln\left(\frac{2-2\xi_{j,extr}}{3-\xi_{j,extr}}\right) - 2 + \frac{2-2\xi_{j,extr}}{3-\xi_{j,extr}} = 0$$

Its numerical solution gives $\xi_{H2,extr} = 0.3960$ and with appropriate it becomes

$$n_{extr,(H2)} = 2.6040 \text{ mol} \qquad \text{and} \qquad x_{H2,extr} = 0.4639$$

- <u>oxygen</u> ($j \equiv O_2$)

$$\nu_j = -1 \qquad n_{j,1} = 1 \qquad n_1 = 3 \qquad \sum_j \nu_j = -1 \qquad x_{j,0} = 0.2095$$

Eq. (01) will be to

$$-\ln\left(\frac{1}{0.2095} \cdot \frac{1-\xi_{j,extr}}{3-\xi_{j,extr}}\right) - 1 + \frac{1-\xi_{j,extr}}{3-\xi_{j,extr}} = 0$$

and its numerical solution gives $\xi_{O2,extr} = 0.8170$ and

$$n_{extr,(O2)} = 2.1829 \text{ mol} \qquad \text{and} \qquad x_{O2,extr} = 0.0838$$

- <u>water steam</u> ($j \equiv H_2O$)

$$\nu_j = 2 \quad n_{j,1} = 0 \qquad\qquad n_1 = 3 \qquad \sum_j \nu_j = -1 \qquad x_{j,0} = 1.0 \quad (\text{,,apparent''})$$

Eq. (01) is to

$$2 \cdot \ln\left(\frac{2\xi_{j,extr}}{3-\xi_{j,extr}}\right) + 2 + \frac{2\xi_{j,extr}}{3-\xi_{j,extr}} = 0$$

and the numerical solution $\xi_{H2O,extr} = 0.4075$. Hence

$$n_{extr,(H2O)} = 2.5925 \text{ mol} \qquad \text{and} \qquad x_{H2O,extr} = 0.3144$$

Appropriate molar fractions change also in the following way:

$$x_{H2,1} = 1/3 = 0.3333 \qquad \rightarrow \qquad x_{H2,2} = 0 \qquad \text{(i.e. below the } x_{H2,extr} \text{ value)}$$
$$x_{O2,1} = 1/3 = 0.3333 \qquad \rightarrow \qquad x_{O2,extr} = 0.0838 \qquad \rightarrow \qquad x_{O2,2} = 0$$
$$x_{H2O,1} = 0 \qquad \rightarrow \qquad x_{H2O,extr} = 0.3144 \qquad \rightarrow \qquad x_{H2O,2} = 1$$

After calculating the hydrogen concentration chemical exergy change (no inversion point), the total amounts of the reactive mixture should be determined, by which molar fractions $x_{j,extr}$ for oxygen and water steam are reached.

Assuming $T_0 = 283.15 \text{ K}$ and $\bar{R} = 0.0083143 \frac{kJ}{mol\,K}$ there will be $\bar{R}T_0 = 2.3542 \frac{kJ}{mol}$ and following concentration chemical exergy changes will be obtained:

- <u>hydrogen</u> H_2

Total exergy change results from the total molar fraction change between the states *1* and *2*, are

$$\Delta\left(n\bar{e}_\mu^x\right)_{H2}^< = \left(n_2 x_{H2,2} \ln\frac{x_{H2,2}}{x_{H2,0}} - n_1 x_{H2,1} \ln\frac{x_{H2,1}}{x_{H2,0}}\right)\bar{R}T_0 = \left(0 - 3 \cdot \frac{2}{3} \cdot \ln\frac{2}{3}\right)\bar{R}T_0 = 0.8109\,\bar{R}T_0$$

because of

$$n_1 = 3 \text{ mol} \quad n_2 = 2 \text{ mol} \quad x_{H2,1} = 2/3 \quad x_{H2,2} = 0 \quad x_{H2,0} = 1.0 \quad (\text{,,apparent fraction''})$$

it will be equal to

$$\Delta\left(n\bar{e}_\mu^x\right)_{H2}^< = 0.8109\,\bar{R}T_0 = 1.9091 \text{ kJ}$$

The zero chemical exergy of hydrogen will change,

$$\nabla\left(n\bar{e}_\mu^0\right)_{H2} = (0-2) \cdot 237.9219 = -475.8438 \text{ kJ}$$

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and will be added to the process expenditures (nominator of the rating quotient).

– <u>oxygen O_2</u>

The total reactive mixture amount while reaching the algebraic sign inversion point $\boldsymbol{K}$ of the concentration chemical exergy change for oxygen equals

$$n_{extr,(O2)} = 2.1829 \text{ mol}$$

and its molar fraction at this process point

$$x_{O2,extr} = 0.0838$$

Thus, the exergy change above the inversion point (superscript $>$) is

$$\nabla\left(n\bar{e}_\mu^x\right)_{O2}^> = \left(n_{extr,(O2)} x_{O2,extr} \ln\frac{x_{O2,extr}}{x_{O2,0}} - n_1 x_{O2,1} \ln\frac{x_{O2,1}}{x_{O2,0}}\right)\bar{R}T_0 =$$

$$= \left(2.1829 \cdot 0.0838 \cdot \ln\frac{0.0838}{0.2095} - 3 \cdot \frac{1}{3} \cdot \ln\frac{1}{3 \cdot 0.2095}\right)\bar{R}T_0 = -0.6320\,\bar{R}T_0 = -1.4879 \text{ kJ}$$

and below it (superscript $<$)

$$\Delta\left(n\bar{e}_\mu^x\right)_{O2}^< = \left(n_2 x_{O2,2} \ln\frac{x_{O2,2}}{x_{O2,0}} - n_{extr,(O2)} x_{O2,extr} \ln\frac{x_{O2,extr}}{x_{O2,0}}\right)\bar{R}T_0 =$$

$$= \left(0 - 2.1829 \cdot 0.0838 \cdot \ln\frac{0.0838}{0.2095}\right)\bar{R}T_0 = 0.1676\,\bar{R}T_0 = 0.3946 \text{ kJ}$$

The zero chemical exergy changes in the process in the following way:

$$\nabla\left(n\bar{e}_\mu^0\right)_{O2} = (0-1)\cdot 3.6798 = -3.6798 \text{ kJ}$$

and will be added to the expenditures (nominator of the thermodynamic effectivity quotient).

– <u>water steam H_2O</u>

The procedure the same as in the case of oxygen, because in the analyzed process the inversion point $\boldsymbol{K}$ will be crossed, and

$$n_{extr,(H2O)} = 2.5925 \text{ mol} \qquad \text{and} \qquad x_{H2O,extr} = 0.3144$$

An appropriate substitution gives further

$$\nabla\left(n\bar{e}_\mu^x\right)_{H2O}^< = \left(n_{extr,(H2O)} x_{H2O,extr} \ln\frac{x_{H2O,extr}}{x_{H2O,0}} - n_1 x_{H2O,1} \ln\frac{x_{H2O,1}}{x_{H2O,0}}\right)\bar{R}T_0 =$$

$$= \left(2.5925 \cdot 0.3144 \cdot \ln\frac{0.3144}{1} - 0\right)\bar{R}T_0 = -0.9431\,\bar{R}T_0 = -2.2203 \text{ kJ}$$

$$\Delta\left(n\bar{e}_\mu^x\right)_{H2O}^> = \left(n_2 x_{H2O,2} \ln\frac{x_{H2O,2}}{x_{H2O,0}} - n_{extr,(H2O)} x_{H2O,extr} \ln\frac{x_{H2O,extr}}{x_{H2O,0}}\right)\bar{R}T_0 =$$

$$= \left(0 - 2.5925 \cdot 0.3144 \cdot \ln\frac{0.3144}{1}\right)\bar{R}T_0 = 0.9431\,\bar{R}T_0 = 2.2203 \text{ kJ}$$

Very interesting case has been occurred here: the total concentration chemical exergy change was equal to zero. It consists of two equal parts — the created and disappearing exergy, because the compositional chemical exergy change occurs between the molar fraction 0 and 1, and the natural environment concentration of water steam has been assumed equal 1, as produced in a devaluation chemical reaction.

The zero chemical exergy of water steam change is

$$\Delta\left(n\bar{e}_\mu^0\right)_{H2O} = (2-0)\cdot 10.3865 = 20.7729 \text{ kJ}$$

– <u>absolute volume work of the chemical reaction</u>

Assuming, the analyzed oxidation reaction occurs isobar at the natural environment pressure p_0, the exergies of the absolute volume work equal to zero. In the case of higher pressures $p>p_0$ (like in the special combustion and/or gasifying technologies), it should be taken into account additionally

$$E_{L,rea}^{+>} = \left(1 - \frac{p_0}{p}\right)L_{rea}^{>} = -(p - p_0)(V_{rea,2} - V_{rea,1}) \text{ if greater than zero } (>0)$$

or

$$E_{L,rea}^{->} = \left(1 - \frac{p_0}{p}\right)L_{rea}^{>} = -(p - p_0)(V_{rea,2} - V_{rea,1}) \quad \text{if less than zero } (<0)$$

Taking the perfect gas relations it becomes

$$V_{rea,2} - V_{rea,1} = (n_2 - n_1)\frac{\overline{R}T}{p} = -1 \cdot \frac{\overline{R}T}{p}$$

whereby T and p are given (isobar–isotherm chemical reaction) and $n_2 - n_1 = -1$.

– heat of the chemical reaction for various T and its exergy (at T_0=283.15 K)
Assuming the heat effect of mixing equal to zero, there is:

T [K]	$Q_{rea}^{->}$ [kJ]	$E_{Q,rea}^{->}$ [kJ]	T [K]	$Q_{rea}^{->}$ [kJ]	$E_{Q,rea}^{->}$ [kJ]
298.15	–483.9000	–24.3451	900	–496.2921	–340.1531
300	–483.9408	–27.1813	1000	–497.8717	–356.8993
400	–486.1968	–142.0302	1100	–499.2931	–370.7705
500	–488.4497	–211.8406	1200	–500.5624	–382.4505
600	–490.6163	–259.0863	1300	–501.6892	–392.4175
700	–492.6575	–293.3775	1400	–502.6872	–401.0187
800	–494.5528	–319.5120	1500	–503.5734	–408.5155

The analyzed chemical reaction is exothermic ($Q_{rea}^{->} < 0$), valid for the temperature range 298–1500 K (because for H_2: 273–1800 K, O_2: 298–1500 K, H_2O: 273–1800 K). Appropriate coefficients, [02], are:

$$\Delta i_{298} = -483900 \qquad \Delta a = -29.92 \qquad \Delta b = 0.00683$$
$$\Delta c' = 431000 \qquad \Delta c = 0.0000131 \qquad \Delta d = -0.00000000544$$

– thermodynamic effectivity
The thermodynamic process effectivity quotient will be generally

$$\varepsilon = \frac{\left|\Delta\left(n\overline{e}_\mu^x\right)_{H2}^<\right| + \left|\Delta\left(n\overline{e}_\mu^x\right)_{O2}^<\right| + \left|\Delta\left(n\overline{e}_\mu^x\right)_{H2O}^>\right| + \left|\Delta\left(n\overline{e}_\mu^0\right)_{H2O}\right| + \left|E_{Q,rea}^{->}\right|}{\left|\nabla\left(n\overline{e}_\mu^x\right)_{O2}^>\right| + \left|\nabla\left(n\overline{e}_\mu^x\right)_{H2O}^<\right| + \left|\nabla\left(n\overline{e}_\mu^0\right)_{H2}\right| + \left|\nabla\left(n\overline{e}_\mu^0\right)_{O2}\right|}$$

or

$$\varepsilon = \frac{1.9091 + 0.3946 + 2.2203 + 20.7729 + \left|E_{Q,rea}^{->}\right|}{1.4879 + 2.2203 + 3.6798 + 475.8438} = \frac{25.2697 + \left|E_{Q,rea}^{->}\right|}{483.2047}$$

In this case the obtained numerical values of the thermodynamic process effectivity quotient are very low, when only concentration chemical exergy changes are taken into account. They are even lower, than for the combustion of element coal (the previous Chapter). Hydrogen as a fuel is more valuable — its zero chemical exergy is higher, and it has been either produced in a devaluation

chemical reaction of liquid water from the natural environment. Putting appropriate values determined above, yields:

process temperature	thermodynamic process effectivity	exergy efficiency	
T [K]	ε	η_{ex}	η_{ex}'
298.15	0.1027	0.0941	0.0508
300	0.1086	0.1000	0.0567
400	0.3463	0.3395	0.2962
500	0.4907	0.4851	0.4418
600	0.5885	0.5836	0.5403
700	0.6595	0.6551	0.6118
800	0.7135	0.7096	0.6663
900	0.7563	0.7527	0.7094
1000	0.7909	0.7876	0.7443
1100	0.8196	0.8165	0.7732
1200	0.8438	0.8409	0.7976
1300	0.8644	0.8617	0.8183
1400	0.8822	0.8796	0.8363
1500	0.8977	0.8952	0.8519

– exergy efficiency

Just like in the previous Chapter the exergy efficiency quotient can be defined in the following way:
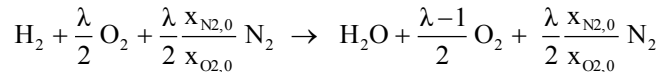
$$\eta_{ex} = \frac{\left|\Delta\left(n\bar{e}_\mu^0\right)_{H2O}\right| + \left|E_{Q,rea}^{\rightarrow}\right|}{\left|\nabla\left(n\bar{e}_\mu^0\right)_{H2}\right| + \left|\nabla\left(n\bar{e}_\mu^0\right)_{O2}\right|} = \frac{20.7729 + \left|E_{Q,rea}^{\rightarrow}\right|}{3.6798 + 475.8438}$$

or

$$\eta_{ex}' = \frac{\left|E_{Q,rea}^{\rightarrow}\right|}{\left|\nabla\left(n\bar{e}_\mu^0\right)_{H2}\right| + \left|\nabla\left(n\bar{e}_\mu^0\right)_{O2}\right|} = \frac{\left|E_{Q,rea}^{\rightarrow}\right|}{3.6798 + 475.8438}$$
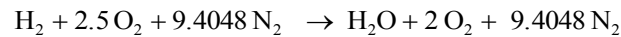
3.2 H$_2$–Combustion in Atmospheric Air

It will be presented in the following the stoichiometric combustion of hydrogen in an atmospheric air with the air excess number λ. The higher pressure of the process will be assumed ($p>p_0$). The chemical reaction can be written down as

$$H_2 + \frac{\lambda}{2}O_2 + \frac{\lambda}{2}\frac{x_{N2,0}}{x_{O2,0}}N_2 \rightarrow H_2O + \frac{\lambda-1}{2}O_2 + \frac{\lambda}{2}\frac{x_{N2,0}}{x_{O2,0}}N_2$$

where $x_{O2,0}$ and $x_{N2,0}$ are the molar concentrations of oxygen O_2 and nitrogen N_2 in the atmospheric air (their values are assumed to be 0.21 and 0.79, respectively). If the air excess number λ will be set to 5, then the above formula will be to

$$H_2 + 2{,}5\,O_2 + 2{,}5\frac{0.79}{0.21}N_2 \rightarrow H_2O + 2\,O_2 + 2{,}5\frac{0.79}{0.21}N_2$$

or

$$H_2 + 2.5\,O_2 + 9.4048\,N_2 \rightarrow H_2O + 2\,O_2 + 9.4048\,N_2$$
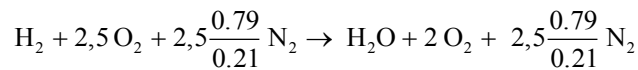
– The molar concentration of hydrogen changes from

$$x_{H2,1} = \frac{1}{1 + 2.5 + 9.4048} = 0.0775 \text{ to } x_{H2,2} = 0$$

and of the oxygen from

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$$x_{O2,1} = \frac{2.5}{1+2.5+9.4048} = 0.1937 \quad \text{to} \quad x_{O2,2} = \frac{2}{1+2+9.4048} = 0.1612$$

The values for the water steam are from

$$x_{H2O,1} = 0 \quad \text{to} \quad x_{H2O,2} = \frac{1}{1+2+9.4048} = 0.0806$$

and for the nitrogen from

$$x_{N2,1} = \frac{9.4048}{1+2.5+9.4048} = 0.7288 \quad \text{to} \quad x_{O2,2} = \frac{9.4048}{1+2+9.4048} = 0.7582$$

The total amount of the reactive mixture changes from

$$n_1 = 1+2.5+9.4048 = 12.9048 \text{ mol} \quad \text{to} \quad n_2 = 1+2+9.4048 = 12.4048 \text{ mol}$$

which means that it will less. The start values are

$$n_{1,H2} = 1 \text{ mol} \quad n_{1,O2} = 2.5 \text{ mol} \quad n_{1,H2O} = 0 \quad n_{1,N2} = 9.4048 \text{ mol}$$

and at the end of the process

$$n_{2,H2} = 0 \quad n_{2,O2} = 2 \text{ mol} \quad n_{2,H2O} = 1 \text{ mol} \quad n_{2,N2} = 9.4048 \text{ mol}$$

To determine the particular concentration exergy changes of reactants the prove should be made if the appropriate algebraic inversion point is crossed in the analyzed process, Eq. (01). For the hydrogen ($j \equiv H_2$) there is for example

$$\nu_j = -1 \quad n_{j,1} = 1 \quad n_1 = 12.9048 \quad \sum_j \nu_j = -1/2 \quad x_{j,0} = 1.0 \quad (\text{,,apparent''})$$

and with Eq. (01)

$$-\ln\left(\frac{1-\xi_{extr}}{12.9048 - \frac{1}{2}\xi_{extr}}\right) - 1 + \frac{1}{2} \cdot \frac{1-\xi_{extr}}{12.9048 - \frac{1}{2}\xi_{extr}} = 0$$

The numerical solution of the non–linear equation leads to the result –6.4929. Thus, the following values can be obtained: $n_{extr,(H2)} = 16.1548$ mol and $x_{H2,extr} = 0.4643$, which means that the expected values cannot be reached at all ($x_{H2,1}=0.0775$ and $x_{H2,2}=0$).

The same calculations will be done for oxygen ($n_{extr,(O2)} = 12.6026$ mol or $x_{O2,extr} = 0.0785$), water steam ($n_{extr,(H2O)} = 11.1517$ mol or $x_{H2O,extr} = 0.3144$) and nitrogen ($n_{extr,(N2)} = 12.6026$ mol or $x_{N2,extr} = 0.2952$). It could be stated that the concentration changes did not lie in the range, in which the inversion point K lies. For the following values: $T_0=283.15$K, $\overline{R} = 0.0083143 \frac{kJ}{mol\,K}$ and hence $\overline{R}T_0 = 2.3542 \frac{kJ}{mol}$ the chemical concentration exergy changes have been determined, and first for the hydrogen H_2:

$$\left(E_{\mu,H2}^x\right)_2 - \left(E_{\mu,H2}^x\right)_1 = \left(n_2 x_{H2,2} \ln\frac{x_{H2,2}}{x_{H2,0}} - n_1 x_{H2,1} \ln\frac{x_{H2,1}}{x_{H2,0}}\right)\overline{R}T_0 =$$

$$= \left(0 - 12.9040 \cdot 0.0775 \cdot \ln\frac{0.0775}{1}\right)\overline{R}T_0 = 2.558\,\overline{R}T_0 = 6.0211 \text{ kJ} = \Delta\left(n\overline{e}_\mu^x\right)_{H2}$$

which can be added to the process advantages (it is greater than zero). The molar concentration of oxygen O_2 changes from $x_{O2,1}=0.1937$ up to $x_{O2,2}=0.1612$, and thus

$$\left(E^{\mathrm{x}}_{\mu,\mathrm{O2}}\right)_2^{>} - \left(E^{\mathrm{x}}_{\mu,\mathrm{O2}}\right)_1^{>} = \left(n_2 x_{\mathrm{O2,2}}\ln\frac{x_{\mathrm{O2,2}}}{x_{\mathrm{O2,0}}} - n_1 x_{\mathrm{O2,1}}\ln\frac{x_{\mathrm{O2,1}}}{x_{\mathrm{O2,0}}}\right)\overline{R}T_0 =$$

$$= \left(12.4048\cdot 0.1612\cdot\ln\frac{0.1612}{0.21} - 12.9048\cdot 0.1937\cdot\ln\frac{0.1937}{0.21}\right)\overline{R}T_0 =$$

$$= -0.3269\overline{R}T_0 = -0.7696\ \mathrm{kJ} = \nabla\left(n\bar{e}^{\mathrm{x}}_{\mu}\right)_{\mathrm{O2}}^{>}$$

It is written down with > index because the whole molar concentration change does occur above $x_{\mathrm{O2,extr}}$ ($x_{\mathrm{O2,extr}}=0.0785$).

For the water steam and oxygen following numerical values have been obtained

$$\left(E^{0}_{\mu,\mathrm{H2O}}\right)_2^{<} - \left(E^{0}_{\mu,\mathrm{H2O}}\right)_1^{<} = \left(n_2 x_{\mathrm{H2O,2}}\ln\frac{x_{\mathrm{H2O,2}}}{x_{\mathrm{H2O,0}}} - n_1 x_{\mathrm{H2O,1}}\ln\frac{x_{\mathrm{H2O,1}}}{x_{\mathrm{H2O,0}}}\right)\overline{R}T_0 =$$

$$= \left(12.4048\cdot 0.0806\cdot\ln\frac{0.0806}{1} - 0\right)\overline{R}T_0 = -2.5181\overline{R}T_0 = -5.9278\ \mathrm{kJ} = \nabla\left(n\bar{e}^{\mathrm{x}}_{\mu}\right)_{\mathrm{H2O}}^{<}$$

and

$$\left(E^{\mathrm{x}}_{\mu,\mathrm{N2}}\right)_2 - \left(E^{\mathrm{x}}_{\mu,\mathrm{N2}}\right)_1 = n_{\mathrm{N2}}\overline{R}T_0\ln\frac{x_{\mathrm{N2,2}}}{x_{\mathrm{N2,1}}} = n_1 x_{\mathrm{N2,1}}\overline{R}T_0\ln\frac{x_{\mathrm{N2,2}}}{x_{\mathrm{N2,1}}} =$$

$$= 12.9048\cdot 0.7288\cdot\overline{R}T_0\ln\frac{0.7582}{0.7288} = 0.3716\overline{R}T_0 = 0.8749\ \mathrm{kJ} = \Delta\left(n\bar{e}^{\mathrm{x}}_{\mu}\right)_{\mathrm{N2}}^{>}$$

Zero exergies of the reactants (except nitrogen) have been taken from the Table 1 in [06] for the natural environment temperature of $T_0=283.15$ K. Thus,

$$\nabla\left(n\bar{e}^{0}_{\mu}\right)_{\mathrm{H2}} = (0-1)\cdot 237.9219 = -237.9219\ \mathrm{kJ}$$

$$\nabla\left(n\bar{e}^{0}_{\mu}\right)_{\mathrm{O2}} = (2.0-2.5)\cdot 3.6798 = -1.8399\ \mathrm{kJ}$$

$$\Delta\left(n\bar{e}^{0}_{\mu}\right)_{\mathrm{H2O}} = (1-0)\cdot 10.3865 = 10.3865\ \mathrm{kJ}$$

where two first values (negative) should be added to thermodynamic expenditures and the last one (positive) to thermodynamic advantages.

The reaction heats for the chosen temperature range up to 1500 K and appropriate exergies are:

T [K]	$Q^{->}_{\mathrm{rea}}$ [kJ]	$E^{->}_{\mathrm{Q,rea}}$ [kJ]	T [K]	$Q^{->}_{\mathrm{rea}}$ [kJ]	$E^{->}_{\mathrm{Q,rea}}$ [kJ]
298.15	−241.95	−12.1727	900	−248.23	−170.1365
300	−241.98	−13.5913	1000	−248.60	−178.2114
400	−243.44	−71.1163	1100	−248.72	−184.6989
500	−244.74	−106.1422	1200	−248.56	−189.9107
600	−245.87	−129.8410	1300	−248.09	−194.0521
700	−246.84	−146.9963	1400	−247.27	−197.2595
800	−247.64	−159.9904	1500	−246.07	−199.6227

The analyzed chemical reaction is exothermic ($Q^{->}_{\mathrm{rea}}<0$) in the valid temperature range 298–1500 K (because for H_2 it is 273–1800 K, for O_2: 298–1500 K, and for H_2O: 273–1800 K). Coefficients of the reaction heat according to [02] have been determined:

$$\Delta i_{298} = -241950 \qquad \Delta a = -14.96 \quad \Delta b = 0.003415 \qquad \Delta c' = 215500$$

$$\Delta c = 0.00000655 \qquad \Delta d = -0.00000000272$$

Hence, the thermodynamic effectivity quotient is to

$$\varepsilon = \frac{\left|\Delta\left(n\bar{e}_\mu^x\right)_{H2}^<\right| + \left|\Delta\left(n\bar{e}_\mu^0\right)_{H2O}\right| + \left|\Delta\left(n\bar{e}_\mu^x\right)_{N2}^>\right| + \left|E_{Q,\,rea}^{->}\right|}{\left|\nabla\left(n\bar{e}_\mu^x\right)_{O2}^>\right| + \left|\nabla\left(n\bar{e}_\mu^x\right)_{H2O}^<\right| + \left|\nabla\left(n\bar{e}_\mu^0\right)_{H2}\right| + \left|\nabla\left(n\bar{e}_\mu^0\right)_{O2}\right|}$$

or

$$\varepsilon = \frac{6.0211 + 0.8749 + 10.3865 + \left|E_{Q,\,rea}^{->}\right|}{0.7696 + 5.9280 + 237.9219 + 1.8399} = \frac{17.2825 + \left|E_{Q,\,rea}^{->}\right|}{246.4595}$$

All the results are presented in the following results matrix, whereas additionally two arts of the so–called exergy efficiencies are calculated according to the formulas

$$\eta_{ex} = \frac{\left|\Delta\left(n\bar{e}_\mu^0\right)_{H2O}\right| + \left|E_{Q,\,rea}^{->}\right|}{\left|\nabla\left(n\bar{e}_\mu^0\right)_{H2}\right| + \left|\nabla\left(n\bar{e}_\mu^0\right)_{O2}\right|} = \frac{10.3865 + \left|E_{Q,\,rea}^{->}\right|}{237.9219 + 1,8399} = \frac{10.3865 + \left|E_{Q,\,rea}^{->}\right|}{239.7618}$$

and

$$\eta_{ex}' = \frac{\left|E_{Q,\,rea}^{->}\right|}{\left|\nabla\left(n\bar{e}_\mu^0\right)_{H2}\right| + \left|\nabla\left(n\bar{e}_\mu^0\right)_{O2}\right|} = \frac{\left|E_{Q,\,rea}^{->}\right|}{237.9219 + 1.8399} = \frac{\left|E_{Q,\,rea}^{->}\right|}{239.7618}$$

process temperature	thermodynamic effectivity	exergy efficiency	
T [K]	ε	η_{ex}	η_{ex}'
298.15	0.1195	0.0941	0.0508
300	0.1253	0.1000	0.0567
400	0.3587	0.3399	0.2966
500	0.5008	0.4860	0.4427
600	0.5969	0.5849	0.5415
700	0.6665	0.6564	0.6131
800	0.7193	0.7106	0.6673
900	0.7604	0.7529	0.7096
1000	0.7932	0.7866	0.7433
1100	0.8195	0.8137	0.7703
1200	0.8407	0.8354	0.7921
1300	0.8575	0.8527	0.8093
1400	0.8705	0.8660	0.8227
1500	0.8801	0.8759	0.8326

If the same reaction of hydrogen combustion with the same air excess number should be analyzed, but at higher process pressure ($p>p_0$), which is the case in gas turbines, in thermodynamic effectivity quotient the appropriate volume work is to be taken into account. Its exergy is to

$$E_{L,rea}^{->} = \left(1 - \frac{p_0}{p}\right)L_{rea}^> = -(p - p_0)(V_{rea,2} - V_{rea,1})$$

and, if it is less than zero (i.e. negative) the volume work and its exergy are produced in the chemical reaction balance area, or

$$E_{L,rea}^{+>} = \left(1 - \frac{p_0}{p}\right)L_{rea}^> = -(p - p_0)(V_{rea,2} - V_{rea,1})$$

if it is greater than zero (i.e. positive) the both quantities are supplied into the chemical reaction balance area. It is in analogy to the heat and its temperature T in relation to the natural environment value T_0. For the above relations has been assumed from the very start that the process pressure p higher is than the natural environment value p_0. Is there the perfect gas considered, then

$$V_{\text{rea},2} - V_{\text{rea},1} = (n_2 - n_1)\frac{\overline{R}T}{p} = -0.5 \cdot \frac{\overline{R}T}{p}$$

where T and p are given values (the isobaric–isotherm chemical reaction) and $n_2 - n_1 = -0.5$. Hence, for the process pressure of $p=10$ bar it yields

$$E_{\text{L,rea}}^{+>} = -\left(10 \cdot 10^5 - 1 \cdot 10^5\right)\left(-0.5 \cdot \frac{0.0083143 \cdot T}{10 \cdot 10^5}\right)\left[\text{Pa} \cdot \text{mol} \cdot \frac{\text{kJ} \cdot \text{K}}{\text{mol} \cdot \text{K} \cdot \text{Pa}}\right] = 0.0037 \cdot T \ [\text{kJ}]$$

The calculated numerical values oft he volume work exergies are to:

T [K]	$E_{\text{L,rea}}^{+>}$ [kJ]		T [K]	$E_{\text{L,rea}}^{+>}$ [kJ]
298.15	1.1155		900	3.3673
300	1.1224		1000	3.7414
400	1.4966		1100	4.1156
500	1.8707		1200	4.4897
600	2.2449		1300	4.8639
700	2.6190		1400	5.2380
800	2.9931		1500	5.6121

The thermodynamic process effectivity of such a high pressure hydrogen combustion equals to

$$\varepsilon = \frac{\left|\Delta(n\overline{e}_\mu^x)_{\text{H2}}^<\right| + \left|\Delta(n\overline{e}_\mu^0)_{\text{H2O}}\right| + \left|\Delta(n\overline{e}_\mu^x)_{\text{N2}}^>\right| + \left|E_{\text{Q,rea}}^{->}\right|}{\left|\nabla(n\overline{e}_\mu^x)_{\text{O2}}^>\right| + \left|\nabla(n\overline{e}_\mu^x)_{\text{H2O}}^<\right| + \left|\nabla(n\overline{e}_\mu^0)_{\text{H2}}\right| + \left|\nabla(n\overline{e}_\mu^0)_{\text{O2}}\right| + \left|E_{\text{L,rea}}^{+>}\right|}$$

or

$$\varepsilon = \frac{6.0211 + 0.8749 + 10.3865 + \left|E_{\text{Q,rea}}^{->}\right|}{0.7696 + 5.9280 + 237.9219 + 1.8399 + \left|E_{\text{L,rea}}^{+>}\right|} = \frac{17.2825 + \left|E_{\text{Q,rea}}^{->}\right|}{246.4595 + \left|E_{\text{L,rea}}^{+>}\right|}$$

The results are presented in the following table (exergy efficiencies η_{ex} and η_{ex}' according to the previously in this Chapter formulas) have been additionally calculated.

Prozeßtemperatur	thermodynamische Prozeßeffektivität	exergetischer Wirkungsgrad	
T [K]	ε	η_{ex}	η_{ex}'
298.15	0.1031	0.0941	0.0508
300	0.1247	0.1000	0.0567
400	0.3565	0.3399	0.2966
500	0.4970	0.4860	0.4427
600	0.5916	0.5849	0.5415
700	0.6595	0.6564	0.6131
800	0.7106	0.7106	0.6673
900	0.7502	0.7529	0.7096
1000	0.7813	0.7866	0.7433
1100	0.8061	0.8137	0.7703
1200	0.8256	0.8354	0.7921
1300	0.8409	0.8527	0.8093
1400	0.8524	0.8660	0.8227
1500	0.8605	0.8759	0.8326

4 EQUILIBRIUM CHEMICAL REACTION OF C–GASIFICATION

The stoichiometric equilibrium chemical reaction

$C + H_2O = CO + H_2$
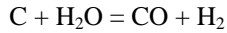
will be analyzed, for which the approximated dependence of the equilibrium constant on process temperature is given by

$$\lg \frac{1}{K_p} = -1.5561 \cdot \lg T - \frac{6740.5}{T} - 2.554 - 0.0001092 \cdot T + 0.028 \cdot 10^{-6} T^2$$

[04]–[05], and which occurs at the unitary pressure. At a given temperature T the equilibrium is characterized by the advancement of the reaction ξ_{eq}, i.e. from

$$K_p = \frac{x_{CO} x_{H2}}{x_{H2O}} \frac{1}{p} = \frac{\xi_{eq}^2}{(1-\xi_{eq})(1+\xi_{eq})} \frac{1}{p} = \frac{\xi_{eq}^2}{1-\xi_{eq}^2} \frac{1}{p} \text{ will be } \xi_{eq} = \sqrt{\frac{K_p}{K_p+1}}$$

The results are put together in the following matrix table:

T [K]	K_p	ξ_{eq}	n_2 gas	n_{H2O} x_{H2O}	n_{CO} x_{CO}	n_{H2} x_{H2}	$Q_{rea}(\xi=1)$ [kJ]	$E_{Q,rea}(\xi=1)$ [kJ]	$\xi_{eq} Q_{rea}$ [kJ]	$\xi_{eq} E_{Q,rea}$ [kJ]	ε
800	0 .0347	0.1832	1.1832	0.8168 0.6903	0.1832 0.1548	0.1832 0.1548	135.24	24.7752	87.38	16.0063	0.9872
850	0.1173	0.3240	1.3240	0.6759 0.5105	0.3240 0.2447	0.3240 0.2447	135.41	43.8817	90.30	29.2639	0.98841
900	0.3473	0.5077	1.5077	0.4923 0.3265	0.5077 0.3367	0.5077 0.3367	135.55	68,8225	92.91	47.1702	0.98628
950	0.9191	0.6920	1.6920	0.3079 0.1820	0.6920 0.4090	0.6920 0.4090	135.67	93.8898	95.23	65.9057	0.9850
1000	2.2110	0.8298	1.8298	0.1702 0.0930	0.8298 0.4535	0.8298 0.4535	135.76	11.657	97.32	80.7580	0.9831
1050	4.9003	0.9113	1.9113	0.0887 0.0464	0.9113 0.4768	0.9113 0.4768	135.83	123.788	99.20	90.4065	0.9809
1100	10.115	0.9539	1.9539	0.0460 0.0236	0.9539 0.4882	0.9539 0.4882	135.88	129.624	10.90	96.2578	0.9785
1150	19.626	0.9754	1.9754	0.0245 0.0124	0.9754 0.4938	0.9754 0.4938	135.90	132.571	102.44	99.9301	0.9760
1200	36.064	0.9864	1.9864	0.0136 0.0068	0.9864 0.4966	0.9864 0.4966	135.91	134.066	103.84	102.432	0.9735
1250	63.161	0.9922	1.9922	0.0078 0.0039	0.9922 0.4980	0.9922 0.4980	135.89	134.835	105.11	104.292	0.9711
1300	106.00	0.9953	1.9953	0.0047 0.0023	0.9953 0.4988	0.9953 0.4988	135.86	135.227	106.27	105.773	0.9695

With a mixing heat of the reactants equal to zero, the heat effect of the reaction is $Q_{rea}>0$, i.e. it is endothermic.

Determining the algebraic sign inversion point **K** for concentration exergy changes:

– water steam ($j \equiv H_2O$) there is

$$\nu_j = -1 \qquad n_{j,1} = 1 \qquad n_1 = 1 \qquad \sum \nu_j = 1 \qquad x_{j,0} = 1 \ (\text{,,apparent''})$$

and the Eq. (01) will be to

$$-\ln\left(\frac{1-\xi_{j,extr}}{1+\xi_{j,extr}}\right) - 1 - \frac{1-\xi_{j,extr}}{1+\xi_{j,extr}} = 0$$

The solution is $\xi_{H2O,extr}=0{,}564376$, from which $n_{extr,(H2O)}=1{,}564376$ and $x_{H2O,extr}=0{,}278464$ can be obtained.

– carbon monoxide ($j \equiv CO$) with

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$$v_j = 1 \qquad n_{j,1} = 0 \qquad n_1 = 1 \qquad \sum v_j = 1 \qquad x_{j,0} = 1 \ (\text{,,apparent''})$$

the Eq. (01) is

$$\ln\left(\frac{\xi_{j,\text{extr}}}{1+\xi_{j,\text{extr}}}\right) + 1 - \frac{\xi_{j,\text{extr}}}{1-\xi_{j,\text{extr}}} = 0$$

which does not give a solution in a solely sensible limits from zero to one (this reactant does not achieve the composition exergy inversion point **K**.

– hydrogen ($j \equiv H_2$) with

$$v_j = 1 \qquad n_{j,1} = 0 \qquad n_1 = 1 \qquad \sum v_j = 1 \qquad x_{j,0} = 1 \ (\text{,,apparent''})$$

will be the same, as with coal monoxide was: in the analyzed chemical reaction the hydrogen does not achieve the appropriate inversion point.

Initial molar fractions of the reactants (substrates) of the gaseous phase are assumed to be

$$x_{H2O,1}=1 \qquad\qquad x_{CO,1}=0 \qquad\qquad x_{H2,1}=0$$

and the end fractions are put in the above table. The appropriate rating quotient, the thermodynamic effectivity for the chemical reaction can be calculated from the formula

$$\varepsilon = \frac{\left|\Delta\left(n\bar{e}_\mu^x\right)_{H2O}^<\right| + \left|\Delta\left(n\bar{e}_\mu^x\right)_{CO}^>\right| + \left|\Delta\left(n\bar{e}_\mu^x\right)_{H2}^>\right| + \left|\Delta\left(n\bar{e}_\mu^0\right)_{CO}\right| + \left|\Delta\left(n\bar{e}_\mu^0\right)_{H2}\right|}{\left|\nabla\left(n\bar{e}_\mu^x\right)_{H2O}^>\right| + \left|\nabla\left(n\bar{e}_\mu^x\right)_{CO}^<\right| + \left|\nabla\left(n\bar{e}_\mu^x\right)_{H2}^<\right| + \left|\nabla\left(n\bar{e}_\mu^0\right)_C\right| + \left|\nabla\left(n\bar{e}_{\text{chem}}^0\right)_{H2O}\right| + \left|E_{Q,\text{rea}}^{+>}\right|}$$

Numerical values of the intermediate and the final results are presented in the above results matrix.

5 NON–STOICHIOMETRIC PROCESSES

The data for the following numerical example have been taken from [05], *Example 3.22*, pages 318–319 where the old, simple, but very efficient calculation method by P. DOLCH from the year 1939 has been presented. The coke layer (assumed as element carbon C) is at the process temperature of 1000 K (T_0=283.15 K) and process pressure 1 ata ($p=p_0$) in a reactive interaction with the gasifying (or converting) agent water steam (1 mol H_2O per 1 mol of carbon) and pure oxygen (0.2 mol O_2 per every 1 mol of carbon). Thus, the total amount of the gaseous phase at the start was n_1=1.2 mol with $x_{H2O,1}$=0.8333 and $x_{O2,1}$=0.1667. At the end of the gasification process n_2=2 moles strong gas has been obtained with following molar fractions: $x_{CO,2}$=0.4112, $x_{CO2,2}$=0.0887, $x_{H2,2}$=0.3887 and $x_{H2O,2}$=0.1112.

The zero–exergy values for T_0=283.15 K for all the species represented in the process (1 mol carbon has been used) are: $\Delta\bar{e}_{\mu,C}^0 = 409.94623 \ \frac{kJ}{mol}$, $\Delta\bar{e}_{\mu,CO}^0 = 275.79287 \ \frac{kJ}{mol}$, $\Delta\bar{e}_{\mu,CO2}^0 = 19.09745 \ \frac{kJ}{mol}$, $\Delta\bar{e}_{\mu,H2}^0 = 237.92189 \ \frac{kJ}{mol}$, $\Delta\bar{e}_{\mu,H2O}^0 = 10.38647 \ \frac{kJ}{mol}$ and $\Delta\bar{e}_{\mu,O2}^0 = 3.67985 \ \frac{kJ}{mol}$, [07], p.57. Concentrations in the natural environment are $x_{O2,0}$=0.21, $x_{CO2,0}$=0.0003 and $x_{H2O,0}$=1.

For the chemical concentration exergy change algebraic sign inversion point **K** will be searched in the same way and with the same assumptions as there has been presented in [08] in the Chapter *Extraction*. The inversion point **K** parameters for all the species are first to find:

– carbon monoxide CO
With parameters

$$n_1\text{=1.2 mol} \quad x_{CO,1}\text{=0} \quad n_2\text{=2.0 mol} \quad x_{CO,2}\text{=0.4114} \quad x_{CO,0}\text{=1} \ (\text{,,apparent''})$$

The coefficients a_{CO} and b_{CO} has been first determined and then the parameters of the inversion point **K**: $x_{CO,K}$=0.501316 and $n_{K(CO)}$=2.17478. It means, the point lies outside the appropriate concentration change between $x_{CO,1}$ and $x_{CO,2}$. Thus, the whole chemical concentration exergy change occurs below the point and is equal to

$$\nabla E_{\mu,CO}^{x<} = \left(n_2 x_{CO,2}\ln x_{CO,2} - n_1 x_{CO,1}\ln x_{CO,1}\right)\bar{R}T_0 = -0.7308\bar{R}T_0 = -0.00608 \text{ kJ}$$

– carbon dioxide CO_2

With parameters
$$n_1=1.2 \text{ mol} \quad x_{CO2,1}=0 \quad n_2=2.0 \text{ mol} \quad x_{CO2,2}=0.088751 \quad x_{CO2,0}=0.0003$$

The same procedure as above leads to the algebraic sign inversion point K lying inside the molar fractions change of CO_2. Its parameters are: $x_{CO2,K}=0.00011$ and $n_{K(CO2)}=1.200996$, which means that the molar fractions and the amount of the reactive mixture change according to the following scheme

x_{CO2}:	0	$\rightarrow$	0.00011	$\rightarrow$	0.088751
n:	1.2 mol	$\rightarrow$	1.200996 mol	$\rightarrow$	0.088751 mol

Thus, the both chemical concentration exergy changes are

$$\Delta E_{\mu,CO2}^{x>} = \left(n_2 x_{CO2,2} \ln \frac{x_{CO2,2}}{x_{CO2,0}} - n_{K(CO2)} x_{CO2,K} \ln \frac{x_{CO2,K}}{x_{CO2,0}} \right) \overline{R} T_0 = 1.010085 \overline{R} T_0 = 0.00840 \text{ kJ}$$

$$\nabla E_{\mu,CO2}^{x<} = \left(n_{K(CO2)} x_{CO2,K} \ln \frac{x_{CO2,K}}{x_{CO2,0}} - n_1 x_{CO2,1} \ln \frac{x_{CO2,1}}{x_{CO2,0}} \right) \overline{R} T_0 = -0.000133 \overline{R} T_0 = -0.0000011 \text{ kJ}$$

- hydrogen H_2

  With parameters
$$n_1=1.2 \text{ mol} \quad x_{H2,1}=0 \quad n_2=2.0 \text{ mol} \quad x_{H2,2}=0.3887 \quad x_{H2,0}=1 \text{ (,,apparent'')}$$

The same procedure as above leads to the algebraic sign inversion point K lying outside the molar fractions change of H_2 (the parameters are: $x_{H2,K}=0.505105$ and $n_{K(H2)}=2.239441$) and the chemical concentration exergy change below the K–point equals to

$$\nabla E_{\mu,H2}^{x<} = \left(n_2 x_{H2,2} \ln x_{H2,2} - n_1 x_{H2,1} \ln x_{H2,1} \right) \overline{R} T_0 = -0.7346 \overline{R} T_0 = -0.00611 \text{ kJ}$$

- water steam H_2O

  With parameters
$$n_1=1.2 \text{ mol} \quad x_{H2O,1}=0 \quad n_2=2.0 \text{ mol} \quad x_{H2O,2}=0.088751 \quad x_{H2O,0}=1$$

The same procedure as above leads to the algebraic sign inversion point K lying inside the molar fractions change of H_2O. Its parameters are: $x_{H2O,K}=0.294638$ and $n_{K(H2O)}=1.796823$, which means that the molar fractions and the amount of the reactive mixture change according to the following scheme

x_{H2O}:	0.8333	$\rightarrow$	0.294638	$\rightarrow$	0.111249
n:	1.2 mol	$\rightarrow$	1.796823 mol	$\rightarrow$	2.0 mol

Thus, the both chemical concentration exergy changes are

$$\Delta E_{\mu,H2O}^{x<} = \left(n_2 x_{H2O,2} \ln x_{H2O,2} - n_{K(H2O)} x_{H2O,K} \ln x_{H2O,K} \right) \overline{R} T_0 = 0.1583 \overline{R} T_0 = 0.00132 \text{ kJ}$$

$$\nabla E_{\mu,H2O}^{x<} = \left(n_{K(H2O)} x_{H2O,K} \ln x_{H2O,K} - n_1 x_{H2O,1} \ln x_{H2O,1} \right) \overline{R} T_0 = -0.4646 \overline{R} T_0 = -0.00386 \text{ kJ}$$

- oxygen O_2

  With parameters
$$n_1=1.2 \text{ mol} \quad x_{O2,1}=0.1667 \quad n_2=2.0 \text{ mol} \quad x_{O2,2}=0 \quad x_{O2,0}=0.21$$

The same procedure as above leads to the algebraic sign inversion point K lying inside the molar fractions change of O_2. Its parameters are: $x_{O2,K}=0.062393$ and $n_{K(O2)}=1.700514$, which means that the molar fractions and the amount of the reactive mixture change according to the following scheme

x_{O2}:	0.1667	$\rightarrow$	0.062393	$\rightarrow$	0
n:	1.2 mol	$\rightarrow$	1.700514 mol	$\rightarrow$	2.0 mol

Thus, the both chemical concentration exergy changes are

$$\Delta E_{\mu,O2}^{x<} = \left(n_2 x_{O2,2} - n_{K(O2)} x_{O2,K} \ln \frac{x_{O2,K}}{x_{O2,0}} \right) \overline{R} T_0 = 0.1288 \overline{R} T_0 = 0.00107 \text{ kJ}$$

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$$\nabla E_{\mu,\mathrm{O2}}^{x>} = \left(n_{\mathrm{K(O2)}} x_{\mathrm{O2,K}} \ln \frac{x_{\mathrm{O2,K}}}{x_{\mathrm{O2,0}}} - n_1 x_{\mathrm{O2,1}} \ln \frac{x_{\mathrm{O2,1}}}{x_{\mathrm{O2,0}}} \right) \overline{R} T_0 = -0.0825 \overline{R} T_0 = -0.00069 \text{ kJ}$$

The zero exergy changes of the particular species are to:

$$\Delta E_{\mu,\mathrm{CO}}^0 = \left(n_2 x_{\mathrm{CO},2} - n_1 x_{\mathrm{CO},1} \right) \Delta \overline{e}_{\mu,\mathrm{CO}}^0 = 226.8391 \text{ kJ} \quad \Delta E_{\mu,\mathrm{CO2}}^0 = \left(n_2 x_{\mathrm{CO2},2} - n_1 x_{\mathrm{CO2},1} \right) \Delta \overline{e}_{\mu,\mathrm{CO2}}^0 = 3.8984 \text{ kJ}$$

$$\Delta E_{\mu,\mathrm{H2}}^0 = \left(n_2 x_{\mathrm{H2},2} - n_1 x_{\mathrm{H2},1} \right) \Delta \overline{e}_{\mu,\mathrm{H2}}^0 = 184.9847 \text{ kJ} \quad \nabla E_{\mu,\mathrm{H2O}}^0 = \left(n_2 x_{\mathrm{H2O},2} - n_1 x_{\mathrm{H2O},1} \right) \Delta \overline{e}_{\mu,\mathrm{H2O}}^0 = -8.0755 \text{ kJ}$$

$$\nabla E_{\mu,\mathrm{O2}}^0 = \left(n_2 x_{\mathrm{O2},2} - n_1 x_{\mathrm{O2},1} \right) \Delta \overline{e}_{\mu,\mathrm{O2}}^0 = -0.7360 \text{ kJ} \quad \nabla E_{\mu,\mathrm{C}}^0 = -\Delta \overline{e}_{\mu,\mathrm{C}}^0 = -409.9462 \text{ kJ}$$

Hence, the thermodynamic effectivity quotient should be equal to

$$\varepsilon = \frac{\left| \Delta E_{\mu,\mathrm{CO2}}^{x>} \right| + \left| \Delta E_{\mu,\mathrm{H2O}}^{x<} \right| + \left| \Delta E_{\mu,\mathrm{O2}}^{x<} \right| + \left| \Delta E_{\mu,\mathrm{CO}}^0 \right| + \left| \Delta E_{\mu,\mathrm{CO2}}^0 \right| + \left| \Delta E_{\mu,\mathrm{H2}}^0 \right|}{\left| \nabla E_{\mu,\mathrm{CO}}^{x<} \right| + \left| \nabla E_{\mu,\mathrm{CO2}}^{x<} \right| + \left| \nabla E_{\mu,\mathrm{H2}}^{x<} \right| + \left| \nabla E_{\mu,\mathrm{H2O}}^{x>} \right| + \left| \nabla E_{\mu,\mathrm{O2}}^{x>} \right| + \left| \nabla E_{\mu,\mathrm{H2O}}^0 \right| + \left| \nabla E_{\mu,\mathrm{O2}}^0 \right| + \left| \nabla E_{\mu,\mathrm{C}}^0 \right| + \left| E_{\mathrm{Q}}^{+>} \right|}$$

or

$$\varepsilon = \frac{0.00840 + 0.00132 + 0.00107 + 226.8391 + 3.8984 + 184.9847}{0.00608 + 0.0000011 + 0.00611 + 0.00386 + 0.00069 + 8.0755 + 0.7360 + 409.9462 + \left| E_{\mathrm{Q}}^{+>} \right|}$$

i.e.

$$\varepsilon = \frac{415.7330}{418.7744 + \left| E_{\mathrm{Q}}^{+>} \right|}$$

This result shows that the analyzed non–stoichiometric gasifying process can occur without any heat supply from outer systems. In such a case the thermodynamic effectivity quotient would be equal to ε=415.7330/418.7744=0.9927, which confirms the *Second Law* condition (P. DOLCH has assumed the chemical reactions set C+H$_2$O=CO+H$_2$ and CO+H$_2$O=CO$_2$+H$_2$, [05]). In fact, the practical values of the quotient are lower, e.g. in the previous Chapter they lie by 0.98 for the same process temperature. Thus, the heat from outside should be supplied, just like more complex examples of gasification processes computed by authors has showed. Assuming that the above quotient should be equal to 0.85, the heat exergy should be

$$\left| E_{\mathrm{Q}}^{+>} \right| = 70.3232 \text{ kJ}$$

and the heat supplied (at 1000 K by T_0=283.15 K) Q_+=98.1 kJ. The both amounts refer to 1 mol of the gasified coke (element carbon C).

6 CONCLUSIONS

The presented examples show the correctness of the theoretical approach worked out in the earlier contribution. The simultaneous stoichiometric chemical reactions, however, will be discussed in another place because the appropriate formulas are very large. They could be proved positive, either. Moreover, the formulation of the thermodynamic quotient can be a sufficient condition for the statement, if the analyzed chemical process can be realized or not. It results from the *Second Law of Thermodynamics*.

In the case of some chemical reactions, just like e.g. the so–called „shift reaction" CO+H$_2$O=CO$_2$+H$_2$ or complex non–stoichiometric gasification processes it can be estimated the particular species amounts and the quantity of heat supply to make the process possible at all, [09].

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