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EXERGY IN CHEMICAL REACTIONS OF COMBUSTION AND GASIFICATION
PART 1: THEORETICAL APPROACH

EXERGIE V CHEMICKÝCH REAKCÍCH SPALOVÁNÍ A ZPLYŇOVÁNÍ
ČÁST 1: TEORETICKÝ PŘÍSTUP

Abstract

The exergy concept applied to chemical reactions of combustion and gasification has been presented and discussed in detail. Especially the building of thermodynamic effectivity quotients has been emphasized. Different cases have been presented: for stoichiometric homogeneous, stoichiometric heterogeneous, simultaneous and non-stoichiometric chemical reactions the special approach was pointed out. Thus, the special procedure of partition exergy changes into vanishing and created exergies (i.e. thermodynamic expenditures and advantages in a process) could be presented. Such an approach makes it possible regarding chemical reactions of combustion and gasification in thermodynamic models of modern power engineering systems, in which these processes have been taken into account only in their simplified form.

Abstrakt

Exergetická koncepce byla aplikována na chemické reakce spalování a zplyňování a byla předložena a projednána detailně. Zvláště bylo zdůrazněno pojetí termodynamických koeficientů efektivity. Různé případy byly prezentovány a zdůrazněné pro: stechiometrické homogenní, stechiometrické heterogenní, simultánní a ne-stechiometrické chemické reakce. Speciální procedury změn energie při tvorbě a ztrátách byly analyzovány (tj. termodynamické výdaje a výhody v procesu). Takový přístup se týká chemických reakcí spalování a zplyňování V termodynamických modelech popisující moderní energetické systémy, v nichž tyto procesy byly vzaty V úvahu pouze ve své zjednodušené formě.

1 INTRODUCTION

The problem of exergy rating of chemical reactions was first discussed even before the name for such a thermodynamic property has been developed (by Z. RANT), [01]. The analysis made by K.G. DENBIGH was the typical *Second-Law Analysis*, which additionally took into account the natural environment with the known intensities T_0 and/or p_0 . Their numerical values were assumed to be equal to the standard chemical ones T^0 or p^0 , respectively, and the example of the stoichiometric ammonia synthesis reaction has been worked out for which the total efficiency of 6% has been obtained (in the sense of the *Second Law*), [02]. There are many further trials to notice, e.g. [03], referring to the chemical synthesis processes, especially the ammonia production, [04]–[08], nitric acid, [04]–[05], [09]–[10], or methanol, [10]. The full spectrum of chemical industry processes, however, was analyzed by V.S. STEPANOV, [11], and by I.L. LEITES ET AL., [12]. All the trials of rating chemical processes, especially the chemical reactions, have been taken as global ones (except that of K.G. DENBIGH), i.e. they considered the whole technological system, in which the analyzed chemical

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reaction took place (further papers: [06], [13]–[23]). Some papers deal with the very important chemical process, the combustion, e.g. [24]–[30]. For the symmetry investigations of thermodynamic cycles, however, it is necessary to know the creation algorithm for an appropriate rating quotient and to apply it to the chemical reaction in the same way, as it is usually done to other thermodynamic processes, typical for the mechanical and power engineering. The goal of such investigations is the presentation of chemical cycles as thermodynamic models of the appropriate energy devices in the way, which can be understandable by a power engineer, and which can be compared with other typical power engineering cycles. For this reason it is important to apply the already worked out universal exergy rating algorithm, [31]–[36], to the stoichiometric chemical reactions. This algorithm has been successfully proved for almost all possible mechanical and chemical engineering processes, and especially to chemical reactions of combustion and gasification presented several times by authors in different application possibilities, eg. [37]–[45].

2 EXERGY BALANCE OF THE CHEMICAL ENERGY CONVERSION

The chemical reaction can be balanced as an open thermodynamic system, characterized both, by the inner energy or the enthalpy. The appropriate general exergy balance equations are:

$$dE_U = \left(1 - \frac{T_0}{T}\right) dQ + \left(1 - \frac{p_0}{p}\right) dL + \sum \left(1 - \frac{\mu_{j,0}}{\mu_j}\right) dL_{\mu,j} - T_0 dS_{\text{irr}}$$

and

$$dE_t = \left(1 - \frac{T_0}{T}\right) dQ + dL_t + \sum \left(1 - \frac{\mu_{j,0}}{\mu_j}\right) dL_{\mu,j} - T_0 dS_{\text{irr}}$$

or, considering the conditions $dT=dp=0$ or $dT=dV=0$ without an external chemical work ($dL_{\mu,j}=0$), viz

$$\Delta E_\mu = \int \left(1 - \frac{T_0}{T}\right) dQ - T_0 \Delta S_{\text{irr}} = \left(1 - \frac{T_0}{T}\right) Q_{\text{rea}} - T_0 \Delta S_{\text{irr}}$$

for $p=p_0$, or

$$\Delta E_\mu = \int \left(1 - \frac{T_0}{T}\right) dQ + \int \left(1 - \frac{p_0}{p}\right) dL - T_0 \Delta S_{\text{irr}} = \left(1 - \frac{T_0}{T}\right) Q_{\text{rea}} + (p - p_0) \Delta V_{\text{rea}} - T_0 \Delta S_{\text{irr}}$$

for $p \neq p_0$, whereby Q_{rea} is the heat of reaction at temperature T and ΔV_{rea} the volume change in the analyzed process, e.g. [46]–[47], and

$$\Delta E_\mu = \int \left(1 - \frac{T_0}{T}\right) dQ + L_t - T_0 \Delta S_{\text{irr}} = \left(1 - \frac{T_0}{T}\right) Q_{\text{rea}} + V \Delta p - T_0 \Delta S_{\text{irr}}$$

in the case, the useful (shaft) work has been done (in a flux system, e.g. combustion chamber of the aircraft engine). The useful (or technical) work L_t can be thought as the appropriate electrical work (e.g. of the galvanic cell or of the MHD/MGD device).

Because of the fundamental exergy equations, [48], it is valid

$$dE_\mu = \sum (\mu_j^0 - \mu_{j,0}^0) dn_j + \bar{R} T_0 \sum \left(\ln \frac{x_j}{x_{j,0}} \right) dn_j \text{ or } E_\mu = \sum n_j (\mu_j^0 - \mu_{j,0}^0) + \bar{R} T_0 \sum n_j \ln \frac{x_j}{x_{j,0}}$$

and in the case $T=T_0$ and $p=p_0$ (or $V=V_0$) with the appropriate equation for the zero-exergy of the specie j

$$E_\mu = \sum n_j \bar{e}_{\mu,j}^0 + \bar{R} T_0 \sum n_j \ln \frac{x_j}{x_{j,0}} = E_\mu^0 + E_\mu^x$$

whereby the first term of the right-hand side is the reactive,

$$E_\mu^0 = \sum n_j \bar{e}_{\mu,j}^0 \text{ or } \bar{e}_\mu^0 = \sum x_j \bar{e}_{\mu,j}^0$$

and the second one the concentration part (constituent) of the system chemical exergy, e.g. [48]–[52],

$$E_{\mu}^x = \sum n_j \bar{e}_{\mu,j}^x = \bar{R}T_0 \sum n_j \ln \frac{x_j}{x_{j,0}} \quad \text{or} \quad \bar{e}_{\mu}^x = \sum x_j \bar{e}_{\mu,j}^x = \bar{R}T_0 \sum x_j \ln \frac{x_j}{x_{j,0}} \quad (01)$$

Hence, the exergy balance will be to

$$\begin{aligned} \sum \Delta n_j \bar{e}_{\mu,j}^0 + \bar{R}T_0 \left(\sum n_{j,2} \ln \frac{x_{j,2}}{x_{j,0}} - \sum n_{j,1} \ln \frac{x_{j,1}}{x_{j,0}} \right) &= \sum \Delta(n\bar{e}_{\mu}^0)_j + \sum \Delta(n\bar{e}_{\mu}^x)_j = \\ &= \int \left(1 - \frac{T_0}{T} \right) dQ - T_0 \Delta S_{\text{irr}} = \left(1 - \frac{T_0}{T} \right) Q_{\text{rea}} - T_0 \Delta S_{\text{irr}} \end{aligned}$$

for $p=p_0$, or to

$$\begin{aligned} \sum \Delta n_j \bar{e}_{\mu,j}^0 + \bar{R}T_0 \left(\sum n_{j,2} \ln \frac{x_{j,2}}{x_{j,0}} - \sum n_{j,1} \ln \frac{x_{j,1}}{x_{j,0}} \right) &= \sum \Delta(n\bar{e}_{\mu}^0)_j + \sum \Delta(n\bar{e}_{\mu}^x)_j = \\ &= \int \left(1 - \frac{T_0}{T} \right) dQ + \int \left(1 - \frac{p_0}{p} \right) dL - T_0 \Delta S_{\text{irr}} = \left(1 - \frac{T_0}{T} \right) Q_{\text{rea}} + (p - p_0) \Delta V_{\text{rea}} - T_0 \Delta S_{\text{irr}} \end{aligned}$$

for $p \neq p_0$ (usually $p \geq p_0$). The concentration exergy, Eq. (01), is a thermodynamic parameter of state, which has been already proved (the SCHWARZ'S conditions) in [52].

3 THERMODYNAMIC EFFECTIVITY QUOTIENT

The presented exergy balances form is a base for the formulation of the so-called thermodynamic transformation in an analyzed energy conversion process. The appropriate mathematical notation of such a transformation will be generally to

$$\begin{aligned} \sum |\nabla(n\bar{e}_{\mu}^0)_j| + \sum |\nabla(n\bar{e}_{\mu}^x)_j^>| + \sum |\nabla(n\bar{e}_{\mu}^x)_j^<| + \left| \left(1 - \frac{T_0}{T} \right) Q_{\text{rea}}^{>} \right| + \left| \left(1 - \frac{T_0}{T} \right) Q_{\text{rea}}^{+<} \right| \rightarrow \\ \rightarrow \sum |\Delta(n\bar{e}_{\mu}^0)_j| + \sum |\Delta(n\bar{e}_{\mu}^x)_j^>| + \sum |\Delta(n\bar{e}_{\mu}^x)_j^<| + \left| \left(1 - \frac{T_0}{T} \right) Q_{\text{rea}}^{<} \right| + \left| \left(1 - \frac{T_0}{T} \right) Q_{\text{rea}}^{+>} \right| - T_0 \Delta S_{\text{irr}} \end{aligned} \quad (02)$$

and

$$\begin{aligned} \sum |\nabla(n\bar{e}_{\mu}^0)_j| + \sum |\nabla(n\bar{e}_{\mu}^x)_j^>| + \sum |\nabla(n\bar{e}_{\mu}^x)_j^<| + \left| \left(1 - \frac{T_0}{T} \right) Q_{\text{rea}}^{>} \right| - \left| \left(1 - \frac{T_0}{T} \right) Q_{\text{rea}}^{+<} \right| + |(p - p_0) \nabla V_{\text{rea}}| \rightarrow \\ \rightarrow \sum |\Delta(n\bar{e}_{\mu}^0)_j| + \sum |\Delta(n\bar{e}_{\mu}^x)_j^>| + \sum |\Delta(n\bar{e}_{\mu}^x)_j^<| + \left| \left(1 - \frac{T_0}{T} \right) Q_{\text{rea}}^{<} \right| - \left| \left(1 - \frac{T_0}{T} \right) Q_{\text{rea}}^{+>} \right| + \\ + |(p - p_0) \Delta V_{\text{rea}}| - T_0 \Delta S_{\text{irr}} \end{aligned} \quad (03a)$$

for pressures $p > p_0$, or

$$\begin{aligned} \sum |\nabla(n\bar{e}_{\mu}^0)_j| + \sum |\nabla(n\bar{e}_{\mu}^x)_j^>| + \sum |\nabla(n\bar{e}_{\mu}^x)_j^<| + \left| \left(1 - \frac{T_0}{T} \right) Q_{\text{rea}}^{>} \right| - \left| \left(1 - \frac{T_0}{T} \right) Q_{\text{rea}}^{+<} \right| \\ + |(p - p_0) \Delta V_{\text{rea}}| \rightarrow \\ \rightarrow \sum |\Delta(n\bar{e}_{\mu}^0)_j| + \sum |\Delta(n\bar{e}_{\mu}^x)_j^>| + \sum |\Delta(n\bar{e}_{\mu}^x)_j^<| + \left| \left(1 - \frac{T_0}{T} \right) Q_{\text{rea}}^{<} \right| - \left| \left(1 - \frac{T_0}{T} \right) Q_{\text{rea}}^{+>} \right| + \\ + |(p - p_0) \nabla V_{\text{rea}}| - T_0 \Delta S_{\text{irr}} \end{aligned} \quad (03b)$$

for pressures $p < p_0$, where $\Delta V_{\text{rea}} > 0$, $\nabla V_{\text{rea}} < 0$, and

$$E_{Q,\text{rea}}^{<} = \left(1 - \frac{T_0}{T}\right) Q_{\text{rea}}^{<} > 0, \text{ i.e. } Q_{\text{rea}}^{<} < 0 \text{ (the process exothermic) at } T < T_0$$

$$E_{Q,\text{rea}}^{>} = \left(1 - \frac{T_0}{T}\right) Q_{\text{rea}}^{>} < 0, \text{ i.e. } Q_{\text{rea}}^{>} < 0 \text{ (the process exothermic) at } T > T_0$$

$$E_{Q,\text{rea}}^{+>} = \left(1 - \frac{T_0}{T}\right) Q_{\text{rea}}^{+>} > 0, \text{ i.e. } Q_{\text{rea}}^{+>} > 0 \text{ (the process endothermic) at } T > T_0$$

$$E_{Q,\text{rea}}^{+<} = \left(1 - \frac{T_0}{T}\right) Q_{\text{rea}}^{+<} < 0, \text{ i.e. } Q_{\text{rea}}^{+<} > 0 \text{ (the process endothermic) at } T < T_0$$

Thermodynamic advantages and expenditures by means of exergy are terms, which fulfill the conditions

$$\text{sign}(\text{advantages}) = \text{sign}(T_0 \Delta S_{\text{irr}}) \quad \text{and} \quad \text{sign}(\text{expenditures}) = -\text{sign}(T_0 \Delta S_{\text{irr}})$$

respectively, and which have been described in detail e.g. in [33]–[35], [46]–[47]. With Eq.(02) it becomes the thermodynamic effectivity

$$\varepsilon = \frac{\sum |\Delta(n\bar{e}_\mu^0)_j| + \sum |\Delta(n\bar{e}_\mu^x)_j^>| + \sum |\Delta(n\bar{e}_\mu^x)_j^<| + \left| \left(1 - \frac{T_0}{T}\right) Q_{\text{rea}}^{<} \right| + \left| \left(1 - \frac{T_0}{T}\right) Q_{\text{rea}}^{+>} \right|}{\sum |\nabla(n\bar{e}_\mu^0)_j| + \sum |\nabla(n\bar{e}_\mu^x)_j^>| + \sum |\nabla(n\bar{e}_\mu^x)_j^<| + \left| \left(1 - \frac{T_0}{T}\right) Q_{\text{rea}}^{>} \right| + \left| \left(1 - \frac{T_0}{T}\right) Q_{\text{rea}}^{+<} \right|}$$

or

$$\varepsilon = \frac{\sum |\Delta(n\bar{e}_\mu^0)_j| + \sum |\Delta(n\bar{e}_\mu^x)_j^>| + \sum |\Delta(n\bar{e}_\mu^x)_j^<| + |E_{Q,\text{rea}}^{<}| + |E_{Q,\text{rea}}^{+>}|}{\sum |\nabla(n\bar{e}_\mu^0)_j| + \sum |\nabla(n\bar{e}_\mu^x)_j^>| + \sum |\nabla(n\bar{e}_\mu^x)_j^<| + |E_{Q,\text{rea}}^{>}| + |E_{Q,\text{rea}}^{+<}|} \quad (04)$$

and from Eq.(03) the appropriate rating quotient considering exergy changes due to the volume changes. Such thermodynamic effectivity quotients are valid for chemical exergy changes in isotherm–isobaric processes. The superscripts > and < refer to the changes above or below the algebraic sign inversion point. In the case of the process heat Q_{rea} , the algebraic sign of the appropriate heat exergy will depend on the natural environment temperature T_0 as the heat exergy change inversion point. In the case of the zero–exergy changes, no inversion point is to state, but in the case of the concentration exergy changes on the contrary: inversion point will be observed, but it does not directly refer to the appropriate natural environment intensity value. It is its functional dependence, [46]–[48], [52]–[58].

The same regularities described for the reaction heat exergy $E_{Q,\text{rea}}$ and its position in the thermodynamic effectivity quotient refer to the volume work exergy $E_{L,\text{rea}}$ in non–equimolar chemical reactions.

3.1 Absolute volume work of the chemical reaction

If the chemical reaction analyzed 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

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

or

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

Assuming the perfect gas relations it becomes

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

whereby T and p are given (isobar–isotherm chemical reaction) and $n_2 - n_1$ results from the chemical reaction formula. The both above expressions for the absolute work of a chemical reaction should be taken into account in the thermodynamic effectivity quotient, i.e. Eq.(04) will be to

$$\varepsilon = \frac{\sum \left| \Delta(n\bar{e}_\mu^0)_j \right| + \sum \left| \Delta(n\bar{e}_\mu^x)_j^> \right| + \sum \left| \Delta(n\bar{e}_\mu^x)_j^< \right| + \left| E_{\text{Q,rea}}^- \right| + \left| E_{\text{Q,rea}}^{+>} \right| + \left| E_{\text{L,rea}}^{+>} \right|}{\sum \left| \nabla(n\bar{e}_\mu^0)_j \right| + \sum \left| \nabla(n\bar{e}_\mu^x)_j^> \right| + \sum \left| \nabla(n\bar{e}_\mu^x)_j^< \right| + \left| E_{\text{Q,rea}}^- \right| + \left| E_{\text{Q,rea}}^{+<} \right| + \left| E_{\text{L,rea}}^- \right|}$$

4 STOICHIOMETRIC CHEMICAL REACTIONS

Advancement of the chemical reaction:

$$d\xi = \frac{dn_r}{\nu_r}$$

whereby the subscript r points to the appropriate reactant. In the reaction analyzed there is for all the reactants:

$$n_r = n_{r,1} + \nu_r \xi$$

and the reaction advancement changes from zero to a certain number of moles, usually one for the special chosen stoichiometric coefficients (for \rightarrow type reactions, i.e. with equilibrium on the products side) and from zero to $\xi_{\text{eq}} = \xi^*$ (for $=$ type reactions, i.e. the equilibrium one).

The whole amount of reactants in a process yields

$$n_\Sigma = \sum_r n_r = \sum_r n_{r,1} + \xi \sum_r \nu_r = n_1 + \xi \sum_r \nu_r$$

In every moment of a process the molar fraction of r reactant equals to

$$x_r = \frac{n_{r,1} + \nu_r \xi}{\sum_r n_{r,1} + \xi \sum_r \nu_r} = \frac{n_{r,1} + \nu_r \xi}{n_1 + \xi \sum_r \nu_r}$$

Thus, the concentration part of chemical exergy of the gaseous reactant r in a gas phase reacting mixture is

$$E_{\mu,r}^x = n_r \bar{R}T_0 \ln \frac{x_r}{x_{r,0}}$$

and its dependence on reaction advancement and the start concentrations

$$E_{\mu,r}^x = (n_{r,1} + \xi \nu_r) \bar{R}T_0 \ln \left(\frac{1}{x_{r,0}} \cdot \frac{n_{r,1} + \xi \nu_r}{n_1 + \xi \sum_r \nu_r} \right) \quad (05)$$

whereby only reactants in the gas phase are taken into account. It does mean the sum $\sum_r \nu_r$

and n_1 refers only to gaseous reactants.

Finding the inversion point ξ_{extr} of the concentration exergy change depends on the chemical reaction type. If only it is non–equimolar in the gas phase, i.e.

$$\sum_r \nu_r \neq 0$$

the procedure is the obvious search for the function minimum

$$\frac{dE_{\mu,r}^x}{d\xi} = 0 \quad \text{or} \quad \frac{d}{d\xi} \frac{E_{\mu,r}^x}{\bar{R}T_0} = 0$$

which is the same. It yields

$$\frac{d}{d\xi} \frac{E_{h,r}^x}{RT_0} = \nu_r \cdot \ln \left(\frac{1}{x_{r,0}} \cdot \frac{n_{r,1} + \xi \nu_r}{n_1 + \xi \sum_r \nu_r} \right) + (n_{r,1} + \xi \nu_r) \cdot \frac{x_{r,0} (n_1 + \xi \sum_r \nu_r)}{(n_{r,1} + \xi \nu_r)} \times$$

$$\times \frac{(n_1 + \xi \sum_r \nu_r) \cdot x_{r,0} \cdot \nu_r - (n_{r,1} + \xi \nu_r) \cdot x_{r,0} \cdot \sum_r \nu_r}{(n_1 + \xi \sum_r \nu_r)^2 \cdot x_{r,0}^2} \quad (06)$$

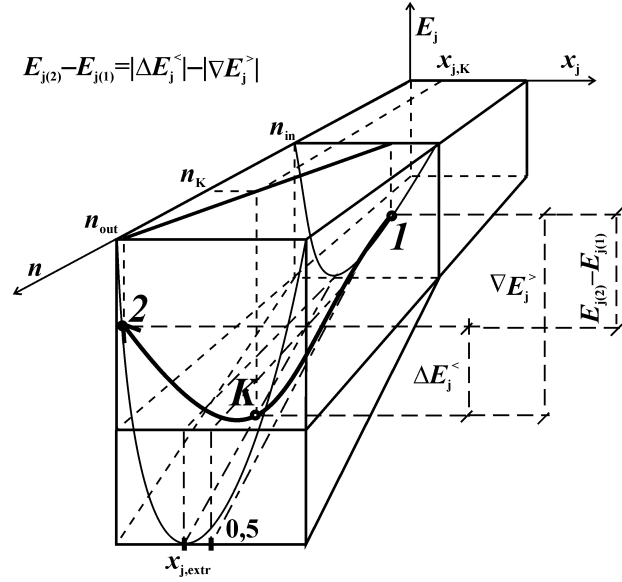


Fig. 1 The **K**-point for the concentration exergy change algebraic sign inversion, [36], page 91.

After rearrangement it follows

$$\nu_r \cdot \ln \left(\frac{1}{x_{r,0}} \cdot \frac{n_{r,1} + \xi_{r,extr} \nu_r}{n_1 + \xi_{r,extr} \sum_r \nu_r} \right) + \nu_r \cdot \frac{n_{r,1} + \xi_{r,extr} \nu_r}{n_1 + \xi_{r,extr} \sum_r \nu_r} \cdot \sum_r \nu_r = 0$$

from which the for the r gas phase reactant the inversion point **K** can be iteratively determined. The appropriate quantity is $\xi_{r,extr}$. It is right, i.e. the concentration exergy inversion point **K** exists, if only the obtained numerical value lies in the only logical range between 0 and 1 (for \rightarrow type reactions the value of ξ at the end can be set as $\xi^* = 1$) or between 0 and ξ^* (for $=$ type reactions). It should be only proved, if in the given range of the r reactant concentration change from $\xi_{r,1}$ to $\xi_{r,2}$ there is the appropriate concentration value $\xi_{r,extr}$.

Parameters of this inversion point **K** are

.) amount of the gaseous reactant r :

$$n_{r,extr} = n_{r,1} + \xi_{r,extr} \nu_r$$

$$n_{extr,(r)} = n_1 + \xi_{r,extr} \sum_r \nu_r$$

.) total amount of the gas phase reaction mixture:

.) molar fraction:

$$x_{r,\text{extr}} = \frac{n_{r,\text{extr}}}{n_{\text{extr}(r)}} = \frac{n_{r,1} + \xi_{r,\text{extr}} \nu_r}{n_1 + \xi_{r,\text{extr}} \sum_r \nu_r}$$

Examples for such chemical reactions are $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$ and $\text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2$. Heterogeneous chemical reactions of combustion (e.g. $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$) and gasification (e.g. $\text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2$) can be analyzed in the same way like just presented above homogeneous ones. The only difference is that the condensed phase (e.g. the solid and/or liquid state) is not taken into account in molar fractions determinations. It follows from the general principles of the so-called chemical thermodynamics, which look somehow strange for the power engineer knowing only the simplified stoichiometric combustion calculations from the so-called engineering-thermodynamics text-books. In fact, the modern text-books take into account the general approach for these calculations, i.e. they do not regret between the so-called chemical and the so-called engineering thermodynamics at all.

The main assumption for the heterogeneous chemical reactions analysis is that there is enough condensed phase reactant in the reactive mixture, i.e. it can be schematically presented as in Fig. 2. After the appropriate chemical reaction has been completed there are no more condensed phase species in the resulting mixture. The same refers to the combustion (or gasification) of sulphur S.

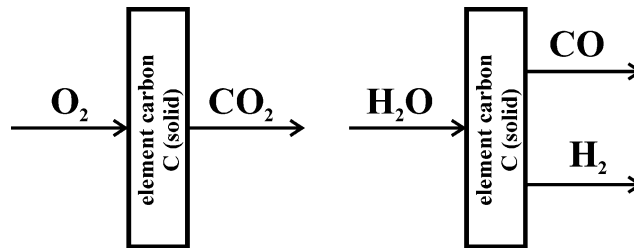


Fig. 2 Schematic diagram of heterogeneous carbon combustion and gasification.

4.1 Equimolar chemical reactions

In the case of an equimolar chemical reaction (in the gas phase) it will be

$$\sum_r \nu_r = 0$$

and the Eq. (05) yields

$$E_{\mu,r}^x = (n_{r,1} + \xi \nu_r) \bar{R} T_0 \ln \left(\frac{1}{x_{r,0}} \cdot \frac{n_{r,1} + \xi \nu_r}{n_1} \right)$$

The first derivative becomes

$$\frac{d}{d\xi} \frac{E_{\mu,r}^x}{\bar{R} T_0} = \nu_r \cdot \ln \left(\frac{1}{x_{r,0}} \cdot \frac{n_{r,1} + \xi \nu_r}{n_1} \right) + (n_{r,1} + \xi \nu_r) \cdot \frac{n_1 \cdot x_{r,0}}{n_{r,1} + \xi \nu_r} \cdot \frac{\nu_r}{n_1 \cdot x_{r,0}} = \nu_r \cdot \ln \left(\frac{1}{x_{r,0}} \cdot \frac{n_{r,1} + \xi \nu_r}{n_1} \right) + \nu_r$$

or from Eq.(06) substituting $\sum_r \nu_r = 0$

$$\frac{d}{d\xi} \frac{E_{\mu,r}^x}{\bar{R} T_0} = \nu_r \cdot \ln \left(\frac{1}{x_{r,0}} \cdot \frac{n_{r,1} + \xi \nu_r}{n_1} \right) + \nu_r$$

which is the same, just like deriving step-by-step the appropriate exergy equation.

The algebraic (so-called analytic) solution of the equation

$$\nu_r \cdot \ln \left(\frac{1}{x_{r,0}} \cdot \frac{n_{r,1} + \xi_{r,\text{extr}} \nu_r}{n_1} \right) + \nu_r = 0$$

can be done, i.e. dividing first by $\nu_r \neq 0$ gives

$$\ln\left(\frac{1}{x_{r,0}} \cdot \frac{n_{r,1} + \xi_{r,\text{extr}} \nu_r}{n_1}\right) = -1 \quad \text{or} \quad \frac{1}{x_{r,0}} \cdot \frac{n_{r,1} + \xi_{r,\text{extr}} \nu_r}{n_1} = e^{-1} = \frac{1}{e}$$

where e is the basis of natural logarithms. Further one becomes

$$n_{r,1} + \xi_{r,\text{extr}} \nu_r = \frac{x_{r,0} \cdot n_1}{e} \quad \text{and finally} \quad \xi_{r,\text{extr}} = \frac{1}{\nu_r} \left(\frac{x_{r,0} \cdot n_1}{e} - n_{r,1} \right)$$

taking into account that anytime yields $n_1 = n_2 = n$. The solution is right, if its numerical value lies in the range between 0 and 1 (for \rightarrow type reactions, i.e. from $\xi=0$ to $\xi^*=1$) or between 0 and ξ^* (for $=$ type reactions).

Thus, parameters of this inversion point K are

$$\begin{aligned} \text{.) amount of the gaseous reactant } r: & \quad n_{r,\text{extr}} = n_{r,1} + \xi_{r,\text{extr}} \nu_r \\ \text{.) total amount of the gas phase reaction mixture:} & \quad n_{\text{extr}(r)} = n_1 + \xi_{r,\text{extr}} \sum_r \nu_r = n \\ \text{.) molar fractions:} & \quad x_{r,\text{extr}} = \frac{n_{r,\text{extr}}}{n} = \frac{n_{r,1} + \xi_{r,\text{extr}} \nu_r}{n} \end{aligned}$$

because always $\sum_r \nu_r = 0$. Examples for such chemical reactions are $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$ and $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$.

4.2 Stoichiometric Chemical Reactions with Inerts

Advancement of the chemical reaction:

$$d\xi = \frac{dn_r}{\nu_r}$$

whereby subscript r points to the appropriate reactant and int to the inert. In the reaction analyzed there is for all the r reactants:

$$n_r = n_{r,1} + \nu_r \xi$$

and for inerts

$$n_{\text{int}} = n_{\text{int},1} = n_{\text{int},2}$$

and the reaction advancement changes from zero to one (for \rightarrow type reactions, i.e. $\xi_{\text{eq}} = \xi^* = 1$) and from zero to $\xi_{\text{eq}} = \xi^*$ (for $=$ type reactions).

The whole amount of reactants and inerts in a process yields

$$n = \sum_r n_r + n_{\text{int},1} = n_{\text{int},1} + \sum_r n_{r,1} + \xi \sum_r \nu_r = n_1 + \xi \sum_r \nu_r$$

because

$$\sum_r n_{r,1} + n_{\text{int},1} = n_1$$

In every moment of a process the molar fraction of reactant r equals to

$$x_r = \frac{n_{r,1} + \nu_r \xi}{n_1 + \xi \sum_r \nu_r}$$

and that of the gaseous inert int

$$x_{\text{int}} = \frac{n_{\text{int}}}{n_{\text{int},1} + \sum_r n_{r,1} + \xi \sum_r \nu_r} = \frac{n_{\text{int}}}{n_1 + \xi \sum_r \nu_r}$$

Thus, the concentration part of chemical exergy of the reaction partner reactant r in a reacting mixture is

$$E_{\mu,r}^x = n_r \bar{R} T_0 \ln \frac{x_r}{x_{r,0}}$$

and its dependence on reaction advancement and the start concentrations of gas phase reactants

$$E_{\mu,r}^x = (n_{r,1} + \xi \nu_r) \cdot \bar{R}T_0 \ln \left(\frac{1}{x_{j,0}} \cdot \frac{n_{r,1} + \xi \nu_r}{n_1 + \xi \sum_r \nu_r} \right)$$

This is the general criterion derived in [36], Eq. (B121), page 90, and the equation has been obtained before (the case without inerts).

After the chemical reaction with inerts has been calculated, obviously there are known all the molar fractions (including inerts, $x_{\text{int},1}$ and $x_{\text{int},2}$) and total amounts n_1 at the beginning and at the end of a process n_2 . The unchanged inerts amount n_{int} is known either. For composition part of chemical exergy determination it is not important, what kind of specie or species are inerts: their molar fraction in total is important. Now the criterion equation should be derived for proving the existence of the inverse K -point for the inert. It is

$$E_{\mu,\text{int}}^x = n_{\text{int}} \bar{R}T_0 \ln \frac{x_{\text{int}}}{x_{\text{int},0}}$$

and

$$E_{\mu,r}^x = \left(n_1 + \xi \sum_r \nu_r \right) \cdot x_{\text{int}} \cdot \bar{R}T_0 \ln \left(\frac{x_{\text{int}}}{x_{\text{int},0}} \right)$$

where

$$n_1 = \sum_r n_{r,1} + n_{\text{int}}$$

The mathematical procedure is the obvious search for the function minimum

$$\frac{dE_{\mu,\text{int}}^x}{dx_{\text{int}}} = 0 \quad \text{or} \quad \frac{d}{dx_{\text{int}}} \frac{E_{\mu,\text{int}}^x}{\bar{R}T_0} = 0$$

which is the same. It yields

$$\frac{d}{dx_{\text{int}}} \frac{E_{\mu,\text{int}}^x}{\bar{R}T_0 \cdot \left(n_1 + \xi \sum_r \nu_r \right)} = x_{\text{int}} \cdot \frac{x_{\text{int},0}}{x_{\text{int}}} \cdot \frac{1}{x_{\text{int},0}} + \ln \frac{x_{\text{int}}}{x_{\text{int},0}} = 1 + \ln \frac{x_{\text{int}}}{x_{\text{int},0}}$$

After rearrangement it follows

$$1 + \ln \frac{x_{\text{int,extr}}}{x_{\text{int},0}} = 0$$

where from

$$x_{\text{int,extr}} = \frac{x_{\text{int},0}}{e}$$

where e is the base of natural logarithms. The result has been first obtained in a monograph [36], page 54–55.

Examples for such chemical reactions are the combustion in the atmospheric air or gasification in the presence of nitrogen, i.e. $\text{H}_2 + \frac{1}{2}\text{O}_2 + \frac{79}{2.21} \text{N}_2 \rightarrow \text{H}_2\text{O} + \frac{79}{2.21} \text{N}_2$ and $\text{C} + \text{H}_2\text{O} + \text{N}_2 = \text{CO} + \text{H}_2 + \text{N}_2$ as non-equimolar (in the gas phase) processes, and again the combustion in the atmospheric air or the so-called CO-shift of the “water gas”, i.e. $\text{C} + \text{O}_2 + \frac{79}{21} \text{N}_2 \rightarrow \text{CO}_2 + \frac{79}{21} \text{N}_2$ and $\text{CO} + \text{H}_2\text{O} + \text{N}_2 = \text{CO}_2 + \text{H}_2 + \text{N}_2$ as the equimolar (in the gas phase) processes.

5 SIMULTANEOUS STOICHIOMETRIC CHEMICAL REACTIONS

Advancements of chemical reactions 1 and 2:

$$d\xi_{r1} = \frac{dn_{r,r1}}{\nu_{r,r1}} \quad \text{and} \quad d\xi_{r2} = \frac{dn_{r,r2}}{\nu_{r,r2}}$$

whereby subscript r points to the appropriate reactant in the stoichiometric reaction system, and subscript $r1$ or $r2$ the stoichiometric chemical reaction 1 and chemical reaction 2 (the set of two simultaneous chemical reactions). In the reaction 1 analyzed there is for all the reactants:

$$n_{r,r1} = n_{r,r1,1} + \nu_{r,r1}\xi_{r1}$$

and in the reaction 2

$$n_{r,r2} = n_{r,r2,1} + \nu_{r,r2}\xi_{r2}$$

Taking into account the both simultaneous chemical reactions $r1$ and $r2$ yields for the r reactant, which can be present either in the reaction 1 or 2 or both:

$$n_r = n_{r,r1,1} + n_{r,r2,1} + \nu_{r,r1}\xi_{r1} + \nu_{r,r2}\xi_{r2} = n_{r,1} + \nu_{r,r1}\xi_{r1} + \nu_{r,r2}\xi_{r2}$$

because

$$n_{r,r1,1} + n_{r,r2,1} = n_{r,1}$$

The whole amount of all reactants in a process (i.e. the reactive mixture) is then to

$$\begin{aligned} n &= \sum_r n_{r,r1} + \sum_r n_{r,r2} = \sum_r n_{r,r1,1} + \xi_{r1} \sum_r \nu_{r,r1} + \sum_r n_{r,r2,1} + \xi_{r2} \sum_r \nu_{r,r2} = \\ &= \sum_r n_{r,1} + \xi_{r1} \sum_r \nu_{r,r1} + \xi_{r2} \sum_r \nu_{r,r2} = n_1 + \xi_{r1} \sum_r \nu_{r,r1} + \xi_{r2} \sum_r \nu_{r,r2} \end{aligned}$$

because there is obviously

$$\sum_r n_{r,r1,1} + \sum_r n_{r,r2,1} = \sum_r n_{r,1} = n_1$$

In every moment of a process the molar fraction of r -th reactant in the gas phase equals to

$$x_r = \frac{n_{r,1} + \nu_{r,r1}\xi_{r1} + \nu_{r,r2}\xi_{r2}}{\sum_r n_{r,1} + \xi_{r1} \sum_r \nu_{r,r1} + \xi_{r2} \sum_r \nu_{r,r2}} = \frac{n_{r,1} + \nu_{r,r1}\xi_{r1} + \nu_{r,r2}\xi_{r2}}{n_1 + \xi_{r1} \sum_r \nu_{r,r1} + \xi_{r2} \sum_r \nu_{r,r2}}$$

The chemical concentration exergy is therefore to

$$E_{\mu,r}^x = n_r \bar{R}T_0 \ln \frac{x_r}{x_{r,0}} = (n_{r,1} + \nu_{r,r1}\xi_{r1} + \nu_{r,r2}\xi_{r2}) \cdot \bar{R}T_0 \ln \left(\frac{1}{x_{r,0}} \cdot \frac{n_{r,1} + \nu_{r,r1}\xi_{r1} + \nu_{r,r2}\xi_{r2}}{n_1 + \xi_{r1} \sum_r \nu_{r,r1} + \xi_{r2} \sum_r \nu_{r,r2}} \right) \quad (07)$$

For the convenience the two simultaneous chemical reactions should be taken in such a form, that the appropriate stoichiometric coefficients refer to the appropriate amounts of species at the process begin.

5.1 Simultaneous Stoichiometric Chemical Reactions with Inerts

Advancements of chemical reactions 1 and 2:

$$d\xi_{r1} = \frac{dn_{r,r1}}{\nu_{r,r1}} \quad \text{and} \quad d\xi_{r2} = \frac{dn_{r,r2}}{\nu_{r,r2}}$$

whereby subscript r points to the appropriate reactant in the stoichiometric reaction $r1$ and $r2$, and so on. In the reaction $r1$ analyzed there is for all the reactants:

$$n_{r,r1} = n_{r,r1,1} + \nu_{r,r1}\xi_{r1}$$

and in the reaction $r2$

$$n_{r,r2} = n_{r,r2,1} + \nu_{r,r2}\xi_{r2}$$

and for inerts

$$n_{\text{int}} = n_{\text{int},1} = n_{\text{int},2}$$

Taking into account the both simultaneous chemical reactions $r1$ and $r2$ it yields for the r reactant, which can be present either in the reaction $r1$ or $r2$, or both:

$$n_r = n_{r,r1,1} + n_{r,r2,1} + \nu_{r,r1} \xi_{r1} + \nu_{r,r2} \xi_{r2} = n_{r,1} + \nu_{r,r1} \xi_{r1} + \nu_{r,r2} \xi_{r2}$$

because

$$n_{r,r1,1} + n_{r,r2,1} = n_{r,1}$$

The whole amount of all reactants in a process (i.e. the reactive mixture) including inerts is then to

$$\begin{aligned} n &= \sum_{\text{int}} n_{\text{int}} + \sum_r n_{r,r1} + \sum_r n_{r,r2} = \sum_{\text{int}} n_{\text{int}} + \sum_r n_{r,r1,1} + \xi_{r1} \sum_r \nu_{r,r1} + \sum_r n_{r,r2,1} + \xi_{r2} \sum_r \nu_{r,r2} = \\ &= n_1 + \xi_{r1} \sum_r \nu_{r,r1} + \xi_{r2} \sum_r \nu_{r,r2} \end{aligned}$$

because there is obviously

$$\sum_{\text{int}} n_{\text{int}} + \sum_r n_{r,r1,1} + \sum_r n_{r,r2,1} = n_1$$

In every moment of a process the molar fraction of r -th gaseous reactant equals to

$$x_r = \frac{n_{r,r1,1} + n_{r,r2,1} + \nu_{r,r1} \xi_{r1} + \nu_{r,r2} \xi_{r2}}{n_1 + \xi_{r1} \sum_r \nu_{r,r1} + \xi_{r2} \sum_r \nu_{r,r2}}$$

and of the inert int

$$x_{\text{int}} = \frac{n_{\text{int}}}{n_1 + \xi_{r1} \sum_r \nu_{r,r1} + \xi_{r2} \sum_r \nu_{r,r2}}$$

The chemical concentration exergy of reactant r in reaction 1 or 2 is therefore to

$$E_{\mu,r}^x = n_r \cdot \bar{R}T_0 \ln \frac{x_r}{x_{r,0}} = (n_{r,1} + \nu_{r,r1} \xi_{r1} + \nu_{r,r2} \xi_{r2}) \bar{R}T_0 \ln \left(\frac{1}{x_{r,0}} \cdot \frac{n_{r,1} + \nu_{r,r1} \xi_{r1} + \nu_{r,r2} \xi_{r2}}{n_1 + \xi_{r1} \sum_r \nu_{r,r1} + \xi_{r2} \sum_r \nu_{r,r2}} \right) \quad (08)$$

and for an inert int

$$E_{\mu,\text{int}}^x = n_{\text{int}} \cdot \bar{R}T_0 \ln \frac{x_{\text{int}}}{x_{\text{int},0}} = n_{\text{int}} \bar{R}T_0 \ln \left(\frac{1}{x_{\text{int},0}} \cdot \frac{n_{\text{int}}}{n_1 + \xi_{r1} \sum_r \nu_{r,r1} + \xi_{r2} \sum_r \nu_{r,r2}} \right)$$

5.2 Searching the Concentration Exergy Inversion Point K

The concentration exergy inversion point K , i.e. $\xi_{1,\text{extr}}$ and $\xi_{2,\text{extr}}$, in a two-dimensional case (for ξ_1 and ξ_2) will be now determined. The equations system should be simultaneously solved and inspected:

$$\frac{dE_{\mu,r}^x}{d\xi_{r1}} = 0 \quad \text{and} \quad \frac{dE_{\mu,r}^x}{d\xi_{r2}} = 0$$

evtl.

$$\frac{dE_{\mu,\text{int}}^x}{d\xi_{r1}} = 0 \quad \text{and} \quad \frac{dE_{\mu,\text{int}}^x}{d\xi_{r2}} = 0$$

for the inert free case of two simultaneous equations $r1$ and $r2$. The case with inerts, however, is a more general one, just like for the simple chemical reaction discussed above. Eqs. (07)–(08) are of the same form. Appropriate derivations are

$$\frac{d}{d\xi_{r1}} \frac{E_{\mu,r}^x}{RT_0} = v_{r,r1} \cdot \ln \left(\frac{1}{x_{r,0}} \cdot \frac{n_{r,1} + v_{r,r1} \xi_{r1} + v_{r,r2} \xi_{r2}}{n_1 + \xi_{r1} \sum_r v_{r,r1} + \xi_{r2} \sum_r v_{r,r2}} \right) + (n_{r,1} + v_{r,r1} \xi_{r1} + v_{r,r2} \xi_{r2}) \times$$

$$\times \frac{x_{r,0} \cdot \left(n_1 + \xi_{r1} \sum_r v_{r,r1} + \xi_{r2} \sum_r v_{r,r2} \right)}{n_{r,1} + v_{r,r1} \xi_{r1} + v_{r,r2} \xi_{r2}} \times$$

$$\times \frac{x_{r,0} \cdot \left(n_1 + \xi_{r1} \sum_r v_{r,r1} + \xi_{r2} \sum_r v_{r,r2} \right) \cdot v_{r,r1} - (n_{r,1} + v_{r,r1} \xi_{r1} + v_{r,r2} \xi_{r2}) \cdot x_{r,0} \cdot \sum_r v_{r,r1}}{\left(n_1 + \xi_{r1} \sum_r v_{r,r1} + \xi_{r2} \sum_r v_{r,r2} \right)^2 \cdot x_{r,0}^2}$$

and

$$\frac{d}{d\xi_{r2}} \frac{E_{\mu,r}^x}{RT_0} = v_{r,r2} \cdot \ln \left(\frac{1}{x_{r,0}} \cdot \frac{n_{r,1} + v_{r,r1} \xi_{r1} + v_{r,r2} \xi_{r2}}{n_1 + \xi_{r1} \sum_r v_{r,r1} + \xi_{r2} \sum_r v_{r,r2}} \right) + (n_{r,1} + v_{r,r1} \xi_{r1} + v_{r,r2} \xi_{r2}) \times$$

$$\times \frac{x_{r,0} \cdot \left(n_1 + \xi_{r1} \sum_r v_{r,r1} + \xi_{r2} \sum_r v_{r,r2} \right)}{n_{r,1} + v_{r,r1} \xi_{r1} + v_{r,r2} \xi_{r2}} \times$$

$$\times \frac{x_{r,0} \cdot \left(n_1 + \xi_{r1} \sum_r v_{r,r1} + \xi_{r2} \sum_r v_{r,r2} \right) \cdot v_{r,r2} - (n_{r,1} + v_{r,r1} \xi_{r1} + v_{r,r2} \xi_{r2}) \cdot x_{r,0} \cdot \sum_r v_{r,r2}}{\left(n_1 + \xi_{r1} \sum_r v_{r,r1} + \xi_{r2} \sum_r v_{r,r2} \right)^2 \cdot x_{r,0}^2}$$

The non-linear equation system ($\xi_{r1,extr}$ and $\xi_{r2,extr}$ are the searched unknown variables) after rearrangement has the following form

$$v_{r,r1} \cdot \ln \left(\frac{1}{x_{r,0}} \cdot \frac{n_{r,1} + v_{r,r1} \xi_{r1,extr} + v_{r,r2} \xi_{r2,extr}}{n_1 + \xi_{r1,extr} \sum_r v_{r,r1} + \xi_{r2,extr} \sum_r v_{r,r2}} \right) + v_{r,r1} - \frac{(n_{r,1} + v_{r,r1} \xi_{r1,extr} + v_{r,r2} \xi_{r2,extr})}{\left(n_1 + \xi_{r1,extr} \sum_r v_{r,r1} + \xi_{r2,extr} \sum_r v_{r,r2} \right)} \cdot \sum_r v_{r,r1} = 0$$

$$v_{r,r2} \cdot \ln \left(\frac{1}{x_{r,0}} \cdot \frac{n_{r,1} + v_{r,r1} \xi_{r1,extr} + v_{r,r2} \xi_{r2,extr}}{n_1 + \xi_{r1,extr} \sum_r v_{r,r1} + \xi_{r2,extr} \sum_r v_{r,r2}} \right) + v_{r,r2} - \frac{(n_{r,1} + v_{r,r1} \xi_{r1,extr} + v_{r,r2} \xi_{r2,extr})}{\left(n_1 + \xi_{r1,extr} \sum_r v_{r,r1} + \xi_{r2,extr} \sum_r v_{r,r2} \right)} \cdot \sum_r v_{r,r2} = 0$$

In the case a reactant r is a reaction partner in the reaction $r1$, the advancement $\xi_{r2,extr}$ of the reaction $r2$ is set to be equal to the original value, e.g. $\xi_{r2,extr} = \xi_{r2}$. The same yields for another case. But if the reactant r is a reaction partner in both the simultaneous reactions, the equation system should be solved and the resulting values $\xi_{r1,extr}$ and $\xi_{r2,extr}$ should be found.

After the values $\xi_{r1,extr}$ and $\xi_{r2,extr}$ have been found, parameters of the concentration exergy inversion point K is given by the following values

.) amount of reactant r :
$$n_{r,extr} = n_{r,1} + v_{r,r1} \xi_{r1,extr} + v_{r,r2} \xi_{r2,extr}$$

.) total amount of the reactive mixture (reactants):
$$n_{extr,(r)} = n_1 + \xi_{r1,extr} \sum_r v_{r,r1} + \xi_{r2,extr} \sum_r v_{r,r2}$$

.) molar fraction of specie reactant r :
$$x_{r,extr} = \frac{n_{r,1} + v_{r,r1} \xi_{r1,extr} + v_{r,r2} \xi_{r2,extr}}{n_1 + \xi_{r1,extr} \sum_r v_{r,r1} + \xi_{r2,extr} \sum_r v_{r,r2}}$$

Subscripts r refer to the reactants only (in the first $r1$ and the second $r2$ chemical reaction). The example of a such simultaneous reactions set is the combustion of the water gas (from gasification), i.e. $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$ & $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$.

For an inert int it has been derived above

$$E_{\mu,int}^x = n_{int} \cdot \bar{R}T_0 \ln \frac{x_{int}}{x_{int,0}} = n_{int} \bar{R}T_0 \ln \left(\frac{1}{x_{int,0}} \cdot \frac{n_{int}}{n_1 + \xi_{r1} \sum_r \nu_{r,r1} + \xi_{r2} \sum_r \nu_{r,r2}} \right)$$

and because

$$n = n_1 + \xi_{r1} \sum_r \nu_{r,r1} + \xi_{r2} \sum_r \nu_{r,r2}$$

it is

$$E_{\mu,int}^x = \left(n_1 + \xi_{r1} \sum_r \nu_{r,r1} + \xi_{r2} \sum_r \nu_{r,r2} \right) \cdot x_{int} \cdot \bar{R}T_0 \ln \left(\frac{x_{int}}{x_{int,0}} \right)$$

Thus

$$\frac{d}{dx_{int}} \left(\frac{E_{\mu,int}^x}{\bar{R}T_0 \left(n_1 + \xi_{r1} \sum_r \nu_{r,r1} + \xi_{r2} \sum_r \nu_{r,r2} \right)} \right) = x_{int} \cdot \frac{x_{int,0}}{x_{int}} \cdot \frac{1}{x_{int,0}} + \ln \frac{x_{int}}{x_{int,0}} = 1 + \ln \frac{x_{int}}{x_{int,0}}$$

where from

$$1 + \ln \frac{x_{int,extr}}{x_{int,0}} = 0$$

The result is (viz. [36], page 54–55)

$$x_{int,extr} = \frac{x_{int,0}}{e}$$

The example of such a simultaneous process is the combustion of a water gas ($\text{CO} + \text{H}_2$) in presence of the atmospheric nitrogen, i.e. $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$ & $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$ & N_2 . It is the combustion in an atmospheric air.

In fact, the complex simultaneous equilibria for combustion and gasification processes can be analyzed using simplified chemical reactions sets, maximum of two reactions, just like pointed above. The exactness of numerical results obtained, especially in case of large technological systems, in which these chemical reactions occur, is practically not reduced. It could be proved in many calculation tests, [46]–[48], [59].

6 NON-STOICHIOMETRIC CHEMICAL REACTIONS

Not always is the chemical reaction stoichiometry given at the hand. There can be a set of reactions solved to get the molar composition of the resulting combustion of gasification products. Such methods are detailed described e.g. in [60]–[61]. The number of simultaneous chemical reactions to solve is usually six up to ten, and the appropriate mathematical non-linear equation system with six up to ten unknown parameters is to solve. In fact, not all the reaction mixture resulting products are important for the thermodynamic analysis: their impact onto the numerical results can be omitted. Taking into account their presence in a calculation procedure, however, is essential. In such calculation methods the combustion of carbon (element C) with an atmospheric air (O_2 and N_2 mixture) needs to take into consideration atomic oxygen (O) and nitrogen (N). Their molar concentrations in flue gases can be set to zero for further analyzes. In this resulting mixture molar concentrations of following species are generally determined: CO, CO_2 , O_2 , N_2 , NO, C_2 (gas), C_7 (gas), N and O. The appropriate non-stoichiometric chemical reaction can be written down as



The nitric oxides NO_x are treated as the only one nitric monoxide NO . This is justified because it has been experimentally proved that in usual combustion processes the nitric monoxide fraction in all possible nitric oxides NO_x equals approximately to 85%.

For such a chemical reaction the exergy balance and the thermodynamic effectivity should be determined. It is not that complicated, as it seems to be, because the gas phase species can be all schematically described as



and so on. Thus, the molar concentrations vary between the start value (mostly zero) and certain values at the end. The appropriate exergy change inversion point can be found without problems and exergy changes (the created and/or diminished ones) calculated. In course of tests made by authors there could be stated that with a rising number of species taken into account the less number of them crossed the algebraic sign inversion point can be observed. The main difficulty in exact analysis and rating of non-stoichiometric chemical reactions is the lack of the resulting heat effect. The appropriate calculation procedure in the case of simultaneous reaction set containing more than two processes is not that easy (that's why it wasn't presented in [60]–[61], the following Band was expected about energy effects, but it was rejected by the publisher), and very often it should be taken from the practice. The general rule is that the thermodynamic effectivity quotient should be greater than one, because only in such a case the *Second Law of Thermodynamics* is fulfilled.

7 CONCLUSIONS

The presented approach to exergy analysis and rating of combustion and gasification processes as common chemical reactions is universal and made in the same way as analyzes of other so-called unit operations, which are important in thermodynamic considerations of modern power engineering systems. But not only these systems can be discussed using the general concept of the thermodynamic effectivity quotient: the concept can be applied to all the chemical reactions in the chemical & process engineering.

Numerous tests made by authors had lead to the statement that the presented method is universal. Some problems occurred in the case of catalytic chemical processes (e.g. for the “shift reaction” $CO + H_2O = CO_2 + H_2$, realized in two–three stages), where the numerical values of the thermodynamic effectivity was greater than one. But such a process is thermodynamically not possible, because of the *Second Law*. It could be stated that even such not directly defined chemical reactions can be analyzed correctly by appropriate reactants quantities, [63].

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