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EXERGY IN SUBSTANCE CHANGE PROCESSES

EXERGIE V PROCESECH ZMĚNY LÁTKY

**Abstract**

The exergy concept applied to substance change processes has been presented and discussed in detail. The very good known exergy partition into the thermal, mechanical and chemical one was revised. The special behavior of all the parts could be stated and the concentration part of the so-called chemical exergy carefully considered. The natural environment was discussed due to its importance for the special behavior of this concentration exergy part. The meaning of the specie concentration in the natural environment has been emphasized and compared with the appropriate role of the natural environment temperature. The considerations presented are the base for generalized analysis and rating of substance change processes.

**Abstrakt**

V článku je exaktně popsána exergetická koncepce v procesech změny látky. Je prodiskutován a ověřen dobře známý podíl exergie na část termickou, mechanickou a chemickou. Speciální vlastnosti těchto částí byly potvrzeny a testovaná tzv. chemická exergie. Byl určen význam životního prostředí na speciální vlastnosti koncentrační části chemické exergie. Význam koncentrace látky v životním prostředí byl zvýrazněn a porovnán s odpovídající roli teploty v životním prostředí. Tyto prezentované úvahy jsou základem pro všeobecnou analýzu a hodnocení procesů změny látky.

**1 INTRODUCTION**

A certain amount of a substance is a system by means of thermodynamics. Open systems can be divided into one-component and in general multi-component ones, the energy state of them can be characterized both by the inner energy  $U$  or the enthalpy  $I$ , as well. Investigating open thermodynamic systems two approaches of their analysis should be emphasized. The first one is typical for the so-called engineering thermodynamics and the power engineering applications, while the second one refers to the general chemical and process engineering analyses. Another word, in the first kind of systems only the substance quantity can change, in the second one, however, additionally its quality alters. The both approaches will be presented.

**2 SIMPLE OPEN SYSTEM WITHOUT SUBSTANCE QUALITY CHANGE**

The one-component open system will be sometimes called open system with accumulation. It is mainly presented in the so-called engineering thermodynamics as a tool for analyzing the gas tankage and/or gas tank emptying processes, e.g. [1]–[8]. The simple one-component open system can exchange energy with its surroundings as heat and/or work, but it can also accumulate the matter (working agent) and/or give it away back to its surroundings. The obvious *First Law* formulas for the closed and the flow systems are

$$dU = dQ + dL = TdS - pdV ; \quad dI = dQ + dL_t = TdS + Vdp \quad (01)$$

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where  $TdS$  is the change of the system energy content due to the reversible heat transfer, the term  $-pdV$  such a change, but due to the reversible absolute volume work, and  $Vdp$  once more such a change, but due to the useful work transfer. While quantities  $U$ ,  $I$ ,  $S$  and  $V$  are the extensive ones, for which the additive rule holds, it yields

$$d\bar{u} = Td\bar{s} - pd\bar{v} \quad \text{and} \quad d\bar{i} = Td\bar{s} + vdp$$

Because of the obvious relations

$$\bar{u} = \frac{U}{n} \quad \bar{s} = \frac{S}{n} \quad \bar{v} = \frac{V}{n} \quad \bar{i} = \frac{I}{n}$$

and assuming condition  $dn \neq 0$  (i.e.  $n \neq 0$ ) the following formulas can be obtained

$$d\left(\frac{U}{n}\right) = Td\left(\frac{S}{n}\right) - pd\left(\frac{V}{n}\right) \quad \text{and} \quad d\left(\frac{I}{n}\right) = Td\left(\frac{S}{n}\right) + \frac{V}{n}dp$$

and

$$\frac{ndU - Udn}{n^2} = \frac{T}{n^2}(ndS - Sdn) - \frac{p}{n^2}(ndV - Vdn); \quad \frac{ndI - Idn}{n^2} = \frac{T}{n^2}(ndS - Sdn) + \bar{v}dp$$

Multiplying both sides by  $n$  and rearranging, one becomes

$$dU = TdS - pdV + (\bar{u} + p\bar{v} - T\bar{s})dn = TdS - pdV + (\bar{i} - T\bar{s})dn \quad (02)$$

$$dI = TdS + Vdp + (\bar{i} - T\bar{s})dn \quad (03)$$

The term  $TdS$  in this equation does characterize the equilibrium thermal interaction, the term  $-pdV$  the mechanical, and the last term  $(\bar{i} - T\bar{s})dn$  the matter (substantial) one. This last term is identical with the specific free enthalpy (GIBBS' energy)

$$\bar{g}_0 = \bar{i}_0 - T_0\bar{s}_0$$

calculated for the intensities of natural environment, if only the system does substantially interact with it (the subscript 0), and multiplied by the differential change of the substance amount in a process. The quantity

$$\mu = \left(\frac{dU}{dn}\right)_{s,v} = \left(\frac{dI}{dn}\right)_{s,p} = \bar{g} = \bar{i} - T\bar{s}$$

is a chemical (or electrochemical) potential (e.g. [9]), although the correct meaning of this concept can be fully motivated only for a multi-component open system.

Eqs.(02)–(03) can be written down on the analogy of Eqs.(01) as

$$dU = dQ + dL + dL_\mu \quad \text{and} \quad dI = dQ + dL_t + dL_\mu$$

whereby  $dL_\mu = (\bar{i} - T\bar{s})dn = \mu dn$  is the so-called substantial (or chemical) work, due to the matter (substance) exchange with the surroundings of the analyzed system.

For the system exergy equations

$$dE_U = dE_Q + dE_L = (T - T_0)dS - (p - p_0)dV; \quad dE_I = dE_Q + dL_t = (T - T_0)dS + Vdp$$

with

$$\bar{e}_U = \frac{E_U}{n} \quad \text{and} \quad \bar{e}_I = \frac{E_I}{n}$$

regarding equations

$$E_U = (U - U_0) - T_0(S - S_0) + p_0(V - V_0) \quad \text{and} \quad E_I = (I - I_0) - T_0(S - S_0)$$

as divided by the mole number

$$\bar{e}_U = (\bar{u} - \bar{u}_0) - T_0(\bar{s} - \bar{s}_0) + p_0(\bar{v} - \bar{v}_0) \quad \text{and} \quad \bar{e}_I = (\bar{i} - \bar{i}_0) - T_0(\bar{s} - \bar{s}_0)$$

it yields

$$d\left(\frac{E_U}{n}\right) = (T - T_0)d\left(\frac{S}{n}\right) - (p - p_0)d\left(\frac{V}{n}\right); \quad d\left(\frac{E_I}{n}\right) = (T - T_0)d\left(\frac{S}{n}\right) + \frac{V}{n}dp$$

or

$$\frac{ndE_U - E_U dn}{n^2} = \frac{T - T_0}{n^2}(ndS - Sdn) - \frac{p - p_0}{n^2}(ndV - Vdn)$$

$$\frac{ndE_I - E_I dn}{n^2} = \frac{T - T_0}{n^2}(ndS - Sdn) + \bar{v}dp$$

and after multiplying the both sides by  $n$  and rearranging

$$\begin{aligned} dE_U &= (T - T_0)dS - (p - p_0)dV + [(\bar{u} - T\bar{s} + p\bar{v}) - (\bar{u}_0 - T_0\bar{s}_0 + p_0\bar{v}_0)] dn = \\ &= (T - T_0)dS - (p - p_0)dV + [(\bar{i} + p\bar{v}) - (\bar{i}_0 + p_0\bar{v}_0)] dn = \\ &= (T - T_0) dS - (p - p_0)dV + (\mu - \mu_0)dn \end{aligned}$$

$$dE_I = (T - T_0)dS + Vdp + [(\bar{i} - T\bar{s}) - (\bar{i}_0 - T_0\bar{s}_0)]dn = (T - T_0)dS + Vdp + (\mu - \mu_0)dn$$

which means, the substantial (or chemical) work exchanged with the system's surrounding, may it be the natural environment, contributes to the system exergy  $E_U$  or  $E_I$ , respectively. The useful chemical work, i.e. its exergy, will be to

$$dE_{L,\mu} = (\mu - \mu_0)dn = \left(1 - \frac{\mu_0}{\mu}\right)dL_\mu = \eta_\mu^C dL_\mu \quad (\equiv dE_\mu)$$

where  $\eta_\mu^C$  is the so-called *chemical CARNOT factor*, by analogy with the *thermal CARNOT factor*  $\eta_{th}^C$  or the *mechanical Carnot factor*  $\eta_m^C$ :

$$dE_Q = \eta_{th}^C dQ \quad (\equiv dE_{U,T} = dE_{I,T}); \quad dE_L = \eta_m^C dL \quad (\equiv dE_{U,p})$$

The terms  $E_\mu$ ,  $E_{U,T}$ ,  $E_{I,T}$  and  $E_{U,p}$  do mean the appropriate parts of the system exergy, namely the chemical, thermal (of the inner energy and of the enthalpy) and mechanical one, respectively, (cf [10]; in [11] the different meaning of the *chemical CARNOT factor* has been used).

### 3 ONE-COMPONENT OPEN SYSTEM

With assumptions

$$dU_{conv} = 0 \quad dS_{conv} = 0 \quad dV_{conv} = 0 \quad dn_{conv} = 0 \quad (04)$$

or

$$dI_{conv} = 0 \quad dS_{conv} = 0 \quad dn_{conv} = 0 \quad (05)$$

in the case of a one-component system, from the energy, entropy, matter or volume balances:

$$dU_{\text{conv}} = dQ + dQ_0 + dL + dL_0 + dL_{\mu} + dL_{\mu,0} = 0 \quad (06)$$

$$dS_{\text{conv}} = \frac{dQ}{T} + \frac{dQ_0}{T_0} + dS_{\text{irr}} = 0 ; \quad dn_{\text{conv}} = \frac{dL_{\mu}}{\mu} + \frac{dL_{\mu,0}}{\mu_0} = 0 ; \quad dV_{\text{conv}} = \frac{dL}{p} + \frac{dL_0}{p_0} = 0$$

or

$$dI_{\text{conv}} = dQ + dQ_0 + dL_t + dL_{\mu} + dL_{\mu,0} = 0 \quad (07)$$

$$dS_{\text{conv}} = \frac{dQ}{T} + \frac{dQ_0}{T_0} + dS_{\text{irr}} = 0 ; \quad dn_{\text{conv}} = \frac{dL_{\mu}}{\mu} + \frac{dL_{\mu,0}}{\mu_0} = 0$$

follow the expressions for the appropriate energy interactions with the natural environment

$$dQ_0 = -\frac{T_0}{T} dQ - T_0 dS_{\text{irr}} ; \quad dL_0 = -\frac{p_0}{p} dL ; \quad dL_{\mu,0} = \frac{\mu_0}{\mu} dL_{\mu}$$

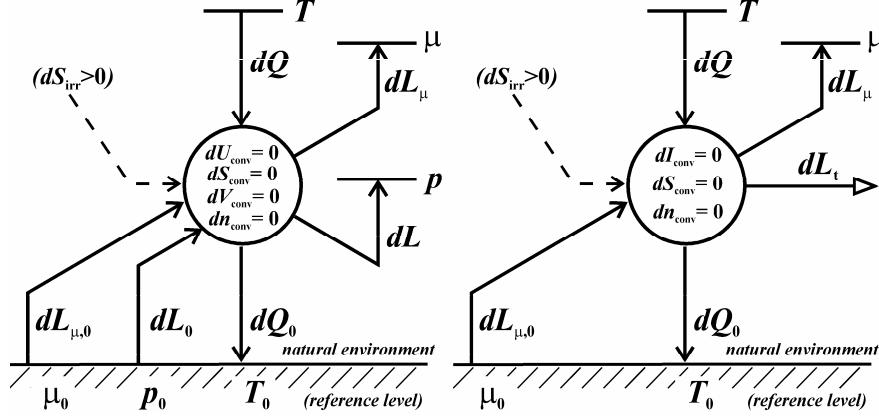


Fig. 1 Energy converter as an open one–component system without accumulation

whereby  $dn=dn_0$  (in a one–component open system no chemical reactions take place, which eventually could change the total matter quantity), Fig. 1. Input and output matter flows can differ only by means of their chemical potential, due to concentrations in external multi–component systems, interacting with the analyzed energy converter (one of these systems is the natural environment, for which  $x=x_0$ , the other one can be for example the pure substance reservoir, in which  $x=1$ ) or phase changes. Putting the above dependencies into Eqs.(06)–(07), respectively, yields

$$\left(1 - \frac{T_0}{T}\right) dQ + \left(1 - \frac{p_0}{p}\right) dL + \left(1 - \frac{\mu_0}{\mu}\right) dL_{\mu} = T_0 dS_{\text{irr}} \quad (08)$$

or

$$\left(1 - \frac{T_0}{T}\right) dQ + dL_t + \left(1 - \frac{\mu_0}{\mu}\right) dL_{\mu} = T_0 dS_{\text{irr}} \quad (09)$$

for the one–component open system. The derived equations are exergy balances of an irreversible energy conversion without accumulation. In this energy conversion do take part the work (volume or shaft, i.e. useful one), the heat and/or the (absolute) chemical work (multiplied by the *chemical CARNOT factor*).

Applying *First Law* formulations for the open system considered,

$$dU = dQ + dL + dL_{\mu} ; \quad dI = dQ + dL_t + dL_{\mu}$$

the exergy equations for it will be to

$$dE_U = dU - T_0 dS + p_0 dV - \mu_0 dn \quad (10)$$

or (with regard to the formula  $dU = TdS - pdV + \mu dn$ )

$$dE_U = (T - T_0) dS - (p - p_0) dV + (\mu - \mu_0) dn \quad (11)$$

and

$$dE_I = dI - T_0 dS - \mu_0 dn \quad (12)$$

or (with regard to  $dI = TdS + \mu dn$ )

$$dE_I = (T - T_0) dS + V dp + (\mu - \mu_0) dn \quad (13)$$

whereby expressions  $dL = -pdV$ ,  $dL_t = Vdp$  and  $dL_\mu = \mu dn$  have been taken into account.

In the case, conditions according to Eqs.(04)–(05) are not valid, i.e. there is an one–component open system with accumulation, and

$$dU_{\text{conv}} \neq 0 \quad dS_{\text{conv}} \neq 0 \quad dn_{\text{conv}} \neq 0 \quad dV_{\text{conv}} \neq 0$$

or

$$dI_{\text{conv}} \neq 0 \quad dS_{\text{conv}} \neq 0 \quad dn_{\text{conv}} \neq 0$$

exergy balances for the irreversible energy conversion processes in such a system can be obtained, viz.

$$dE_U = \left(1 - \frac{T_0}{T}\right) dQ + \left(1 - \frac{p_0}{p}\right) dL + \left(1 - \frac{\mu_0}{\mu}\right) dL_\mu - T_0 dS_{\text{irr}} \quad (14)$$

$$dE_I = \left(1 - \frac{T_0}{T}\right) dQ + dL_t + \left(1 - \frac{\mu_0}{\mu}\right) dL_\mu - T_0 dS_{\text{irr}} \quad (15)$$

or

$$d\bar{e}_U = \left(1 - \frac{T_0}{T}\right) d\bar{q} + \left(1 - \frac{p_0}{p}\right) d\bar{l} + \left(1 - \frac{\mu_0}{\mu}\right) d\bar{l}_\mu - T_0 d\bar{s}_{\text{irr}}$$

$$d\bar{e}_I = \left(1 - \frac{T_0}{T}\right) d\bar{q} + d\bar{l}_t + \left(1 - \frac{\mu_0}{\mu}\right) d\bar{l}_\mu - T_0 d\bar{s}_{\text{irr}}$$

The useful (shaft or technical) work  $dI_t$ , which is necessary to „produce“ 1 kilo–mole (or 1 mole) of the substance in a pure state from the natural environment at  $T_0$  and  $p_0$  by  $dS_{\text{irr}}=0$  in an energy converter without accumulation ( $dE_I=0$ ), is thus from the last equation to

$$dL_t = -\left(1 - \frac{\mu_0}{\mu}\right) dL_\mu = -(\mu - \mu_0) dn \quad \text{or} \quad \frac{dL_t}{dn} = \bar{l}_t = -(\mu - \mu_0) \quad (16)$$

and the useful (shaft) work obtained in a reversible process of devaluating this substance from the pure state ( $x=1$ ) to the natural environment state (where  $x=x_0$ ) at  $T_0$  and  $p_0$ , Eq.(11) and Eq.(13), is the so–called zero–exergy of this substance, i.e.

$$\bar{e}_\mu^0 \equiv -\bar{l}_t = \mu - \mu_0 \quad (17)$$

For the atmospheric oxygen O<sub>2</sub> it will be for example

$$\bar{e}_{\mu, O_2}^0 = \mu_{O_2}^0 + \bar{R}T_0 \ln 1 - \mu_{O_2}^0 - \bar{R}T_0 \ln x_{O_2,0} = -\bar{R}T_0 \ln x_{O_2,0} \quad (18)$$

The reverse chemical reaction can be called the revaluation one, e.g. [12].

For better understanding the exergy concept of the one-component open system, in the above equations, the electrical work  $dL_{el}=U_{el}dq_{el}$  will be taken into account instead of the chemical one  $dL_{\mu}$ , [13], [29]. It is obvious, that the electrical potential of the natural environment (the Earth) equals to zero, i.e.  $U_{el,0}=0$ , so Eqs.(08)–(09) will be to

$$\left(1 - \frac{T_0}{T}\right)dQ + \left(1 - \frac{p_0}{p}\right)dL + dL_{el} = T_0 dS_{irr} \quad \text{or} \quad \left(1 - \frac{T_0}{T}\right)dQ + dL_t + dL_{el} = T_0 dS_{irr}$$

and instead of Eqs.(10)–(13) one becomes following expressions

$$\begin{aligned} dE_U &= dU - T_0 dS + p_0 dV; & dE_U &= (T - T_0)dS - (p - p_0)dV - U_{el}dq_{el} \\ dE_I &= dI - T_0 dS; & dE_I &= (T - T_0)dS - Vdp - U_{el}dq_{el} \end{aligned}$$

Finally, the exergy balance Eqs.(14)–(15), will change to

$$dE_U = \left(1 - \frac{T_0}{T}\right)dQ + \left(1 - \frac{p_0}{p}\right)dL + dL_{el} - T_0 dS_{irr}; \quad dE_I = \left(1 - \frac{T_0}{T}\right)dQ + dL_t + dL_{el} - T_0 dS_{irr}$$

Thus, the electrical work is equivalent to the useful work, which is very good known and commonly experienced as a shaft work.

It is interesting, that although the already very often discussed in the subject literature problem of the form of relations

$$E_{U,0} = U_0 - T_0 S_0 + p_0 V_0 - \mu_0 n_0 = 0 \quad E_{I,0} = I_0 - T_0 S_0 - \mu_0 n_0 = 0$$

or

$$E_{U,0} = U_0 - T_0 S_0 + p_0 V_0 = 0 \quad E_{I,0} = I_0 - T_0 S_0 = 0 \quad (19)$$

the last two for  $dn=0$ , when the state of natural environment is assumed, that is by its intensities  $T_0$ ,  $p_0$  and/or  $\mu_0$ , the appropriate exergy values should equal to zero, but it is not the case. For the ideal gas e.g. yields

$$i_0 = c_p T_0; \quad s_0 = c_p \ln T_0 - R \ln p_0$$

and with Eq.(19) these relations will be to

$$e_{1,0} = c_p T_0 - c_p T_0 \ln T_0 + R T_0 \ln p_0$$

Assuming the obvious fact, the natural environment pressure equals to 1 (unitary pressure), then the solution of such an equation,

$$c_p T_0 (1 - \ln T_0) = 0$$

will give the strictly mathematical result:  $T_0=0$  or  $T_0=e$ , whereby  $e=2.71828$  is the base of natural logarithms. Such an unexpected result will be obtained due to the common and fundamental mistake. Setting the last relation equal to zero should take into account not only the natural environment state, but also another, a different thermodynamic state. Only then the numerical value of such an expression will be equal to zero, namely the natural environment state has to be taken as a limit of the relation

$$e_{1,0} = c_p(T - T_0) - c_p T_0 \ln \frac{T}{T_0} + RT_0 \ln \frac{p}{p_0}$$

i.e.

$$e_{1,0} = \lim_{\substack{T \rightarrow T_0 \\ p \rightarrow p_0}} \left[ c_p(T - T_0) - c_p T_0 \ln \frac{T}{T_0} + RT_0 \ln \frac{p}{p_0} \right] = 0$$

In this place the analogy of the last expression with the formula for the chemical potential can be mentioned. It is namely

$$\mu = \mu^0 + RT \ln \frac{p}{p^0} = \mu^0 + RT \ln p$$

whereby  $p^0$  is the unitary pressure of the referred state, the numerical value of which is assumed in a fully arbitrary way, and usually it equals to the standard chemical pressure of 1 ata, or better to express, the right-hand side of the last relation is a limit for  $p^0 \rightarrow 1$ , [9], [14], [29]. In the above relation the appropriate temperature of referred state is hidden, the so-called standard chemical temperature of  $T^0=293.15$  K, for which there is  $\mu^0=g^0$ . In exergy equations the roles of the standard chemical intensities take over the intensities of the natural environment.

The mentioned at the begin of this discussion equations for the exergy of the inner energy and of the enthalpy for the natural environment state should be treated as changing limits of appropriate intensities, i.e.  $T \rightarrow T_0$ ,  $p \rightarrow p_0$ , and eventually  $\mu \rightarrow \mu_0$ . Only this interpretation ensures the only logically motivated numerical value at  $T_0$ ,  $p_0$  and  $\mu_0$ . It is possible, that the statement discussed above is one of the most important reasons for the promoting complicated exergy definitions and the desperate fight against exergy definitions, which are simple, easy understandable, clear and very universal.

#### 4 GENERALIZED MULTI-COMPONENT OPEN SYSTEM

The more interesting case of the thermodynamic open system is the multi-component one, in which chemical reactions can occur. In such a system the inlet species  $j$  from the natural environment (the reference level 0) in the Fig. 2 are not in general identical with the outlet species  $j$ . They can differ in quantity and quality, as well.

For conditions Eqs.(04)–(06), whereby in the case of the lack of chemical reactions

$$dn_{j,\text{conv}} = 0 \quad (20)$$

is valid, the appropriate exergy balance of the multi-component open system will be on the analogy of Eqs.(08)–(09) to

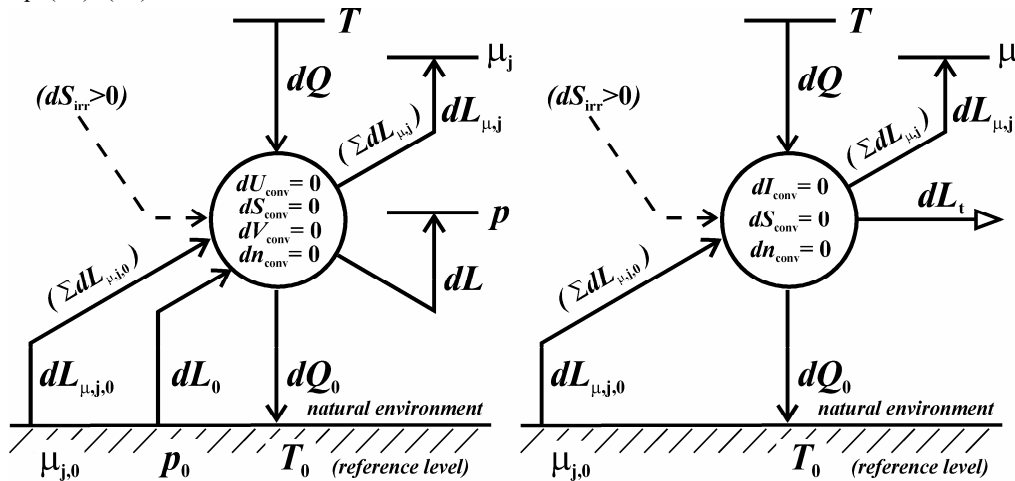


Fig. 2 Energy converter as an open multi-component system without accumulation

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

or

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

The absolute chemical work of a specie  $j$ , equal to  $dL_{\mu,j} = \mu_j dn_j$ , means a chemical energy change of this specie while crossing the converter between its inlet and outlet, [15], [29].

Using the *First Law* formula for a multi-component system with chemical work similarly to Eqs.(16)–(17), i.e.

$$dU = dQ + dL + \sum dL_{\mu,j} \quad \text{and} \quad dI = dQ + dL_t + \sum dL_{\mu,j}$$

for the exergy of such a system yields

$$dE_U = dU - T_0 dS + p_0 dV - \sum \mu_{j,0} dn_j \quad (21)$$

or

$$dE_U = (T - T_0)dS - (p - p_0)dV + \sum (\mu_j - \mu_{j,0})dn_j \quad (22)$$

and

$$dE_I = dI - T_0 dS - \sum \mu_{j,0} dn_j \quad (23)$$

or

$$dE_I = (T - T_0)dS + V dp + \sum (\mu_j - \mu_{j,0})dn_j \quad (24)$$

To formulate appropriate exergy balances, the system is to be analyzed as an energy converter with accumulation of all properties. The last are given by conditions (04)–(06) and (20). After easy algebraic operations it will be similar to Eqs.(14)–(15)

$$dE_U = \left(1 - \frac{T_0}{T}\right)dQ + \left(1 - \frac{p_0}{p}\right)dL + \sum \left(1 - \frac{\mu_{j,0}}{\mu_j}\right)dL_{\mu,j} - T_0 dS_{\text{irr}} \quad (25)$$

and

$$dE_I = \left(1 - \frac{T_0}{T}\right)dQ + dL_t + \sum \left(1 - \frac{\mu_{j,0}}{\mu_j}\right)dL_{\mu,j} - T_0 dS_{\text{irr}} \quad (26)$$

Are there chemical reactions in such a system present, the particular species will disappear, produced, or remain unchanged, and instead of the condition (20) three general cases are possible, i.e.

$$dn_{j,\text{conv}} < 0 \quad dn_{j,\text{conv}} > 0 \quad \text{or} \quad dn_{j,\text{conv}} = 0$$

The special case will result from the stoichiometry of the analyzed chemical reaction.

## 5 NATURAL ENVIRONMENT — THE REFERENCE SYSTEM

The important source of difficulties in applying, when not even understanding the exergy concept, is the natural environment, which occurs in the proper exergy definition. Many trials were undertaken to define the main environment intensities  $T_0$  or  $p_0$  in an objective way, especially the first of



them, but they were not generally accepted. Discussions in the literature have been stopped, but the problem did not disappear. For example the temperature of 9.30 °C ( $T_0=282.45$  K) has been suggested as a weighted year average environment temperature of the atmospheric air in the city of Dresden (Germany), [33]–[34], and in the city of Tarnów (ca. 600 km eastwards, in Poland) 8.80 °C ( $T_0=281.95$  K). For an environment temperature  $T_0$  as a reference one, there was very often applied the lowest temperature in the analyzed process, but in such a case there is not an exergy analysis at all! The further trials to obtain an exact mean value of the environment pressure are not known, because of the very poor effect of this intensity on the thermo–mechanical exergy.

The importance of taking into account the natural environment state as a reference state into thermodynamic analyses is generally known and appreciated. It allows more accurate statements about power processes, which always take place in the given natural environment. The concept of the useful work can be considered as an origin of such understanding of the role of the natural environment in the engineering thermodynamic analysis. In the older engineering thermodynamics text–books concepts of three forms of work were usually introduced: the volume work (as physical or absolute), the technical (shaft) and the useful work. The first of them is the known concept of the volume absolute work relating to the closed system ( $dL=-pdV$ ), the second one is the shaft work relating to the so–called flow system ( $dL_t=Vdp$ ). The useful work in such a presentation is the absolute volume work of the closed system being in mechanical interaction with the natural environment. The performed absolute work  $dL$  was not the work amount, one could directly apply in the engineering (power) system, because the work of the natural environment  $dL_0=-p_0dV$  should be taken into account to become

$$dL_{\text{use}} = dL - dL_0 = -(p - p_0)dV = \frac{p - p_0}{p} dL \quad (27)$$

The useful work is equivalent to the shaft (or technical) work  $dL_t$  of the flow system, which can be fully utilized for practical purposes, i.e.  $dL_{\text{use}} \equiv dL_t$ . From the above reminder can be stated, that the numerical value of the natural environment pressure  $p_0$  in fact is not of the decisive meaning in the flow systems thermodynamic analysis, and just these systems are the most important ones for the power engineering.

The very similar problem concerns the heat conversion into (useful) work in the so–called CARNOT engine, the thermodynamic model of which is the (reversible) CARNOT cycle. In many engineering thermodynamics text–books there is not strictly distinguished between the general work concept and the useful work concept. The CARNOT engine univocally produces the useful work  $dL_{\text{use}}$  from the heat  $dQ$  supplied at the temperatures  $T>T_0$ . The heat  $dQ_0$  is carried away from this engine at  $T_0$ . Generally, the last temperature is called often *the temperature of the lower heat source*, but for the power engineering processes it is equivalent to the natural environment intensity  $T_0$ . Thus

$$dL_{\text{use}} = dQ - dQ_0 = (T - T_0)dS = \frac{T - T_0}{T} dQ \quad (28)$$

The numerical value of the temperature  $T_0$  is usually fixed in analyses, although its changes are of the great importance for practical results. It can be proved in which grade the change of the environment temperature  $T_0$  in Eq.(28) and the environment pressure  $p_0$  in Eq.(27) do have an effect on the useful work amount in both cases. The so–called

$$\text{mechanical} \quad \eta_m^c = \frac{p - p_0}{p} \quad \text{and} \quad \text{thermal} \quad \eta_{\text{th}}^c = \frac{T - T_0}{T}$$

CARNOT factor (e.g. [16]–[17]) in above equations changes then as follows:

$$d\eta_{\text{th}}^c = \frac{\partial \eta_{\text{th}}^c}{\partial T} dT + \frac{\partial \eta_{\text{th}}^c}{\partial T_0} dT_0 = \frac{T_0}{T^2} dT - \frac{1}{T} dT_0 = \frac{T_0}{T} \left( \frac{dT}{T} - \frac{dT_0}{T_0} \right)$$

and

$$d\eta_m^c = \frac{\partial \eta_m^c}{\partial p} dp + \frac{\partial \eta_m^c}{\partial p_0} dp_0 = \frac{p_0}{p^2} dp - \frac{1}{p} dp_0 = \frac{p_0}{p} \left( \frac{dp}{p} - \frac{dp_0}{p_0} \right)$$

The influence weight of the system (source) pressure  $p$  or the environment pressure  $p_0$  and the system (source) temperature  $T$  or the environment temperature  $T_0$  in the second case onto the *CARNOT factor* change is equivalent, if there is only

$$dT = \frac{T}{T_0} dT_0 \quad \text{or} \quad dp = \frac{p}{p_0} dp_0$$

Are temperatures  $T > T_0$  (or pressures  $p > p_0$ ), it is evident, that the influence of the  $T_0$  or  $p_0$  change onto the *CARNOT factor* numerical value is much greater, than that of the  $T$  or  $p$  change (the multiplicity is equal to the ratio of  $T$  and  $T_0$  or  $p$  and  $p_0$ , respectively). At  $T < T_0$  (or  $p < p_0$ ) however, on the contrary, the influence of the change of the natural environment intensities on the *CARNOT factor* is less, then that of the  $T$  (or  $p$ ) change. Hence, the conclusion can be made, that the numerical values of natural environment intensities are very important for thermodynamic analysis results of the thermo–mechanical (power) processes, for which usually  $T > T_0$  and/or  $p > p_0$ . The problem, however, has not been solved in a satisfactory way. But the lack of universal, univocal numerical values of the natural environment intensities  $T_0$  and  $p_0$  is paradoxically the advantage of the exergy concept and the whole exergy method. This circumstance allows investigations of the influence of their changes on the power system operation, e.g. [18]–[20] and lately [21].

The exact definition of the natural environment temperature  $T_0$  and pressure  $p_0$  was really not such in a focus of investigators' interest, as this is observed in the case of its chemical composition, expressed by molar concentrations  $x_{j,0}$ . Various models of the natural environment have been proposed. It can be stated, however, that each of them has its advantages and disadvantages. No one of them fulfils all needs; but each of them seems to be an interesting particular idea, which enriches the whole problem understanding. For species represented in the mostly assumed natural environment, the atmospheric air, there are not so many problems in the exact definition of their so–called chemical exergies, especially the normal chemical standard exergy and the chemical zero–exergy, which are the useful work amounts obtained in a reversible process of moving them from the pure state ( $x_j=1$ ) to the natural environment ( $x_j=x_{j,0}$ ), first at  $T_0$  and  $p_0$ , and for the second one at  $T^0$  and  $p^0$ . Because of the assumed reversibility, it refers to the useful work amount necessary to produce the pure state from the natural environment. The atmospheric nitrogen  $N_2$  is represented in the air (the obvious natural environment) at its molar concentration  $x_{N_2,0}$ , the oxygen  $O_2$  at  $x_{O_2,0}$ , the carbon dioxide  $CO_2$  at  $x_{CO_2,0}$ , and so on. The exergy definition presented in previous author's contributions says that the exergy of the natural environment equals univocally to zero. The symmetry of the very good known expression for the chemical potential of the specie  $j$  as its molar free enthalpy (or GIBBS' energy)

$$\mu_j = \mu_j^0 + \bar{R}T \ln x_j \quad (29)$$

and of the expression for the chemical part of the system exergy in a flow system for  $T=T_0$  and  $p=p_0$  yields

$$\bar{e}_{\mu,j,0}(T_0, p_0, x_{j,0}) = \bar{e}_{\mu,j}^0(T_0, p_0, x_j=1) + \bar{R}T_0 \ln x_{j,0} = 0$$

where the first term of the right–hand side is the so–called zero–exergy and the second one the so–called chemical concentration exergy part, e.g. [17], [22]–[23], [29], [32], because of

$$\bar{e}_{\mu,j,0}(T_0, p_0, x_{j,0}) = \mu_{j,0}(T_0, p_0, x_{j,0}) = \Delta \bar{g}_{j,0}(T_0, p_0) = \Delta \bar{i}_j(T_0, p_0) - T_0 \Delta \bar{s}_j(T_0, p_0) = 0$$

and hence for the above mentioned components of the atmospheric air one becomes the following zero–exergy values:

$$\bar{e}_{\mu, N_2}^0 = -\bar{R}T_0 \ln x_{N_2,0}; \quad \bar{e}_{\mu, O_2}^0 = -\bar{R}T_0 \ln x_{O_2,0}; \quad \bar{e}_{\mu, CO_2}^0 = -\bar{R}T_0 \ln x_{CO_2,0} \quad (30)$$

Appropriate standard chemical exergies, calculated for the standard chemical temperature  $T^0=293.15$  K and  $p^0=1$  ata, respectively, will be to

$$\bar{e}_{\mu, N_2}^n = -\bar{R}T^0 \ln x_{N_2,0}; \quad \bar{e}_{\mu, O_2}^n = -\bar{R}T^0 \ln x_{O_2,0}; \quad \bar{e}_{\mu, CO_2}^n = -\bar{R}T^0 \ln x_{CO_2,0} \quad (31)$$

The Eqs.(30)–(31) refer to useful work amounts needed to the reversible isothermal (at  $T_0$  or  $T^0$ , respectively) compression of the particular specie  $j$  from the pressure  $x_{j,0}p_0$  to  $p_0$ , or to obtain the pure specie  $j$  ( $x_j=1$ ) from the natural environment (atmospheric air), in which it occurs at  $x_{j,0}<1$ . Hence, the above zero–exergies and the standard chemical exergies are positive (i.e. greater zero) and stand for the negative isobaric–isotherm change of the appropriate system exergy. The problem under discussion is the atmospheric air humidity: the air can be assumed as saturated (i.e.  $\varphi=1$ ) one at  $T_0$ ,  $p_0$  or an arbitrary value can be assumed, e.g. [24]. Because of the very poor effect of the air natural humidity on the exergy value, this air can be assumed as to be dry.

It can be stated, that there are no problems calculating the zero–exergy for species, if only the natural environment temperature  $T_0$ , the pressure  $p_0$  and their molar concentrations, the  $x_{j,0}$  values, are known. Is the analyzed compound **A** not present in the obvious natural environment, it must be produced in the so–called devaluation chemical reaction by JAN SZARGUT, e.g. [24], or more exact to say, devaluated into the natural environment species. Thus, the general form of such a reaction can be symbolically expressed as



where the subscript *nes* refers to substances  $\mathbf{B}_{\text{nes}}$  present in the assumed natural environment (at  $x_{j,0}$ ). The **A** is the compound not present in this natural environment, devaluated into substances  $\mathbf{B}_{\text{nes}}$  in the chemical reaction taking place in the natural environment ( $T_0, p_0$ ) itself to determine the zero–exergy, or at chemical normal (standard) conditions, i.e.  $T^0$  and  $p^0$ , to determine the standard chemical exergy. The above devaluation reaction differs slightly from that presented by WOLFGANG FRATZSCHER ([23], p.122), but there is no need here to use his procedure of determining zero–exergies, which is based on the JAN SZARGUT'S scheme, modified to be more convenient and useful.

In fact, this procedure requires a very well defined natural environment as a reference state. Similar to problems with the exact determination of natural environment intensities  $T_0$  and  $p_0$ , there is not possible to give generally valid molar concentration values of the reference substances, characterizing their occurrence in the natural environment. Many different models have been proposed in the literature (e.g. [25]–[26]), each investigator tried to make his model work for assumed particular purposes, but it cannot be stated, such–and–such one is more general — the same situation has been presented above, and referred to the generally valid numerical values of  $T_0$  and  $p_0$ . Because of the great importance of the chemical energy conversions in the engineering process analysis, an interesting way of solution for the natural multi–component environment model is to find in [27], pp.217–218. ADRIAN BEJAN introduces a so–called *restricted dead state* of the mixture system, which is *the state where only temperature and pressure match the corresponding environmental values*. The zero–exergies calculated for such a state are not then necessarily equal to the zero–exergies enjoyed by the multi–component natural environment in its ultimate (proper) dead state.

From the above discussion can be concluded, that the natural environment problem cannot be solved in a general form and there is not possible to give universal numerical values of its intensities and composition. For the exergy method of thermodynamic analysis it is enough to state, that in time of analysis the assumed values of  $T_0, p_0$  and  $x_{j,0}$  do not change.

One more very important statement should be mentioned, which refers to the molar concentration of species produced by the devaluation chemical reaction, Eq.(32). It equals always to one ( $x_{A,0}=1$ ), for this reaction is a stoichiometric one with the extent  $\xi=1$  (the appropriate assumptions,

e.g. [24]). This is an important statement, especially for the investigation of energy conversions in mixing processes, or generally, chemical ones.

## 6 CHEMICAL REACTION OF DEVALUATION

The so-called devaluation chemical reaction, Eq.(32), is a process at  $T_0$  and  $p_0$ , in which the chemical compound **A** will be decomposed into species **B**<sub>nes</sub> represented in the assumed natural environment. The special exergy value, the so-called zero-exergy of the specie **A**, results from Eq.(21) or Eq.(23). For constant  $T$  and  $p$  or  $V$ , one becomes the chemical exergy equation as

$$dE_{U,\mu} = dE_{I,\mu} = dE_{\mu} = -\sum \mu_{j,0} dn_j$$

which, used for the devaluation reaction according to Eq.(32) is to

$$dE_{\mu} = -\sum v_j \mu_{j,0} d\xi = -\sum (v_{nes}^{(A)} \mu_{nes,0} + \mu_{A,0}^0) d\xi$$

because of  $dn_j = v_j^{(A)} d\xi$ , or after integration from  $\xi=0$  to  $\xi=1$

$$E_{\mu,A} = \bar{e}_{\mu,A}^0 = -\sum v_{nes}^{(A)} \mu_{nes,0} + \mu_{A,0}^0 \quad (33)$$

because  $v_A = -1$  and 1 kilo-mole (or 1 mole) of the compound **A** has been devaluated at  $T_0$  and  $p_0$ . The system exergy change according to the last equation does also correspond to the amount of the useful work, obtained in a reversible process of converting **A** into substances **B**<sub>nes</sub>, which are common in the natural environment, Eq.(32). This statement results also from the exergy balance, Eq.(26), at appropriate conditions, because of  $\bar{e}_{\mu,A}^0 \equiv -\bar{l}_{t,A}$ , viz. Eq.(17), [17], [22], [29], [32]. Is for example the carbon (graphite) **C** produced in a devaluation chemical reaction from the in assumed natural environment existing specie oxygen  $O_2$  ( $x_{O_2,0}$ ) and carbon dioxide  $CO_2$  ( $x_{CO_2,0}$ ), then according to Eq.(32) it can be written down



and thus from Eq.(33)

$$\bar{e}_{\mu,C}^0 = -\mu_{CO_2,0} + \mu_{O_2,0} + \mu_{C,0}^0$$

whereby  $v_{CO_2}=1$ ,  $v_{O_2}=-1$  and  $v_C=-1$ . Considering Eq.(29) for all reactants, it yields

$$\bar{e}_{\mu,C}^0 = -\mu_{CO_2,0}^0 + \mu_{O_2,0}^0 + \mu_{C,0}^0 + \bar{R}T_0 \ln \frac{x_{O_2,0}}{x_{CO_2,0}} = -\Delta \bar{g}_{CO_2,0}^0 + \bar{R}T_0 \ln \frac{x_{O_2,0}}{x_{CO_2,0}} \quad (34)$$

because at the assumed natural environment conditions (i.e.  $T_0$  and  $p_0$ ) there is

$$\mu_{O_2,0}^0 \equiv \Delta \bar{g}_{O_2,0}^0 = 0 \quad \text{and} \quad \mu_{C,0}^0 \equiv \Delta \bar{g}_{C,0}^0 = 0$$

Similar operations can be made to determine the next important stable element of the natural environment, which is not represented in it, the hydrogen  $H_2$ . The devaluation reaction producing  $H_2$  is according to Eq.(32)



and the Eq.(33) becomes with Eq.(29) to

$$\begin{aligned} \bar{e}_{\mu,H_2}^0 &= -\mu_{H_2O,0} + \frac{1}{2} \mu_{O_2,0} + \mu_{H_2,0} = -\mu_{H_2O,0}^0 + \frac{1}{2} \mu_{O_2,0}^0 + \mu_{H_2,0}^0 + \bar{R}T_0 \ln \frac{x_{O_2,0}}{x_{H_2O,0}} = \\ &= -\Delta \bar{g}_{H_2O,0}^0 + \bar{R}T_0 \ln \frac{x_{O_2,0}^{1/2}}{x_{H_2O,0}} \end{aligned} \quad (35)$$

In Eqs.(34)–(35) the molar concentration of the compound **A**, for which the devaluation reaction has been realized, and which is not represented in the natural environment, was set as equal to one, e.g. [17], [22], [29], [32]. Thus  $x_{C,0}=1$  and  $x_{H_2,0}=1$ . This is the so-called „apparent” molar concentration of a compound produced in devaluation reactions. The molar concentration of water in the natural environment can be assumed to be one either, if only such an environment has been chosen (generally, molar concentrations of species in a condensed state, i.e. liquids or solids, are in the chemical thermodynamics assumed to be equal to one). The following devaluation chemical reaction can be formulated to determine the zero-exergy of the carbon monoxide CO:



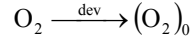
and applying Eq.(33),

$$\bar{e}_{\mu,\text{CO}}^0 = -\mu_{\text{CO}_2,0} + \frac{1}{2}\mu_{\text{O}_2,0} + \mu_{\text{CO},0}^0$$

whereby  $\nu_{\text{CO}_2}=1$ ,  $\nu_{\text{O}_2}=-\frac{1}{2}$  and  $\nu_{\text{CO}}=-1$ . Considering Equation (29) for all reactants, it yields

$$\bar{e}_{\mu,\text{CO}}^0 = -\mu_{\text{CO}_2,0}^0 + \frac{1}{2}\mu_{\text{O}_2,0}^0 + \mu_{\text{CO},0}^0 + \bar{R}T_0 \ln \frac{x_{\text{O}_2,0}^{1/2}}{x_{\text{CO}_2,0}} = \Delta\bar{g}_{\text{CO},0}^0 - \Delta\bar{g}_{\text{CO}_2,0}^0 + \bar{R}T_0 \ln \frac{x_{\text{O}_2,0}}{x_{\text{CO}_2,0}} \quad (36)$$

Two more general conclusions considering the devaluation chemical reaction can be made. The first of them is the „apparent” devaluation reaction of the specie, which is present in the natural environment, e.g. the oxygen O<sub>2</sub>. The appropriate devaluation reaction is then

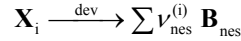


and the zero-exergy expression from Eq.(33) to

$$\bar{e}_{\mu,\text{O}_2}^0 = -\mu_{\text{O}_2,0}^0 + \mu_{\text{O}_2,0}^0 - \bar{R}T_0 \ln x_{\text{O}_2,0} = -\bar{R}T_0 \ln x_{\text{O}_2,0}$$

The result obtained here does fully agree with Eq.(30b) and Eq.(18), that have been derived in a different way.

The second conclusion is a very easy zero-exergy calculation method using zero-exergy values of the stable (in the assumed natural environment) elements, like e.g. O<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub> or C, for which the appropriate free enthalpy (the GIBBS' energy) equals to zero. Using again the general devaluation reaction for these stable species **X<sub>i</sub>**,



the Eq.(33) will be to

$$\bar{e}_{\mu,i}^0 = -\sum \nu_{\text{nes}}^{(i)} \mu_{\text{nes},0} + \mu_{i,0}^0 = -\sum \nu_{\text{nes}}^{(i)} \mu_{\text{nes},0} \quad (\text{for } \mu_{i,0}^0 \equiv \Delta\bar{g}_{i,0}^0 = 0)$$

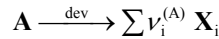
Eq.(32) gives the devaluation reaction, in which the compound **A** resolves into simple substances **B<sub>nes</sub>**. Thus, substituting the last expression for the zero-exergy of the simple stable substances into Eq.(33), it becomes

$$\bar{e}_{\mu,A}^0 = -\sum \nu_{\text{nes}}^{(A)} \mu_{\text{nes},0} + \mu_{A,0} = \mu_{A,0} - \sum \nu_i^{(A)} \sum \nu_{\text{nes}}^{(i)} \mu_{\text{nes},0} = \Delta\bar{g}_{A,0}^0 + \sum \nu_i^{(A)} \bar{e}_{\mu,i}^0 \quad (37)$$

whereby the obvious condition is valid

$$\sum \nu_{\text{nes}}^{(A)} \nu_{\text{nes}}^{(i)} = \nu_{\text{nes}}^{(A)}$$

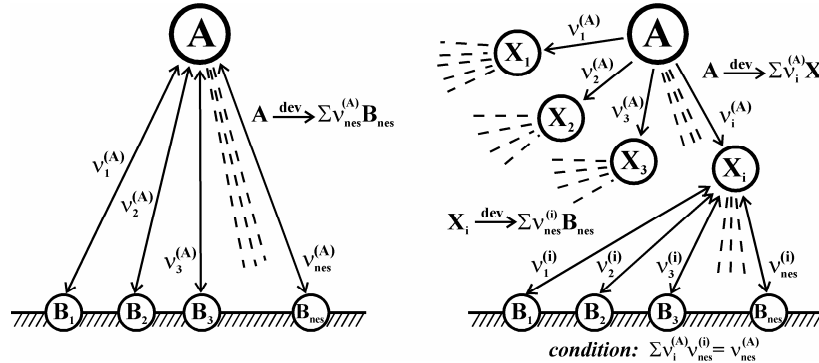
(also [23], p.126). The appropriate devaluation chemical reaction is then to



and can be called the indirect devaluation reaction of the compound **A**, e.g. [17], [22]–[23], [29], [32]. This indirect devaluation procedure has been derived in different ways, e.g. in [23], pp.125–126 (Bild 3.31.) or [22]. In Fig. 3 the two particular procedures, the direct and the indirect devaluation reactions are shown, whereas the apparent devaluation is a special case of the direct procedure. For carbon monoxide CO it is for example

$$\bar{e}_{\mu, \text{CO}}^0 = \Delta \bar{g}_{\text{CO}, 0}^0 + \bar{e}_{\mu, \text{C}}^0 + \frac{1}{2} \bar{e}_{\mu, \text{O}_2}^0 \quad (38)$$

which gives the same expression, Eq.(36), using zero–exergies calculated by Eqs.(34)–(35).



**Fig. 3** The direct (*left*) and indirect (*right*) devaluation chemical reaction of the compound **A**, the „apparent” devaluation is a special case of the direct process

## 7 CONSTITUENTS OF THE CHEMICAL EXERGY AND THEIR BEHAVIOR

From the derived Eqs.(15)–(16) for a multi–component system yields

$$d\bar{l}_t = -\frac{dE_{L,\mu}}{n} = -d\bar{e}_\mu = -\sum \left( 1 - \frac{\mu_{j,0}}{\mu_j} \right) d\bar{l}_{\mu,j} = -\sum (\mu_j - \mu_{j,0}) dx_j$$

and for a specie *j*

$$\bar{e}_{\mu,j} = \mu_j - \mu_{j,0}$$

which does mean the so–called chemical exergy of a homogeneous specie *j* that is represented in the natural environment. For the ideal mixtures of ideal gases the chemical potential of a specie *j* equals to

$$\mu_j = \mu_j^0 + \bar{R}T \ln x_j$$

The first right–hand side term takes into account chemical structural characteristics of the substance (specie) in a pure state ( $x_j=1$ ) and in the standard chemical conditions (the superscript 0, i.e. the temperature of  $T^0=283.15$  K and the pressure of  $p^0=1$  ata), the second one its properties in an (ideal) mixture. In the thermodynamic analyses it will be usually assumed, that the standard chemical conditions are approximately equal to the natural environment conditions, i.e.  $T^0 \cong T_0$  and  $p^0 \cong p_0$ , e.g. [23]–[24], [27]–[30], [32]. In special cases such an assumption leads to difficulties with simultaneous energy and exergy balancing, but very often makes the application of exergy method simple because of the possibility of the direct use of thermo–chemical tables. That is why the distinguishing between the zero–exergy and the standard chemical exergy is necessary.

The chemical exergy of a specie *j* in a multi–component open system consists of two parts, the constituents, by analogy with the form of a chemical potential relation. If then there are no differences in the chemical structure between the specie analyzed and the same specie represented in the natural environment, the only important exergy constituent is the exergy part, which results from

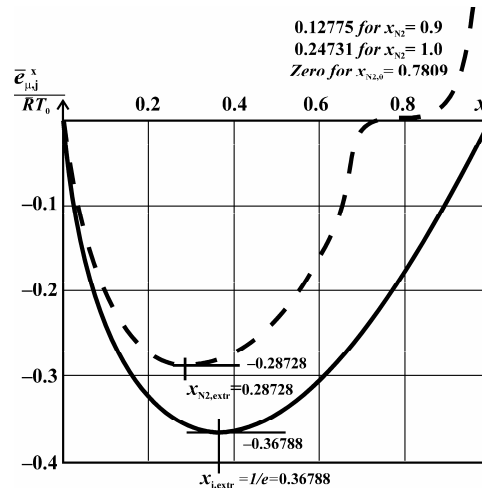
its molar fraction in the mixture. In this place should the fact be emphasized, that the substance produced in the devaluation chemical reaction according to JAN SZARGUT, which is not represented in the natural environment, is characterized by the molar fraction  $x_{j,0}=1$  in the so-called apparent natural environment. The reason why such a result will be obtained is the analysis typical for the so-called chemical thermodynamics, namely the stoichiometric formation chemical reaction, e.g. [31].

If then in an open multi-component thermodynamic system all the analyzed substances, even the produced ones (in a stoichiometric chemical devaluation reaction described above) do not differ from these present in the natural environment (even in the apparent one), then the whole chemical exergy of this system results from the molar fractions of components in the system and their molar fractions in the natural environment (also in the apparent one), i.e.

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

As like in the case of the thermo-mechanical exergy and its constituents the chemical composition exergy  $\bar{e}_{\mu,j}^x$  of the specie  $j$  in a mixture is characterized by the algebraic inversion sign plus or minus. The appropriate diagram of the concentration chemical exergy constituent dependence in the only sensible range from 0 to 1 in an ideal mixture of ideal species is presented in Fig. 4. The algebraic sign inversion point is reached in the point  $x_{j,\text{extr}}=1/e=0.36788$  for species with the molar fraction in the natural environment  $x_{j,0}=1$  (even in the case of the apparent natural environment). The value of  $e=2.71828$  is the base of natural logarithms. For substances represented in the natural environment the inversion point refers to the following values of the molar fraction in a process:

– oxygen	O <sub>2</sub>	$x_{\text{O}_2,0} = 0.2095$	$x_{\text{O}_2,\text{extr}} = 7.7071 \cdot 10^{-2}$
– nitrogen	N <sub>2</sub>	$x_{\text{N}_2,0} = 0.7809$	$x_{\text{N}_2,\text{extr}} = 2.8728 \cdot 10^{-1}$
– carbon dioxide	CO <sub>2</sub>	$x_{\text{CO}_2,0} = 0.0003$	$x_{\text{CO}_2,\text{extr}} = 1.1036 \cdot 10^{-4}$



**Fig. 4** Concentration chemical exergy change vs. molar fraction change of nitrogen N<sub>2</sub>

All the above numerical values can be easily determined investigating the function

$$y = f(x_j) = \frac{\bar{e}_{\mu,j}^x}{\bar{R}T_0} = x_j \ln \frac{x_j}{x_{j,0}}$$

The first derivative for  $x_j$  equals to

$$y' = 1 + \ln \frac{x_j}{x_{j,0}}$$

where from (after setting  $y'$  equal to zero) yields

$$x_j = x_{j,\text{extr}} = e^{\ln x_j - 1} = \exp(\ln x_{j,0} - 1) = \frac{x_{j,0}}{e}$$

with the value of  $e$  as the base of natural logarithms.

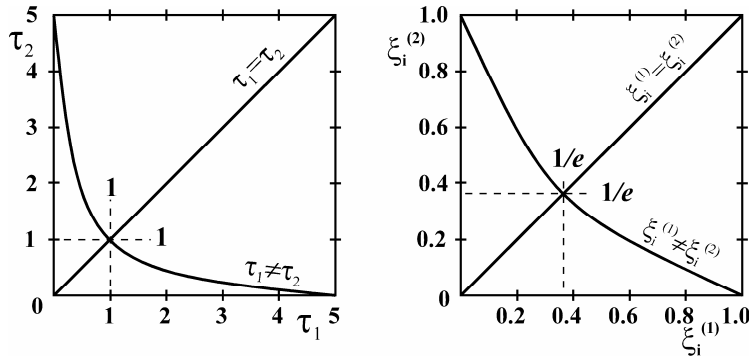
Changing in a process its molar fraction from the state (1) to the state (2), the chemical concentration exergy of the specie  $j$  changes, and this change will be zero, if only

$$\bar{R}T_0 x_j^{(1)} \ln \frac{x_j^{(1)}}{x_{j,0}} = \bar{R}T_0 x_j^{(2)} \ln \frac{x_j^{(2)}}{x_{j,0}} \quad \text{or} \quad \xi_j^{(1)} \ln \xi_j^{(1)} = \xi_j^{(2)} \ln \xi_j^{(2)} \quad (39)$$

whereby  $\xi_j = x_j/x_{j,0}$ . The solution of the last algebraic equation gives the result  $\xi_{j,\text{extr}} = 1/e$ , i.e.  $x_{j,\text{extr}} = x_j/x_{j,0}$  (see the right-hand side graphical solution diagram in Fig. 5). By analogy with this circumstance, the zero change of the thermal (temperature) exergy constituent of the thermo-mechanical system exergy between the states (1) and (2) is to

$$c_p(T_2 - T_1) - c_p T_0 \ln \frac{T_2}{T_1} = 0 \quad \text{or} \quad (\tau_2 - \tau_1) - \ln \frac{\tau_2}{\tau_1} = 0 \quad (40)$$

and the result is  $\tau = 1$  or  $T_1 = T_2$  (the left-hand side graphical solution presented in the diagram in Fig. 5).



**Fig. 5** Graphical solutions of Eqs.(39)–(40)

By analogy with the thermal (temperature) and mechanical (pressure) constituents of the thermo-mechanical system exergy (exergy  $E_I$  of enthalpy  $I$  and/or exergy  $E_U$  of inner energy  $U$ ) the appropriate table can be built, where directions of concentration chemical exergy changes vs. changes of concentrations of the specie  $j$  in certain ranges will be presented:

range of molar fraction changes	molar fraction increase	molar fraction decrease
	$\Delta x_j > 0$ ( $x_j^{(2)} > x_j^{(1)}$ )	$\Delta x_j < 0$ ( $x_j^{(2)} < x_j^{(1)}$ )
$x_j < x_{j,\text{extr}}$	$\nabla \bar{e}_{\mu,j}^{x<} < 0$	$\Delta \bar{e}_{\mu,j}^{x<} > 0$
$x_j > x_{j,\text{extr}}$	$\Delta \bar{e}_{\mu,j}^{x>} > 0$	$\nabla \bar{e}_{\mu,j}^{x>} < 0$

When in a process  $1 \rightarrow 2$  for a specie  $j$  the molar fraction value of  $x_{j,\text{extr}}$  will be crossed, then the whole concentration chemical exergy change will consist of two parts, namely of the part observed in the range from  $x_j^{(1)}$  to  $x_{j,\text{extr}}$  and of the part in a range from  $x_{j,\text{extr}}$  to  $x_j^{(2)}$ .



## 8 CONCLUSIONS

The above discussion has introduced the special behavior of the substantial part of the exergy. This part, known as the concentration part of the chemical exergy, determines exergy balancing of mixing and separation processes and even chemical reactions. The appropriate applications will be presented very soon as the continuation of the present work (the special case of chemical reactions has been already worked out within the research project INTERVIRON, e.g. [35]).

The special behavior of exergy — not known in the case of energy or entropy — was the main reason of hitherto troubles in applying the concept for processes (and systems) analysis and rating regarding the *Second Law*. The rating quotients less than zero and greater than one have been obtained for very good known processes. Such a result was in fact useless. The unique method of thermodynamic analysis should take into account the above presented special behavior of all the parts of exergy: the thermal, mechanical (pressure) and chemical (substantial) one.

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***Evaluation, Verification and Interpretation of the Environmental Loads of the Czech Republic – INTERVIRON 2B06068***

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