

Jaroslav KOZACZKA*, Pavel KOLAT**

EXERGY IN MIXING PROCESSES

EXERGIE V MÍCHACÍCH PROCESECH

Abstract

The exergy concept applied to mixing processes has been presented and discussed in detail. The goal of the following discussion is, how to apply the simple exergy balance of these processes to build an appropriate thermodynamic transition formula and hence, the generalized exergy rating quotient, the thermodynamic effectivity. The procedure should match the idea used for other processes of power and chemical engineering, as well. Thus, the possibility of taking into account mixing processes in the complex system analyzes will be realized.

Abstrakt

V článku je exaktně popsána exergetická koncepce v míchacích procesech. Cílem diskuze je odpovědět na dotazy týkající se formulace jednoduché bilance energie a zformulování vztahů termodynamických přenosů a odtud všeobecného exergetického hodnocení termodynamické efektivity. Procedura musí odpovídat metodě aplikovatelné u jiných inženýrských procesů chemických, energetických a procesních technologií. Takto může být provedena, aby zohlednila míchací procesy v analýze komplexních systémů.

1 INTRODUCTION

It has been previously stated a special behavior of substance (or chemical) exergy changing its concentration [1]. There exists a certain extreme-point, in which the exergy change while altering the concentration starts to continue in an opposite direction. E.g. in a process of nitrogen N_2 concentration change in a mixture from zero to 1 its so-called concentration exergy first diminishes (negative numerical values) until the nitrogen mole fraction reaches the exergy change algebraic sign inversion point ($x_{N_2, \text{extr}}=0.28728$), and from this point up, it rises (negative numerical values) until the concentration exergy reaches the value of 0 at $x_{N_2,0}=0.7809$, which is the mole (volume) concentration of nitrogen in an atmospheric air (the natural environment). Thereafter it rises in the positive numerical values range till the concentration reaches 1, i.e. until the pure nitrogen has been produced. The end numerical value at $x_{N_2}=1$ and at the natural environment temperature T_0 is the so-called nitrogen zero exergy.

In the following general mixing processes will be discussed, and especially how they can be balanced, analyzed and rated using exergy concept. The special concept of the thermodynamic transition and thermodynamic effectivity will be used to make the presented processes comparable with others, which have been analyzed and rated with the exergy, either.

2 MIXING STREAMS IN GENERAL

Two streams 1 and 2 can be mixed continuously to a resulting steam (without any subscript) so that the appropriate exergy balance in an adiabatic process will be to

* Prof. Ing., Dr. (Prof. dr hab. inž), AGH – University of Science and Technology, Faculty of Mechanical Engineering and Robotics, Department of Power Engineering and Environmental Protection, Mickiewicza 30, 30-059 Kraków, Poland – corresponding author (kozaczka@agh.edu.pl)

** Prof. Ing., DrSc., VŠB – Technical University of Ostrava, Faculty of Mechanical Engineering, Department of Power Engineering, 17 listopadu 15, 708 33 Ostrava–Poruba, Czech Republic

$$E_{1,1} + E_{1,2} = E_1 + T_0 \Delta S_{\text{irr}}$$

or more detailed

$$n_1 \bar{e}_{1,1} + n_2 \bar{e}_{1,2} = (n_1 + n_2) \bar{e}_1 + T_0 \Delta S_{\text{irr}}$$

which can be to

$$x_1 \bar{e}_{1,1} + x_2 \bar{e}_{1,2} = \bar{e}_1 + T_0 \Delta \bar{s}_{\text{irr}}$$

The stream at the end of the process contains substances of the stream 1 and of the stream 2 so that above Equations can be written down as

$$-x_1(\bar{e}_1 - \bar{e}_{1,1}) - x_2(\bar{e}_1 - \bar{e}_{1,2}) = T_0 \Delta \bar{s}_{\text{irr}} \quad \text{or} \quad -x_1 \Delta \bar{e}_{1,1} - x_2 \Delta \bar{e}_{1,2} = T_0 \Delta s_{\text{irr}} \quad (1)$$

The both exergy changes $\Delta \bar{e}_{1,1}$ and $\Delta \bar{e}_{1,2}$ are sums of the thermal, mechanical (pressure) and concentration chemical changes, because the (molar) exergy of enthalpy is a caloric parameter of state, if only the natural environment parameters do not vary in a time of analysis. Thus,

$$\Delta \bar{e}_1 = \Delta \bar{e}_{1,T} + \Delta \bar{e}_{1,p} + \Delta \bar{e}_{1,\mu}^x$$

and the Eq.(1) will be to

$$-x_1(\Delta \bar{e}_{1,T} + \Delta \bar{e}_{1,p} + \Delta \bar{e}_{1,\mu}^x) - x_2(\Delta \bar{e}_{1,T} + \Delta \bar{e}_{1,p} + \Delta \bar{e}_{1,\mu}^x) = T_0 \Delta s_{\text{irr}} \quad (2)$$

Each term of the last equation, however, can be presented as the sum of the positive exergy changes (rises) and negative ones (falls) due to the appropriate parameter causing its algebraic sign inversion. In the case of the thermal exergy change the parameter is the temperature T_0 of the natural environment, in the case of the mechanical exergy change there is no such a criterion and in the case of the concentration chemical exergy change it is the value $x_{j,\text{extr}}=1/e$ for species that do not exist in the natural environment (e is the base of natural logarithms) or $x_{j,\text{extr}}=x_{j,0}/e$, where $x_{j,0}$ is the concentration of analyzed specie in the natural environment. In general there is

$$\begin{aligned} \Delta \bar{e}_{1,T} &= |\Delta \bar{e}_{1,T}^>| + |\Delta \bar{e}_{1,T}^<| - |\nabla \bar{e}_{1,T}^>| - |\nabla \bar{e}_{1,T}^<| \\ \Delta \bar{e}_{1,p} &= |\Delta \bar{e}_{1,p}| - |\nabla \bar{e}_{1,p}| \\ \Delta \bar{e}_{1,\mu}^x &= |\Delta \bar{e}_{1,\mu}^{x>}| + |\Delta \bar{e}_{1,\mu}^{x<}| - |\nabla \bar{e}_{1,\mu}^{x>}| - |\nabla \bar{e}_{1,\mu}^{x<}| \end{aligned}$$

Putting above formulas into Eq.(2) yields a somehow large equation

$$\begin{aligned} -x_1 \left(|\Delta \bar{e}_{1,T}^>| + |\Delta \bar{e}_{1,T}^<| - |\nabla \bar{e}_{1,T}^>| - |\nabla \bar{e}_{1,T}^<| + |\Delta \bar{e}_{1,p}| - |\nabla \bar{e}_{1,p}| + |\Delta \bar{e}_{1,\mu}^{x>}| + |\Delta \bar{e}_{1,\mu}^{x<}| - |\nabla \bar{e}_{1,\mu}^{x>}| - |\nabla \bar{e}_{1,\mu}^{x<}| \right) - \\ -x_2 \left(|\Delta \bar{e}_{1,T}^>| + |\Delta \bar{e}_{1,T}^<| - |\nabla \bar{e}_{1,T}^>| - |\nabla \bar{e}_{1,T}^<| + |\Delta \bar{e}_{1,p}| - |\nabla \bar{e}_{1,p}| + |\Delta \bar{e}_{1,\mu}^{x>}| + |\Delta \bar{e}_{1,\mu}^{x<}| - |\nabla \bar{e}_{1,\mu}^{x>}| - |\nabla \bar{e}_{1,\mu}^{x<}| \right) = T_0 \Delta s_{\text{irr}} \end{aligned}$$

which can be formed into the so-called thermodynamic transition equation, i.e.

$$\begin{aligned} x_1 \left(|\nabla \bar{e}_{1,T}^>| + |\nabla \bar{e}_{1,T}^<| + |\nabla \bar{e}_{1,p}| + |\nabla \bar{e}_{1,\mu}^{x>}| + |\nabla \bar{e}_{1,\mu}^{x<}| \right) + x_2 \left(|\nabla \bar{e}_{1,T}^>| + |\nabla \bar{e}_{1,T}^<| + |\nabla \bar{e}_{1,p}| + |\nabla \bar{e}_{1,\mu}^{x>}| + |\nabla \bar{e}_{1,\mu}^{x<}| \right) \rightarrow \\ \rightarrow x_1 \left(|\Delta \bar{e}_{1,T}^>| + |\Delta \bar{e}_{1,T}^<| + |\Delta \bar{e}_{1,p}| + |\Delta \bar{e}_{1,\mu}^{x>}| + |\Delta \bar{e}_{1,\mu}^{x<}| \right) + x_2 \left(|\Delta \bar{e}_{1,T}^>| + |\Delta \bar{e}_{1,T}^<| + |\Delta \bar{e}_{1,p}| + |\Delta \bar{e}_{1,\mu}^{x>}| + |\Delta \bar{e}_{1,\mu}^{x<}| \right) + T_0 \Delta s_{\text{irr}} \end{aligned}$$

where from the thermodynamic effectivity quotient can be determined

$$\varepsilon = \frac{x_1 \left(|\Delta \bar{e}_{1,T}^>| + |\Delta \bar{e}_{1,T}^<| + |\Delta \bar{e}_{1,p}| + |\Delta \bar{e}_{1,\mu}^{x>}| + |\Delta \bar{e}_{1,\mu}^{x<}| \right) + x_2 \left(|\Delta \bar{e}_{1,T}^>| + |\Delta \bar{e}_{1,T}^<| + |\Delta \bar{e}_{1,p}| + |\Delta \bar{e}_{1,\mu}^{x>}| + |\Delta \bar{e}_{1,\mu}^{x<}| \right)}{x_1 \left(|\nabla \bar{e}_{1,T}^>| + |\nabla \bar{e}_{1,T}^<| + |\nabla \bar{e}_{1,p}| + |\nabla \bar{e}_{1,\mu}^{x>}| + |\nabla \bar{e}_{1,\mu}^{x<}| \right) + x_2 \left(|\nabla \bar{e}_{1,T}^>| + |\nabla \bar{e}_{1,T}^<| + |\nabla \bar{e}_{1,p}| + |\nabla \bar{e}_{1,\mu}^{x>}| + |\nabla \bar{e}_{1,\mu}^{x<}| \right)}$$

For m streams it can be rewritten as

$$\varepsilon = \frac{\sum_i^m x_i \left(|\Delta \bar{e}_{i,T}^>| + |\Delta \bar{e}_{i,T}^<| + |\Delta \bar{e}_{i,p}| + |\Delta \bar{e}_{i,\mu}^{x>}| + |\Delta \bar{e}_{i,\mu}^{x<}| \right)}{\sum_i^m x_i \left(|\nabla \bar{e}_{i,T}^>| + |\nabla \bar{e}_{i,T}^<| + |\nabla \bar{e}_{i,p}| + |\nabla \bar{e}_{i,\mu}^{x>}| + |\nabla \bar{e}_{i,\mu}^{x<}| \right)} \quad (3)$$

If additionally heat Q_+ will be supplied (heating) while the mixing process is running, or heat Q_- will be carried away (cooling), the rating quotient can be in general to

$$\varepsilon = \frac{\sum_i^m x_i \left(|\Delta \bar{e}_{i,T}^>| + |\Delta \bar{e}_{i,T}^<| + |\Delta \bar{e}_{i,p}| + |\Delta \bar{e}_{i,\mu}^{x>}| + |\Delta \bar{e}_{i,\mu}^{x<}| \right) + |E_{Q_+}^>| + |E_{Q_-}^<|}{\sum_i^m x_i \left(|\nabla \bar{e}_{i,T}^>| + |\nabla \bar{e}_{i,T}^<| + |\nabla \bar{e}_{i,p}| + |\nabla \bar{e}_{i,\mu}^{x>}| + |\nabla \bar{e}_{i,\mu}^{x<}| \right) + |E_{Q_+}^>| + |E_{Q_-}^<|} \quad (4)$$

because the heat supplied below the natural environment temperature T_0 (superscript $<$) means decreasing of the analyzed system exergy, supplied above T_0 its increasing, and so on.

The last equations do seem a little bit complex, but they can be reduced for known main process parameters. If for example an adiabatic ($dQ=0$) and isobaric ($dp=0$) mixing process of the same substances in each stream will be considered, the above thermodynamic effectivity quotient can be reduced to

$$\varepsilon = \frac{\sum_i^m x_i \left(|\Delta \bar{e}_{i,T}^>| + |\Delta \bar{e}_{i,T}^<| \right)}{\sum_i^m x_i \left(|\nabla \bar{e}_{i,T}^>| + |\nabla \bar{e}_{i,T}^<| \right)}$$

If the process runs above the natural environment temperature T_0 , all the terms with superscript $<$ will be set to zero, i.e.

$$\varepsilon = \frac{\sum_i^m x_i \left(|\Delta \bar{e}_{i,T}^>| \right)}{\sum_i^m x_i \left(|\nabla \bar{e}_{i,T}^>| \right)}$$

and for only two streams 1 and 2,

$$\varepsilon = \frac{x_1 \left(|\Delta \bar{e}_{i,T}^>| \right)_1 + x_2 \left(|\Delta \bar{e}_{i,T}^>| \right)_2}{x_1 \left(|\nabla \bar{e}_{i,T}^>| \right)_1 + x_2 \left(|\nabla \bar{e}_{i,T}^>| \right)_2}$$

Finally it has to be assumed, which stream is hotter. If there is $T_1 > T_2$, than the temperature of the resulting mixture lies in the range between T_1 and T_2 , and the thermodynamic effectivity yields

$$\varepsilon = \frac{x_2 \left(|\Delta \bar{e}_{i,T}^>| \right)_2}{x_1 \left(|\nabla \bar{e}_{i,T}^>| \right)_1} \quad (5)$$

3 MIXING TWO STREAMS — SPECIAL CASES

There are two streams 1 and 2 in gas phase of different composition. The first stream consists of two components a and b , the second stream either, but appropriate molar fractions are different. Assuming an adiabatic isotherm–isobaric process it can be according to above Eq.(3)

$$\varepsilon_{\substack{dT=0 \\ dp=0 \\ dq=0}} = \frac{x_1 \left(|\Delta \bar{e}_{i,\mu 1a}^{x>}| + |\Delta \bar{e}_{i,\mu 1a}^{x<}| + |\Delta \bar{e}_{i,\mu 1b}^{x>}| + |\Delta \bar{e}_{i,\mu 1b}^{x<}| \right) + x_2 \left(|\Delta \bar{e}_{i,\mu 2a}^{x>}| + |\Delta \bar{e}_{i,\mu 2a}^{x<}| + |\Delta \bar{e}_{i,\mu 2b}^{x>}| + |\Delta \bar{e}_{i,\mu 2b}^{x<}| \right)}{x_1 \left(|\nabla \bar{e}_{i,\mu 1a}^{x>}| + |\nabla \bar{e}_{i,\mu 1a}^{x<}| + |\nabla \bar{e}_{i,\mu 1b}^{x>}| + |\nabla \bar{e}_{i,\mu 1b}^{x<}| \right) + x_2 \left(|\nabla \bar{e}_{i,\mu 2a}^{x>}| + |\nabla \bar{e}_{i,\mu 2a}^{x<}| + |\nabla \bar{e}_{i,\mu 2b}^{x>}| + |\nabla \bar{e}_{i,\mu 2b}^{x<}| \right)} \quad (6)$$

The thermodynamic effectivity quotient will be not that complex after all the terms have been investigated. The following numerical example makes it clear and understandable.

3.1 Numerical Example I — Mixing two gaseous oxygen/nitrogen streams

Let assume the mixing process of two streams 1 and 2 consisting of nitrogen N_2 (a) and oxygen O_2 (b). The first stream is 2 kilo moles per time unit and the second one 8 kilo moles. They contain following amounts of N_2 and O_2 , expressed by their molar fractions:

component	stream	
	1	2
a (N_2)	$x_{1a}=0.79$	$x_{2a}=0.10$
b (O_2)	$x_{1b}=0.21$	$x_{2b}=0.90$

The resulting stream of 10 kilo moles contains $x_a=0.238$ and $x_b=0.762$ nitrogen and oxygen, respectively. Concentrations of the two species in the natural environment are

$$x_{N_2,0}=x_{a,0}=0.79 \quad \text{and} \quad x_{O_2,0}=x_{b,0}=0.21$$

Hence, appropriate concentrations, by which the exergy change algebraic sign inverts [01], are

$$x_{N_2,extr} = x_{a,extr} = 0.2906 \quad \text{and} \quad x_{O_2,extr} = x_{b,extr} = 0.0725$$

Thus, the molar concentrations of the both species considered change like follows:

component	stream	
	1	2
a (N_2)	$0.79 \rightarrow x_{a,extr} \rightarrow 0.238$	$0.10 \rightarrow 0.238$
b (O_2)	$0.21 \rightarrow 0.762$	$0.90 \rightarrow 0.762$

Appropriate concentration exergy changes are —

For nitrogen contents change in the first stream from the start to the exergy change inversion point, i.e. above the $x_{N_2,extr}$ value:

$$n_1 \cdot \nabla \bar{e}_{1,\mu 1a}^{x>} = 2 \cdot \left(0.2906 \ln \frac{0.2906}{0.79} - 0.79 \ln \frac{0.79}{0.79} \right) \bar{R} T_0 = -0.58125 \bar{R} T_0 < 0$$

and for nitrogen contents change from the exergy change inversion point to the end, i.e. below the $x_{N_2,extr}$ value:

$$n_1 \cdot \Delta \bar{e}_{1,\mu 1a}^{x<} = 2 \cdot \left(0.238 \ln \frac{0.238}{0.79} - 0.2906 \ln \frac{0.2906}{0.79} \right) \bar{R} T_0 = 0.01016 \bar{R} T_0 > 0$$

The resulting exergy change algebraic signs in the two ranges do determine if the change is a rising (Δ) or diminishing (∇) one. The symbolic \bar{R} points here to the universal gas constant. For oxygen contents change in the first stream yields (above the $x_{O_2,extr}$ value)

$$n_1 \cdot \Delta \bar{e}_{1,\mu 1b}^{x>} = 2 \cdot \left(0.762 \ln \frac{0.762}{0.21} - 0.21 \ln \frac{0.21}{0.21} \right) \bar{R} T_0 = 1.96419 \bar{R} T_0 > 0$$

In the second stream the exergy change inversion point is not crossed neither for nitrogen nor for oxygen, and the appropriate exergy changes are

$$n_2 \cdot \nabla \bar{e}_{1,\mu 2a}^{x<} = 8 \cdot \left(0.238 \ln \frac{0.238}{0.79} - 0.10 \ln \frac{0.10}{0.79} \right) \bar{R} T_0 = -0.63086 \bar{R} T_0 < 0$$

$$n_2 \cdot \nabla \bar{e}_{1,\mu 2b}^{x>} = 8 \cdot \left(0.762 \ln \frac{0.762}{0.21} - 0.90 \ln \frac{0.90}{0.21} \right) \bar{R} T_0 = -2.62130 R T_0 \quad < 0$$

So, the previously formulated general thermodynamic effectivity equation for the adiabatic isotherm–isobaric mixing process, Eq.(6), will be shortened to its special form

$$\varepsilon_{\substack{dq=0 \\ dT=0 \\ dp=0}} = \frac{n_1 |\Delta \bar{e}_{1,\mu 1a}^{x<}| + n_1 |\Delta \bar{e}_{1,\mu 1b}^{x>}|}{n_1 |\nabla \bar{e}_{1,\mu 1a}^{x>}| + n_2 |\nabla \bar{e}_{1,\mu 2a}^{x<}| + n_2 |\nabla \bar{e}_{1,\mu 2b}^{x>}|} = \frac{0.01016 + 1.96419}{0.58125 + 0.63086 + 2.62130} = \underline{0.5150}$$

3.2 Numerical Example II — Mixing water steam and condensate

In a RANKINE cycle with heat regenerative the heat exchanger can be used that in fact is a mixing vessel. In this apparatus the steam extracted from the steam turbine at certain pressure p_{sex} and amount of M_{sex} will be added to the condensate, the pressure of which has been raised from the condensation pressure (e.g. 0.04 bar) to the extracted steam pressure p_{sex} . The amount of the condensate by only one steam extraction is the rest of the steam on turbine inlet, e.g. M_{con} . The usually saturated water steam behind the regenerative heat exchanger will be further pumped to the steam boiler (a deaerating device should be used). In RANKINE cycles with several steam extractions membrane heat exchanger are commonly used. In this example, however, the $p_{\text{sex}}=1.2$, water steam enthalpy $i_{\text{sex}}=2592$ kJ/kg, $M_{\text{sex}}=0.128$ kg and from the i – s –diagram $s_{\text{sex}}=7.075$ kJ/(kg·K). The condensate enthalpy equals to $i_{\text{con}}=121.42$ kJ/kg and the entropy $s_{\text{con}}=0.4225$ kJ/(kg·K); the numerical values have been taken from water steam tables for $p_{\text{con}}=0.04$ bar as i' and s' (the energy/exergy supplied by the condensate pump can be assumed as negligible). The condensate enthalpy behind the mixer is $i_{\text{mix}}=439.4$ kJ/kg and its entropy $s_{\text{mix}}=1.3606$ kJ/(kg·K), which has been taken from the water steam tables for $p_{\text{sex}}=1.2$ bar as i' and s' , either. The amount of condensate from the turbine is $M_{\text{con}}=0.872$ kg (calculations are usually made for 1 kg water steam in the turbine inlet). The mixing process thermodynamic effectivity for the adiabatic–isobaric conditions should be determined.

The substance is the same, although existing in two phases, the condensed (liquid) and the gaseous one. Thus, Eq.(5) will be applied. There are two streams, for which following exergy changes can be calculated (the exergy change algebraic sign inversion point is excluded because the whole process runs above the natural environment temperature T_0 , e.g. equal to 293.15 K). They are:

$$\begin{aligned} \nabla E_{1,T\text{sex}}^{\>} &= M_{\text{sex}} [i_{\text{mix}} - i_{\text{sex}} - T_0 (s_{\text{mix}} - s_{\text{sex}})] = \\ &= 0.128 \cdot [439.4 - 2592 - 293.15 \cdot (1.3606 - 7.075)] = -61.110 \text{ kJ} \quad < 0 \end{aligned}$$

$$\begin{aligned} \Delta E_{1,T\text{con}}^{\>} &= M_{\text{con}} \cdot [i_{\text{mix}} - i_{\text{con}} - T_0 (s_{\text{mix}} - s_{\text{con}})] = \\ &= 0.872 \cdot [439.4 - 121.42 - 293.15 \cdot (1.3606 - 0.4225)] = 37.475 \text{ kJ} \quad > 0 \end{aligned}$$

Hence, the thermodynamic effectivity of the process is to

$$\varepsilon_{\substack{dq=0 \\ dp=0}}^{\>} = \frac{|\Delta E_{1,T\text{con}}^{\>}|}{|\nabla E_{1,T\text{sex}}^{\>}|} = \frac{37.475}{61.110} = \underline{0.6132}$$

In the case the mixing vessel (the regenerative heat exchanger) is cooled, the heat exergy at temperatures above T_0 will be carried away from the balance area and the appropriate term should be placed in the denominator of the quotient, according to Eq.(4). Thus, the thermodynamic effectivity of such a process will be less (greater exergy losses due to heat taken away to the surroundings).

Special analysis of mixing processes has been presented in [2], but in somehow different form. The discussed above so–called thermodynamic transition process and the thermodynamic effectivity

quotient, however, are needed for thermodynamic analysis an rating complex power and chemical engineering systems, not only main processes themselves.

4 CONCLUSION

The thermodynamic transition and the appropriate thermodynamic effectivity quotient can be formulated in the same way as for main power processes, i.e. compression and expansion, which have been presented in the earlier author's contribution [3]. In fact the thermodynamic effect of mixing is not that important and very often can be neglected to achieve clear system presentation. In some cases, however, they need to be taken into account, especially while analyzing a particular process on which the mixing does influence it. The problem of analyzing such processes is similar to the sense of analyzing e.g. the flow whirls from the exergy point of view. The last problem has been very detailed presented in [4], but it could be stated, they are not that important in system analyzes. The exergy concept is first of all useful in analyzing systems and pointing processes that mostly influence the whole system effectiveness, but not in analyzing particular processes itself. The conclusion could be formulated after a huge number of numerical cases have been calculated and critically discussed by the authors.

Some of the exergy analysis and rating of mixing processes have been presented at scientific conferences, where they have been discussed with auditory, [5]–[7]. Exergy analyzes of technological mixing processes are very rare in the literature, and they usually discuss mixing streams of different temperature, e.g. [8].

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