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A non-equilibrium phenomenological theory of the mass and heat transfer in physical and chemical interactions Part I — application to NH_3/H_2O and other working systems

M.D. Staicovici

Thermopower Equipment Research and Design Institute (SC ICPET — CERCETARE SA), 236 Vitan Road, 74369 Bucharest, Romania

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Abstract

The paper presents an original non-equilibrium phenomenological theory of mass and heat transfer. The theory is particularized to a few case studies including physical binary gas–liquid interactions in non-ideal mixtures (e.g., working system NH_3/H_2O), pure components (NH_3, H_2O), as well as an independent chemical interaction (ammonia synthesis). All applications emphasize an important feature of the mass and heat coupled currents, that is the ideal point approaching (i.p.a.) effect, not mentioned so far in the specialized literature. The i.p.a. effect consists of a continuous increase of the mass and heat currents of an interaction evolving towards an ideal point, by several percentages (pure component case) to several hundreds of times (working pairs case), as compared to the states which are far from the same ideal point. On the contrary, the forces of systems with non-coupled mass and heat currents tend to zero when evolve to equilibrium. The paper raises the problem of the ammonia bubble absorption, not satisfactorily explained by the 'two films' theory. The existence of the i.p.a. effect satisfactorily explains it from a qualitative point of view. This explanation throws a new light on the absorption phenomenon encountered by the working pairs used in the thermal absorption technology: (i) absorption process is not a surface phenomenon, as it is usually considered and (ii) the actual estimation of the interface mass transfer by analogy with heat transfer is improper. The non-equilibrium approach, outlined in this paper, is not contradictory to the classic equilibrium phenomenological theory. On the contrary, it may be an equivalent alternative or it may be combined with the classic approach in order to assess mass and heat transfer processes. Its main investigation tool, the natural thermodynamical force, has specific important features in the neighbourhood of an ideal point. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

The NH_3/H_2O system is the most common working combination in the thermal absorption technology. Although there is quite a comprehensive theoretical and practical experience in the use of such combination, the gas–liquid interaction in this medium is, most surprisingly, still dealt with empirically. The analogy with heat transfer is commonly used for the

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E-mail address: staicovici@dnt.ro (M.D. Staicovici).

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Nomenclature

A	reduced excess heat, dimensionless, chemical affinity, kJ/kmol
a, b, c, d	factors intervening in Eqs. (A1)–(A4)
c_p	specific heat at constant pressure, kJ/kmol K
C	local thermal capability, kJ/kmol
f	figure of merit quantifying the increase of a phenomenological function approaching an ideal state, as compared to its far equilibrium states
h	specific enthalpy, kJ/kmol
j	interface current (mass, heat, etc.), mol/s, kg/s, W
k	global mass transfer coefficient, kg/m^2 s
M	match function intervening in the natural thermodynamical force equation, molar mass of a specie involved in a chemical reaction, kg/kmol
$L_{i,\,j}$	phenomenological coefficient associated with the coupled currents i and j, mol^2 K/J s, kg K s/m^2
n	number of species or moles of a specie involved in a chemical reaction and time unit, mol/s
N	mass flux, kg/m^2 s
Nu	Nusselt number
p	partial pressure, kPa, bar, ata
Pr	Prandtl number
R	gas constant, kJ/kmol K
Re	Reynolds number
s	specific entropy, kJ/kmol K
Sc	Schmidt number
Sh	Sherwood number
$\dot{S}$	entropy source, W/K
t	time, s
T, t	temperature, K, °C
U	total internal energy, J
V	volume, molar volume, m^3, m^3/kmol

x, x^*	liquid phase molar fraction, and that in equilibrium with gas phase molar fraction y, respectively, mol/mol
X	generalized thermodynamic force, kJ/kmol K
y, y^*	gas phase molar fraction, and that in equilibrium with liquid phase molar fraction x, respectively, mol/mol
z	point in the X definition domain

Greek symbols

δ	finite difference (variation)
Δ	driving force (according to classical interpretation)
$\dot{\Lambda}$	exergy destruction velocity, W
μ	chemical potential, kJ/kmol
ν	stoichiometric coefficient
σ	superficial tension, N/m

Subscripts and superscripts

abs	absorption
c	condensation
e	equilibrium
i	mass
q	heat
g	gas, gaseous phase
gen	generation
l	liquid, liquid phase
max	maximum
p	constant pressure, pure
ph	phenomenological
r	reduced
T	constant temperature
v	vaporization
$'$	before interaction
$''$	after interaction
0	environmental
1, 2	mixture species

calculation of interface mass transfer,

$$N = k\Delta \tag{1}$$

In Eq. (1), N is the mass flow transferred as a result of the action of the motive force Δ. The motive force is equal to the deviation from the equilibrium conditions. Proportionality factor k is the mass transfer coefficient. According to the well-known concept of the ‘two films’ [1], N is proportional to the difference of the concentrations of the gas or liquid phases and to the global mass transfer coefficients of the phases

$$N = K_{\mathrm{g}}\left(y - y^*\right) = K_{\mathrm{l}}(x - x^*) \tag{2}$$

In Eq. (2), x^* and y^* are the concentrations of the liquid and gas phases in equilibrium with the gas phase of concentration y and the liquid phase of concentration x, respectively. Coefficients K_{g} and K_{l} are expressed as functions of the global resistance to mass transfer, which have additive properties to the partial resistance of the phases, similar to the heat transfer. More often than not it is considered that mass transfer is controlled by the phase with the greatest partial resistance. In order to decrease global resistance, the dispersion of the process controlling phase is usually used. That is why, according to the classic interpretation, it is implicitly admitted that the NH_3/H_2O gas–liquid interaction is a surface phenomenon.

The literature referring to mass transfer has mainly dealt with the dependence of transfer coefficients on molecular diffusivity. This approach includes the 'two films' concept referred to above, as well as the theory of penetration [2] and renewal [3]. Specialized literature has paid less attention to the relation between absorption rate and hydrodynamic conditions. So far it has been experimentally proved that in certain given conditions there is a Reynolds analogy in the case of mass transfer

$$Sh = a_m Re^{b_m} Sc^{c_m} \tag{3}$$

and

$$Nu = a_h Re^{b_h} Pr^{c_h} \tag{4}$$

in the case of heat transfer, in two-phase gas–liquid flow in pipes [4,5]. Eq. (3) does not hold good, for instance, when shear stresses exist at the gas–liquid interface, but successfully applies for the gas-phase controlled mass transfer in wetted-wall columns.

Several authors have studied heat and mass transfer in the NH_3/H_2O system [5–11]. Most of them express their results by means of correlations similar to Eqs. (3) and (4). A detailed study was conducted by Keizer [12] for two-phase NH_3/H_2O flow of the slug type in vertical pipe absorbers. For the purpose of evaluating mass transfer, first he made use of prediction correlations of partial coefficient k_l, which were derived from past works by others [13–18]. Comparing his experimental data with the ones predicted and finding that they sensibly differ, sometimes even by an order of magnitude, Keizer questions the applicability of the correlations of the authors mentioned in Refs. [13–18] to the prediction of mass transfer in the case of the NH_3/H_2O system and comes to the conclusion that it cannot be precisely determined whose partial resistance — that of the liquid phase or of the gas phase — controls the NH_3/H_2O absorption process. Finally, his correlations are satisfactory by adapting Eq. (3).

In an attempt to find a more accurate method of prediction of NH_3/H_2O gas–liquid interactions, this paper will take into consideration the non-equilibrium thermodynamics [19]. Although it seems to be a natural direction of investigation, it has not been used in the analysis of the NH_3/H_2O system so far.

A simple experiment made by the author is described below. The experiment strengthens the conviction that the method of approaching the interactions which form the main object of this study should be reviewed. The experiment consists of injecting a single gaseous ammonia bubble into the NH_3/H_2O solution at normal pressure, ambient temperature and small molar fractions. Based upon the numerous observations recorded, it has been found that, according to the gas phase feeding rate, the evolution of the bubble may be characterized as follows: (i) at low and moderate feeding rates (10^{-8}–10^{-7} kg/s), the dynamics of the bubble takes place in two distinct stages: (a) *growth*, when the bubble progressively expands its volume up to a maximum value, concurrently with gas absorption, followed by (b) *collapse*, when the bubble is rapidly absorbed, reducing its volume to zero, although it continues to be fed with gas through the injection nozzle; throughout its evolution the bubble does not detach itself from the nozzle and has an almost spherical shape; in the case of a continuous gas feeding, the phenomenon becomes quasi-periodical; the frequency of complete evolution grows up with the increase of the flow rate; the duration of the *growth* stage is much longer than that of the *collapse* stage; (ii) at high flow rates, *collapse* does no longer occur, but a phenomenon of oscillation of the bubble volume between two values, a maximum and a minimum one, is noticed; the bubble is no longer spherical but elongates in the direction of the nozzle axis and has an irregular contour. The study of the bubble in its complete *growth–collapse* evolution gives rise to two questions which are difficult to answer by means of the current theory of interface mass transfer and absorption as a surface phenomenon, synthesized by Eqs. (1) and (2) (the problem of the ammonia bubble absorption [20]): (i) if during the *growth* phase, as the bubble increases its volume, the molar fraction x of the interface approaches the saturation point so that the difference in the concentration of phases $(x^* - x)$ and implicitly the current absorbed decrease, then how could the occurrence of the *collapse* phase, which, quite on the contrary, assumes a continuous increase of the current absorbed in order to exceed the relatively constant value of the feeding flow rate, be explained?; (ii) if absorption is considered to be a surface phenomenon, then, yet again, how could *collapse*, a process during which the current absorbed, proportional to the gas–liquid contact area, decreases by the radius second power, instead of increasing as noted in the first question above, be explained? As it will be further demonstrated, these questions may be accurately answered by applying a non-equilibrium phenomenological theory, outlined in this work, to the interface of the subject interactions. The theory is not contradictory to the classic equilibrium phenomenological approach, but it completes it, highlighting new important features of the mass and heat transport near an equilibrium state, like the ideal point approaching (i.p.a.) effect, not mentioned so far in the specialized literature and included in this work too.

2. A non-equilibrium phenomenological theory of the coupled mass and heat transfer in physical mono-, bi- and particular polycomponent gas–liquid interactions

In the general case, interacting polycomponent, biphase evolution phenomena of gas–liquid, solid–liquid, solid–gas or gas–gas, liquid–liquid type may be considered. For the sake of clarity, here we shall use the notations for the binary physical interactions of gas–liquid type. The liquid phase may additionally contain other dissolved non-volatile components. The state parameters characterizing the interface, i.e., temperature, pressure and molar fraction, marked as T_g, p_g and y for gas and as T_l, p_l and x for liquid, are time functions. At the interface, surface tension forces, given by Laplace equation, or in a new approach [21], by equality

$$\Delta p = -\mathrm{div}\,\vec{\sigma} \tag{5}$$

where $\vec{\sigma}$ is a normal positive vector to the surface and equal to the surface tension of the liquid, are generated. The two-phase system is considered to be open. It evolves towards the state of equilibrium through a finite sequence of stationary states. It is also assumed that the total energy of the system is approximately equal to its internal energy, that is, its macroscopic kinetic energy, the external fields of any nature which act on it as well as its internal tensions are negligible. Under these circumstances, when the mechanical work exchanged by the system with the exterior is negligible, the heat exchanged between the system and, the environment and between its various areas is sensibly equal to the total enthalpy exchange. Here a coupled mass and heat transfer process means a process involving the existence of (a) a phase (nature) change of components (reactants), (b) an interaction heat and (c) simultaneous mass and heat currents influencing each other. The gas-liquid interaction involves the simultaneous existence of coupled mass and heat currents 'j', noted by subscripts 'i' and 'q', respectively, and of gas and liquid, marked by subscripts 'g' and 'l', respectively, which get in and out of the system, marked as prime (′) and secondary (″), respectively. The coupled currents are vectors, but here they will be treated as scalars, without loss of much information. Additionally, because energy is carried by the mass currents, they are considered the coupling currents and those of energy (heat, etc.) are the coupled ones. Finally, the classic notion of 'equilibrium' point (state) will be referred to as ideal point (state).

The entropy source, $\dot{S}$, shows the contribution of the currents to the global entropy yield. In a stationary state this is written as [22]

$$\dot{S} = -\frac{\dot{\Lambda}}{T_0} = -\left(\sum j_i' s_i' + \sum j_i'' s_i''\right) - \left(\sum \frac{j_q'}{T'} + \sum \frac{j_q''}{T''}\right) \tag{6}$$

where $\dot{\Lambda}$ is the exergy dissipation velocity and T_0 is the temperature of the infinite reservoir. Dimensionally j_i' and j_q' are expressed in mol/s or kg/s and in W, respectively. Eq. (6) is particularized to two opposed elementary processes which are permanently encountered in the heat absorption technology: (i) the gas interacts with the liquid, resulting in a liquid with new properties (absorption); (ii) the liquid decomposes in liquid and gas with new properties (generation). Taking the abovementioned things into account, as well as the common conventional signs in thermodynamics, Eq. (6) can be rewritten for case (i) as

$$\dot{S} = -\left(j'_{i,g}\cdot s'_g + j'_{i,l}\cdot s'_l - j''_{i,l}\cdot s''_l\right) - \left[j'_{q,g}\cdot\frac{1}{T'_g} + j'_{q,l}\cdot\frac{1}{T'_l} - \left(j''_{q,l} + j_q\right)\cdot\frac{1}{T''_l}\right] \tag{7}$$

where j_q is a heat current, considered as an excess element resulting out of the deviation from the ideal state of the mixture. The following current balances are considered in the system

process heat

$$j'_{q,g} + j'_{q,l} = j''_{q,l} + j_q \tag{8}$$

total mass

$$j'_{i,g} + j'_{i,l} = j''_{i,l} \tag{9}$$

mass for one of the species

$$y j'_{i,g} + x j'_{i,l} = (x + \delta x)\cdot j''_{i,l} \tag{10}$$

In Eq. (10) δx is the finite variation of molar fraction, undergone by the liquid as a result of its interaction with the gas phase. The heat flows are extensive elements. Taking into account the previous observation concerning the calculation of the heat exchange by means of total enthalpy, they can be written as

$$j'_{q,g} = j'_{i,g}\cdot h'_g$$

$$j'_{q,l} = j'_{i,l}\cdot h'_l$$

$$j''_{\mathrm{q,\,l}} = j''_{\mathrm{i,\,l}} \cdot h''_{\mathrm{l}} \tag{11}$$

Taking into consideration Eqs. (9) and (10), the first bracket of Eq. (7) can be written as

$$-\left(j'_{\mathrm{i,\,g}} \cdot s'_{\mathrm{g}} + j'_{\mathrm{i,\,l}} \cdot s'_{\mathrm{l}} - j''_{\mathrm{i,\,l}} \cdot s''_{\mathrm{l}}\right) = -j'_{\mathrm{i,\,g}}\left[\left(s'_{\mathrm{g}} - s'_{\mathrm{l}}\right) - (y-x)\frac{s''_{\mathrm{l}} - s'_{\mathrm{l}}}{\delta x}\right] \tag{12}$$

It is noted that the first bracket of Eq. (7) represents the contribution of the mass currents to the entropy source only, therefore the ratio on the right side of Eq. (12) becomes

$$\frac{s''_{\mathrm{l}} - s'_{\mathrm{l}}}{\delta x} \cong \left(\frac{\partial s_{\mathrm{l}}}{\partial x}\right)_{\mathrm{p,\,T}} \tag{13}$$

Temperature T''_{l} is related to the finite variation of liquid temperature due to the deviation from the ideal state $\delta T = T''_{\mathrm{l}} - T'_{\mathrm{l}}$ by

$$\frac{1}{T''_{\mathrm{l}}} = \frac{1}{T'_{\mathrm{l}}\left(1 + \frac{\delta T}{T'_{\mathrm{l}}}\right)} = \frac{1}{T'_{\mathrm{l}}}\left[1 - \frac{\delta T}{T'_{\mathrm{l}}} + \left(\frac{\delta T}{T'_{\mathrm{l}}}\right)^2 - \cdots\right] \tag{14}$$

Following simple calculations by means of Eqs. (14) and (8)–(11), the second bracket of Eq. (7) may be written as

$$-\left[j'_{\mathrm{q,\,g}}\frac{1}{T'_{\mathrm{g}}} + j'_{\mathrm{q,\,l}}\frac{1}{T'_{\mathrm{l}}} - \left(j''_{\mathrm{q,\,l}} + j_{\mathrm{q}}\right)\frac{1}{T''_{\mathrm{l}}}\right] = -j'_{\mathrm{i,\,g}}\left\{\left(\frac{1}{T'_{\mathrm{g}}} - \frac{1}{T'_{\mathrm{l}}}\right)h'_{\mathrm{g}} + \frac{1}{T'_{\mathrm{l}}}\left(h'_{\mathrm{g}} - h'_{\mathrm{l}} + \frac{h'_{\mathrm{l}}}{j_{\mathrm{r}}}\right)\frac{\delta T}{T'_{\mathrm{l}}\left(1 + \frac{\delta T}{T'_{\mathrm{l}}}\right)}\right\} \tag{15}$$

where

$$j_{\mathrm{r}} = \frac{j'_{\mathrm{i,\,g}}}{j''_{\mathrm{i,\,l}}} \tag{16}$$

is the reduced mass current of gas (mol. mol^{-1}) involved in the interaction. The ratio $\frac{\delta T}{T'_{\mathrm{l}}}$ is calculated by means of the liquid specific heat equation at constant pressure

$$c_{\mathrm{p,\,l}} = \left(\frac{\partial h_{\mathrm{l}}}{\partial T}\right)_{\mathrm{p,\,x}} \tag{17}$$

resulting in

$$\frac{\delta T}{T'_{\mathrm{l}}} = \frac{\delta h'_{\mathrm{l}}}{T'_{\mathrm{l}} \cdot c_{\mathrm{p,\,l}}} = A j_{\mathrm{r}} \tag{18}$$

where the non-dimensional factor A in Eq. (18), herein called 'reduced excess heat', is obtained with Eqs. (9), (10) and (16) and has the expression

$$A = (y-x)\left(\frac{\partial h'_{\mathrm{l}}}{\partial x}\right)_{\mathrm{p,\,T}} \cdot \frac{1}{T'_{\mathrm{l}} \cdot c_{\mathrm{p,\,l}}} \tag{19}$$

Eqs. (12)–(19) are introduced in Eq. (7) and the entropy source [22,23] is written as

$$\dot{S} = j'_{\mathrm{i,\,g}}(-X) \tag{20}$$

where

$$-X = -\left\{\left[\left(s'_{\mathrm{g}} - s'_{\mathrm{l}}\right) - (y-x)\left(\frac{\partial s'_{\mathrm{l}}}{\partial x}\right)_{\mathrm{p,\,T}}\right] + h'_{\mathrm{g}}\left(\frac{1}{T'_{\mathrm{g}}} - \frac{1}{T'_{\mathrm{l}}}\right) + \frac{A}{T'_{\mathrm{l}}(1 + Aj_{\mathrm{r}})}\left[\left(h'_{\mathrm{g}} - h'_{\mathrm{l}}\right) \cdot j_{\mathrm{r}} + h'_{\mathrm{l}}\right]\right\}. \tag{21}$$

Eq. (20) points out the proportionality of the entropy source with the coupling gas mass current $j'_{\mathrm{i,\,g}}$ and with factor $(-X)$, identified as a thermodynamic force and named here as non-equilibrium (natural) thermodynamic force. This force differs from the forces governing the coupled heat and mass transfer in continuous media, originating from Fourier's and Fick's laws, respectively and established with equilibrium thermodynamics tools. It only depends on the entry values of the system, a reason for which the marking primary (′) is hereinafter given up. Because it depends only on the interface p, T, x and y state parameters, force is a path independent function, and therefore a state function. According to Eqs. (8)–(11), the coupled heat current j_{q} has the expression

$$j_{\mathrm{q}} = j'_{\mathrm{i,\,g}} \cdot C \tag{22}$$

where C is the local thermal capacity (availability) of the binary mixture [24] obtained from Eqs. (8)–(11)

$$C = \left(h'_{\mathrm{g}} - h'_{\mathrm{l}}\right) - (y-x)\left(\frac{\partial h'_{\mathrm{l}}}{\partial x}\right)_{\mathrm{p,\,T}}. \tag{23}$$

This paper is confined to considering that the currents involved are linear functions of the thermodynamical forces. Later on, this consideration will be justified. Hence, the phenomenological equations are reduced to the simplest linear expression

$$j'_{\mathrm{i,\,g}} = L_{11}(-X) \tag{24}$$

where L_{11} is the strictly positive phenomenological coefficient of proportionality, having the dimension of $\mathrm{mol}^2\ \mathrm{K}\ \mathrm{J}^{-1}\ \mathrm{s}^{-1}$. In a first approximation L_{11} is considered to be a constant, independent of X. With Eq. (24), the entropy source (Eq. (20)) acquires the definite positive form

$$\dot{S} = L_{11} X^2 \tag{25}$$

for all interface p, T, x and y values, except the ideal points, given by

$$p_{\mathrm{l}} = p_{\mathrm{g}} = p_{\mathrm{e}}$$

$$T_{\mathrm{l}} = T_{\mathrm{g}} = T_{\mathrm{e}}$$

$$\mu_{1(2),\,\mathrm{l}} = \mu_{1(2),\,\mathrm{g}}$$

where it is not defined, according to the non-equilibrium phenomenological approach outlined in this work. It is useful to proceed to the non-dimensioning of the equations referred to above. In order to do this, the following reduced elements are considered

$$L_{11,\,\mathrm{r}} = \frac{L_{11}}{(j''_{\mathrm{i,\,l}}/R)}; \quad X_{\mathrm{r}} = \frac{X}{R}; \quad \dot{S}_{\mathrm{r}} = \frac{\dot{S}}{R j''_{\mathrm{i,\,l}}}$$

$$h_{\mathrm{r}} = \frac{h}{T_b R}; \quad c_{\mathrm{p,\,r}} = c_{\mathrm{p}}/R; \quad s_{\mathrm{r}} = s/R$$

$$p_{\mathrm{r}} = \frac{p}{p_b}; \quad T_{\mathrm{r}} = \frac{T}{T_b} \tag{26}$$

In Eq. (26) R, p_b and T_b are the gas constant, reduction pressure and absolute reduction temperature, respectively. The previously deduced equations can be re-written in a reduced form (subscript 'r') as follows

$$\dot{S}_r = j_{\mathrm{r}}(-X_{\mathrm{r}}) = L_{11,\,\mathrm{r}} \cdot X_{\mathrm{r}}^2 \tag{27}$$

$$j_{\mathrm{r}} = L_{11,\,\mathrm{r}}(-X_{\mathrm{r}}) \tag{28}$$

$$\begin{aligned} X_{\mathrm{r}} = {} & \left[(s_{\mathrm{g,\,r}} - s_{\mathrm{l,\,r}}) - (y - x)\left(\frac{\partial s_{\mathrm{l,\,r}}}{\partial x}\right)_{p_{\mathrm{r}} T_{\mathrm{r}}} \right] \\ & + h_{\mathrm{g,\,r}}\left(\frac{1}{T_{\mathrm{g,\,r}}} - \frac{1}{T_{\mathrm{l,\,r}}}\right) + \frac{A_{\mathrm{r}}}{T_{\mathrm{l,\,r}}(1 + A_{\mathrm{r}} \cdot j_{\mathrm{r}})} \\ & \times \left[\left(h_{\mathrm{g,\,r}} - h_{\mathrm{l,\,r}}\right) \cdot j_{\mathrm{r}} + h_{\mathrm{l,\,r}} \right] \end{aligned} \tag{29}$$

$$A_{\mathrm{r}} = \left(\frac{\partial h_{\mathrm{l,\,r}}}{\partial x}\right)_{p_{\mathrm{r}} T_{\mathrm{r}}} \frac{y - x}{T_{\mathrm{l,\,r}} \cdot c_{\mathrm{p,\,l,\,r}}} \tag{30}$$

$$j_{\mathrm{q,\,r}} = j_{\mathrm{r}} \cdot C_{\mathrm{r}} \tag{31}$$

where

$$C_{\mathrm{r}} = \left(h_{\mathrm{g,\,r}} - h_{\mathrm{l,\,r}}\right) - (y - x)\left(\frac{\partial h_{\mathrm{l,\,r}}}{\partial x}\right)_{p_{\mathrm{r}} T_{\mathrm{r}}} \tag{32}$$

The partial reduced thermodynamical force of a purely mass nature, given by the first square bracket on the right side of Eq. (29) is marked as $X_{\mathrm{i,\,r}}$

$$X_{\mathrm{i,\,r}} = (s_{\mathrm{g,\,r}} - s_{\mathrm{l,\,r}}) - (y - x)\left(\frac{\partial s_{\mathrm{l,r}}}{\partial x}\right)_{p_{\mathrm{r}} T_{\mathrm{r}}} \tag{33}$$

We have to remark here about the similarity between the Eqs. (32) and (33).

Taking into account that $L_{11,\,\mathrm{r}}$ must be in a first approximation independent of X_{r}, from Eqs. (28) and (29) the reduced natural thermodynamical force is expressed in an implicit form as [20,25]

$$-X_{\mathrm{r}} = -\frac{X_{\mathrm{i,\,r}} + h_{\mathrm{g,\,r}}\left(\frac{1}{T_{\mathrm{g,\,r}}} - \frac{1}{T_{\mathrm{l,\,r}}}\right) + \frac{A_{\mathrm{r}} h_{\mathrm{l,\,r}}}{T_{\mathrm{l,\,r}}\left[1 + A_{\mathrm{r}} L_{11,\,\mathrm{r}}(-X_{\mathrm{r}})\right]}}{1 + \frac{A_{\mathrm{r}}\left(h_{\mathrm{g,\,r}} - h_{\mathrm{l,\,r}}\right)}{T_{\mathrm{l,\,r}}\left[1 + A_{\mathrm{r}} L_{11,\,\mathrm{r}}(-X_{\mathrm{r}})\right]} M(p_{\mathrm{r,\,e}}, x_{\mathrm{e}})} \tag{34}$$

where $M(p_{\mathrm{r,\,e}}, x_{\mathrm{e}})$ is a new function discussed later in Section 3. It may be derived, solving Eq. (34) with respect to $-X_{\mathrm{r}}$, by means of a simple iterative method [26], or as a second degree algebraic equation (see Appendix A). The set of ideal points separates the strictly positive forces ($-X_{\mathrm{r}} > 0$), characterized by absorption currents, $j_{\mathrm{r}} > 0$, from the strictly negative ones ($-X_{\mathrm{r}} < 0$), a fact which gives rise to generating currents, $j_{\mathrm{r}} < 0$. Force is useful in approaching interaction mass and heat currents of mono-, bi- and particular polycomponent gas–liquid interactions with a non-ideal mixture, coupling it with Eqs. (28) and (31) and the classic hydro-gaso-dynamics. For instance, the last two types of interactions are encountered in the binary systems NH_3/H_2O, $H_2O/LiBr$, $NH_3/LiNO_3$, $NH_3/NaSCN$, CH_3NH_2/H_2O, etc., or in the ternary systems such as $NH_3/H_2O{-}LiBr$, $CH_3NH_2/H_2O{-}LiBr$, etc.

The case of pure component interactions is important and it is worth paying a little bit more attention to. The Eq. (34) holds good here too, simply considering that x and y take values close to 0 or 1. However, the reduced excess heat A_{r} and the term $(y - x)(\frac{\partial s_{\mathrm{l,\,r}}}{\partial x})_{p_{\mathrm{r}} T_{\mathrm{r}}}$ in Eq. (33) are vanishing when x and y approach 0 or 1, so that Eq. (34) simplifies in case of pure components, namely

$$-X_{\mathrm{r,\,p}} = -(s_{\mathrm{g,\,r}} - s_{\mathrm{l,\,r}}) - h_{\mathrm{g,\,r}}\left(\frac{1}{T_{\mathrm{g,\,r}}} - \frac{1}{T_{\mathrm{l,\,r}}}\right) \tag{35}$$

In Eq. (35), the two terms of the right member have different signs, but $-X_{\mathrm{r,\,p}}$ is strictly negative and holds for vaporization

$$-X_{\mathrm{r,\,p,\,v}} = -X_{\mathrm{r,\,p}}$$

$$j_{\mathrm{r,\,v}} = L_{11,\,\mathrm{r}}\big(-X_{\mathrm{r,\,p,\,v}}\big)$$

$$T_{\mathrm{g,\,r}} > T_{\mathrm{l,\,r}} \tag{36}$$

In case of condensation, the currents are changing the sign, therefore

$$-X_{\mathrm{r,\,p,\,c}} = -\big(-X_{\mathrm{r,\,p}}\big)$$

$$j_{\mathrm{r,\,c}} = L_{11,\,\mathrm{r}}\big(-X_{\mathrm{r,\,p,\,c}}\big)$$

$$T_{\mathrm{g,\,r}} > T_{\mathrm{l,\,r}} \tag{37}$$

When the system approaches an ideal point, the second term on the right side of Eq. (35) vanishes and force takes maximum absolute values, according to a postulate to follow. Section 4 includes case studies for binary and pure component interactions.

The phenomenological coefficient may be theoretically estimated by making a simple imaginary experiment. Let us consider an isolated gaseous mixture bubble of volume $V_{\mathrm{g}}(t)$, at pressure $p_{\mathrm{g}}(t)$ and temperature T_{g}, which interacts with the liquid phase surrounding it. For convenience, it is assumed that the bubble has an isotherm adiabatic evolution in the liquid. According to the first principle of thermodynamics, the variation of its internal energy within the time unit is equal to the power exchanged between the gas and its environment, presented as

$$\dot{U}_{\mathrm{g}} = p_{\mathrm{g}}\dot{V}_{\mathrm{g}}$$

or,

$$-j_{\mathrm{r}}\rho_{\mathrm{l}}|\dot{V}_{\mathrm{g}}|u_{\mathrm{g}} = p_{\mathrm{g}}\dot{V}_{\mathrm{g}} \tag{38}$$

where $u_{\mathrm{g}} = c_{\mathrm{v,\,g}}\ T_{\mathrm{g}}$ is the gas specific internal energy. Upon absorption $\dot{V}_{\mathrm{g}} < 0$, and upon generation $\dot{V}_{\mathrm{g}} > 0$ and Eq. (38) is simplified to the expression

$$j_{\mathrm{r}} = \pm\frac{p_{\mathrm{g}}}{\rho_{\mathrm{l}}c_{\mathrm{v,\,g}}T_{\mathrm{g}}} \tag{39}$$

Eq. (39) shows that positive reduced currents are obtained in absorption and negative ones in generation processes, as previously mentioned herein. This equation is valid when the homobaricity condition in the bubble is met [27], i.e., when $(\dot{R}/C)^2 \ll 1$, where $\dot{R}$ and C are the interface velocity and the velocity of sound in gas, respectively. Physically, the above condition is met where the pressure from the wall is sensibly equal to the pressure in the rest of the gas volume and has a known value. In this case the mass currents have low values and anticipating the further expressed conclusions, are far from the state of equilibrium. The determination of the phenomenological coefficient is not affected by the position of the system relative to the point of equilibrium in respect to which it has been assumed that $L_{11,\,\mathrm{r}}$ is independent X_{r}. $L_{11,\,\mathrm{r}}$ is calculated by means of Eq. (28)

$$L_{11,\,\mathrm{r}} = \frac{j_{\mathrm{r}}}{-X_{\mathrm{r}}} \tag{40}$$

where j_{r} and X_{r} are determined through an iterative process from Eqs. (39) and (34), respectively [20]. A similar result is obtained if, instead of the energy equation, the mass balance in the bubble is written as

$$-j_{\mathrm{r}}\rho_{\mathrm{l}}|\dot{V}| = \rho_{\mathrm{g}}\dot{V} \tag{41}$$

resulting in

$$j_{\mathrm{r}} = \pm\frac{\rho_{\mathrm{g}}}{\rho_{\mathrm{l}}} \tag{42}$$

For an ideal gas

$$\rho_{\mathrm{g}} = \frac{p_{\mathrm{g}}}{RT_{\mathrm{g}}} \tag{43}$$

and the reduced mass flow acquires the form

$$j_{\mathrm{r}} = \pm\frac{p_{\mathrm{g}}}{\rho_{\mathrm{l}}RT_{\mathrm{g}}} \tag{44}$$

which is equally valid and useful in homobaricity conditions.

3. A non-equilibrium phenomenological approach of the coupled mass and heat transfer in chemical interactions

As soon as a chemical reaction is identified, much of a chemical problem involves coupled mass and heat transfer. The entropy source of a chemical interaction is expressed in a classic way by means of the chemical affinity, A [22,23]. The linear form of equations is confined to cases having the ratio (A/RT) much less than unity. For our non-equilibrium approach, let us consider the general case of an independent stoichiometric chemical interaction:

$$\nu'_1 A'_1 + \nu'_2 A'_2 + \cdots + \nu'_{n'} A'_{n'} \Leftrightarrow \nu''_1 A''_1 + \nu''_2 A''_2 + \cdots + \nu''_{n''} A''_{n''} \tag{45}$$

In the conventional equation (45) we shall consider the direct reaction, where reactants, A'_i, $i = 1, \ldots, n'$, marked as prime ($'$), are to the left and the products of reaction, A''_i, $i = 1, \ldots, n''$, marked as secondary ($''$), are to the right. Symbols ν'_i and ν''_i stand for the stoichiometric coefficients of the reactants and products of reaction, respectively. The inverse reaction has inverted prime and secondary superior index. Eq. (45) implies the following mass and heat balances:

$$\sum_{i=1}^{n'} j'_i = \sum_{i=1}^{n''} j''_i \tag{46}$$

and

$$\sum_{i=1}^{n'} j'_{i,q} = j_q + \sum_{i=1}^{n''} j''_{i,q} \tag{47}$$

respectively. The mass currents j'_i and j''_i are given by

$$j'_i = n\nu'_i M_{A'_i}, \quad i = 1, \ldots, n' \tag{48}$$

and

$$j''_i = n\nu''_i M_{A''_i}, \quad i = 1, \ldots, n'', \tag{49}$$

respectively, where n is the number of moles of each species involved in interaction which is the same for all species. The heat flows, coupled with the mass ones, are extensive elements here too. Similarly to the physical interactions, they can be written as

$$j'_{i,q} = h'_i j'_i, \quad i = 1, \ldots, n'$$

$$j''_{i,q} = h''_i j''_i, \quad i = 1, \ldots, n'' \tag{50}$$

Next it is supposed that all reactants and products of reaction have the same pressure, equal to that of equilibrium, p_e. Additionally, the reactants have the temperatures T'_i, $i = 1, \ldots, n'$, which can have different values, in a general case, but the products of reaction have the same pre-established (controlled) temperature, equal to that of equilibrium, T_e. The state parameters may or may not be time dependent. For given external conditions, an independent chemical reaction is a fixed, unique combination, where each mass current of the reactants is dependent of the other $n' - 1$ only through the number n of moles involved in reaction, and the same applies to the mass currents of the products of reaction. In this case, the interaction behaves like having a single degree of freedom, for example that of a coupling mass current of one of the reactants, coupled with its corresponding heat current. Let us suppose that this current is j'_1. The interaction is completely determined from the mass and heat transfer point of view if we assess this current, and further the number n of moles involved in reaction. Using current j'_1, we define the following reduced mass currents of reactants and of the products of reaction

$$j'_{i,r} = \frac{j'_i}{j'_1}, \quad i = 1, \ldots, n' \tag{51}$$

$$j''_{i,r} = \frac{j''_i}{j'_1}, \quad i = 1, \ldots, n'' \tag{52}$$

from where it results

$$j'_i = j'_{i,r} j'_1, \quad i = 1, \ldots, n' \tag{53}$$

$$j''_i = j''_{i,r} j'_1, \quad i = 1, \ldots, n'' \tag{54}$$

The entropy source is expressed again with Eq. (6), considering the same hypothesis as in Section 2. Further, taking into account the Eqs. (46), (47), (50), (53) and (54) the entropy source can be written as

$$\dot{S} = j'_1(-X) \tag{55}$$

where $(-X)$ will be termed non-equilibrium (natural) thermodynamical force of an independent chemical interaction. It is a function of p_e, T'_i, $i = 1, \ldots, n'$ and T_e, and is given by

$$-X = -\left\{ \sum_{i=1}^{n'} j'_{i,r}\left[s'_i + h'_i\left(\frac{1}{T'_i} - \frac{1}{T_e}\right)\right] - \sum_{i=1}^{n''} j''_{i,r} s''_i \right\} \tag{56}$$

Force exhibits the same important property as that of the physical interactions, namely it is a function of state. The entropy and enthalpy in Eq. (56) must be evaluated on the basis of an absolute zero reference state, if the right measure of the interaction is desired to be obtained. The mass currents and reaction heat current are calculated by

$$j'_1 = L_{11}(-X) \tag{57}$$

$$j'_i = L_{11} j'_{i,r}(-X), \quad i = 2, \ldots, n' \tag{58}$$

and

$$j_q = j'_1\left(\sum_{i=1}^{n'} h'_i j'_{i,r} - \sum_{i=1}^{n''} h''_i j''_{i,r}\right) \tag{59}$$

respectively. The phenomenological coefficient is analytically assessed using appropriate methods. This subject is not the main topic of this section. Eqs. (48) and

(57) are finally used to calculate the number n of moles involved in reaction

$$j_1' = L_{11}(-X) = n\nu_1' M_{A_1'} \tag{60}$$

A reduced form of Eqs. (57)–(60) may be easily obtained if the reducing equations (26) are applied here too.

4. Non-equilibrium phenomenological theory applications: case studies of NH_3/H_2O, NH_3, H_2O and other working pairs gas–liquid interactions. Case study of a chemical interaction force

The thermal factors involved in the calculation of the natural thermodynamic force (Eq. (34)) have been expressed analytically in the case of ammonia–water system [20] by means of Ziegler and Trepp state equation [28]. From the experience, the process at hand is non-linear and the assumption of a linear set of phenomenological equations needs to be justified. Indeed, the currents are linear with respect only to the force. In fact, they are strongly non-linear with respect to all interface variables through the thermal factors s_r, h_r, A_r and C_r intervening in the calculation of the thermodynamical force, [28]. The phenomenological coefficient has been estimated by means of Eqs. (40), (39) and (34), resulting in $L_{11,\,r} = 10^{-3}|R|^{-1} = 1/8314$. Before starting the application, we paid special attention to the consistency of the force with respect to the equilibrium thermodynamics, regarding the ideal points calculation of a gas–liquid system and particularly of the ammonia–water mixtures. As it will be further mentioned, force is not defined in an ideal point and never cancels. Practically, such a point is determined by progressively restricting the interval of definition throughout which the function has finite values, of equal absolute value and contrary signs, up to the desired level of accuracy (here usually obtained up to the sixth decimal). In principle, the two thermodynamical approaches, the equilibrium and the non-equilibrium phenomenological ones, are equivalent, as far as the determination of the ideal point is concerned. However, although in both cases the same state equation for the binary mixture under study has been used, the non-equilibrium phenomenological calculations has lead to sensibly different results in some parts of the solubility field [20] because the Ziegler and Trepp equation has an arbitrarily chosen zero reference of state. First attempts to approach the results of the two methods failed when a non-linear dependence of the mass current with respect to the natural force was considered. This explains why we used just only a linear dependence of the mass current with respect to the force (Eq. (24)). Best results were obtained by amplifying the second term of the denominator in Eq. (34) by a match function $M(p_{r,\,e}, x_e)$, already mentioned in Section 3. Several values of the match function are given in Fig. 1 for five reduced ideal pressures and five ideal solution mass fractions. These values were well correlated by a four-order double polynomial expansion

$$M(p_{r,\,e}, x_e) = \exp\left(\sum_{i,\,j=0}^{4} A_{i,\,j} p_{r,\,e}^{i} x_e^{j}\right) \tag{61}$$

The coefficients $A_{i,\,j}$ are given below:

$A_{00} = -1.55107 \times 10^{0}$; $A_{01} = 4.30114 \times 10^{0}$; $A_{02} = -2.50709 \times 10^{1}$; $A_{03} = 5.14562 \times 10^{1}$; $A_{04} = 3.53064 \times 10^{1}$;
$A_{10} = 2.20458 \times 10^{1}$; $A_{11} = -3.43605 \times 10^{2}$; $A_{12} = 2.15534 \times 10^{3}$; $A_{13} = -5.56704 \times 10^{3}$; $A_{14} = 4.87992 \times 10^{3}$;
$A_{20} = -5.72617 \times 10^{1}$; $A_{21} = 9.54441 \times 10^{2}$; $A_{22} = -6.00841 \times 10^{3}$; $A_{23} = 1.54652 \times 10^{4}$; $A_{24} = -1.35339 \times 10^{4}$;
$A_{30} = 5.53949 \times 10^{1}$; $A_{31} = -9.34452 \times 10^{2}$; $A_{32} = 5.88969 \times 10^{3}$; $A_{33} = -1.51448 \times 10^{4}$; $A_{34} = 1.32402 \times 10^{4}$;
$A_{40} = -1.74164 \times 10^{1}$; $A_{41} = 2.94977 \times 10^{2}$; $A_{42} = -1.86140 \times 10^{3}$; $A_{43} = 4.78901 \times 10^{3}$; $A_{44} = -4.18852 \times 10^{3}$

The relative differences (%) in the approximation of equilibrium mass fraction of the mixture solution with Eq. (34), are plotted in Fig. 2. The differences could come also from the different units used for x_e, namely mass fraction in h–x diagram, and molar fraction in the equation of state of Ziegler and Trepp, respectively, and the use of a unique computing value for the phenomenological coefficient. $M(p_{r,\,e}, x_e)$ compensates the arbitrarily chosen zero reference state of a system entropy and enthalpy. To this extent, considering the absolute zero temperature as zero reference state of an interacting system enthalpy and entropy can be a goal for the future non-equilibrium phenomenological approach applications, because in this case $M(p_{r,\,e}, x_e)$ is no more needed and the computation simplifies. However, in our case, before using Eq. (34) in an evolution process assessment, we need the 'nearest' ideal point which the system evolves to, in order to calculate the match function. Here, the Prigogine theorem is helpful, relative to the minimization of the entropy source in an irreversible stationary process, and the computation becomes an iterative one. However, practically with a good initial guess of the nearest ideal

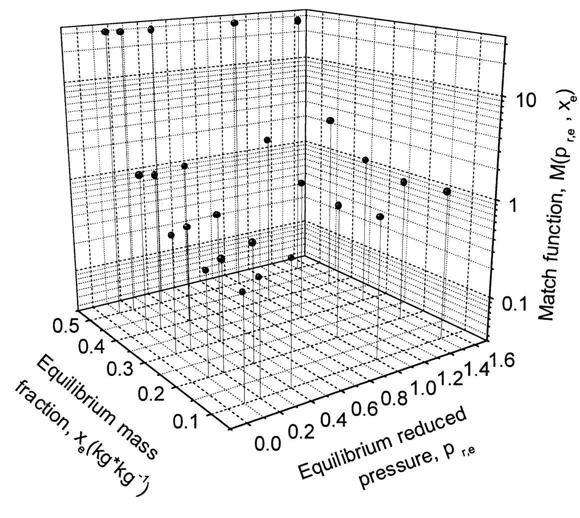


Fig. 1. Several values of the match function in Eq. (34) for ammonia/water gas–liquid mixtures ($p_b = 10$ bar; $T_b = 100$ K).

point, the use of this theorem would not be necessary and the computation is correspondingly simplified. Further comments on this are included in a paper to follow [29]. For our application, Eq. (34) covers a usual domain for refrigeration purposes with the NH_3/H_2O system, namely of $1 \leq p \leq 15$ bar, $0.1 \leq x \leq 0.45$ and $0.5 \leq y \leq 0.998$.

The Eqs. (27), (28), (31) and (34) have been represented for exemplification as partial functions of the reduced state parameters x, $t_{l,\,r}$, y and $t_{g,\,r}$, respectively in Figs. 3–7 (at interface, gas and liquid are in mechanical equilibrium, $p_l \cong p_g$, and no pressure partial functions exist in fact). For completeness, the natural thermodynamic force of pure components (water and ammonia) is given in two study cases in Fig. 8. The curves are different in shape, depending upon the variable used in the abscissa and the nature of the system. Partial functions which depend on the parameters of the same phase have the same monotonous absorption or generation variation. According to the postulate (see Section 5) and its consequence, the diagrams show the continuous increase of force, Figs. 3b and 5b–7b, entropy source, Figs. 3a and 5a–7a, and of the coupled mass and heat currents, Fig. 4a and b, respectively, approaching an ideal state. In case of currents, an ideal point approaching (i.p.a) effect is emphasized: depending on how strong the currents coupling is, the approach to an ideal state determines an increased effect of the function absolute value by several percentages (in case of pure components), to several hundred times (for the binary system), as compared to the states which are far from the same ideal point. In this way, referring to currents, the term of 'far from equilibrium state' changes here its classical meaning and corresponds to its opposite, namely to the low interaction. The i.p.a. effect has been brought to light also in the case of other working combinations, namely $NH_3/LiNO_3$ and NH_3/NaSCN, Figs. 9–10, respectively (first mentioned in Ref. [30]). An i.p.a. effect behaviour has also been observed while calculating Eq. (56) for an independent chemical reaction. In this work we present a case study concerning the natural force of ammonia synthesis from nitrogen and hydrogen. The results are given in Fig. 11, where force (Eq. (56)) is plotted against several values of the reactants temperature ($T'_1 = T'_2$) and several pressures. The equilibrium temperature is equal to 600 K. The direct reaction, between hydrogen and nitrogen to form ammonia, has

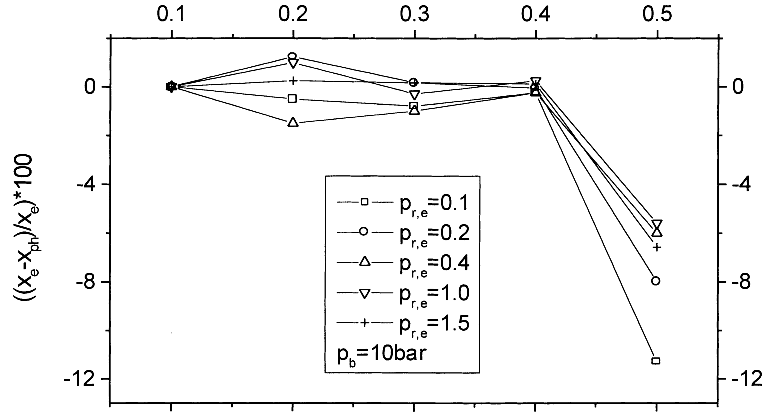


Fig. 2. The relative differences % in the approximation of equilibrium mass fraction of ammonia/water solutions with Eq. (34).

negative forces and currents and takes place until the temperature of reactants, hydrogen and nitrogen, is lower than that of equilibrium. The inverse reaction, when ammonia decomposes to form hydrogen and nitrogen, has positive forces and currents and takes place as long as the temperature of the reactant ammonia is higher than that of equilibrium. The mass and heat currents assessment needs the phenomenological coefficient of a gas–gas interaction, which is not deduced here because the purpose of this example is only to emphasize the common feature of the natural forces approaching an ideal point and not to go deeper into a chemical reaction.

The i.p.a. effect may be quantified, in the case of a single interaction type, by a figure of merit, 'f', equal to the ratio of two same type (e.g., absorption/condensation or generation/vaporization) function values, corresponding to the states closer, and farther, respectively, to the ideal state. Figs. 3–11 include also the maximal 'f' values for the chosen examples. Besides an 'f' evaluation, our phenomenological approach creates also the opportunity to compare the intensity of

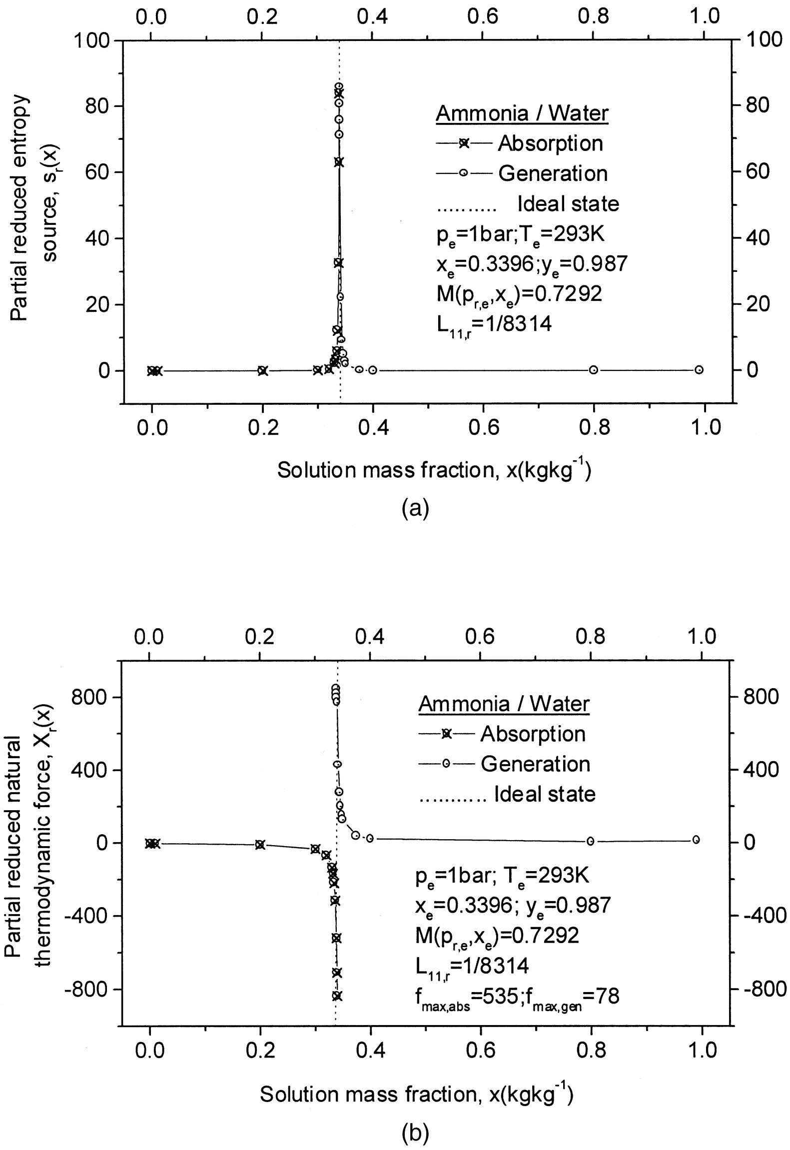
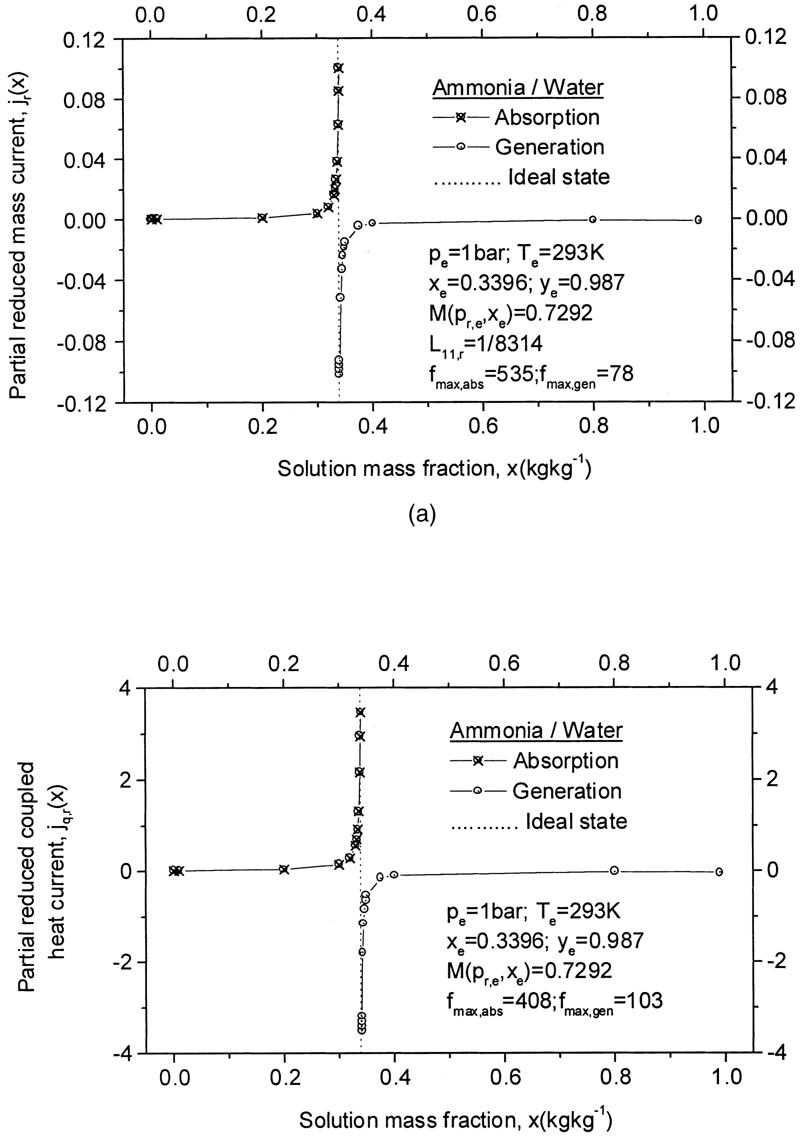


Fig. 3. The i.p.a. effect behaviour for the reduced entropy source (a) and natural thermodynamic force (b) as functions of solution mass fraction.

different interaction types, comparing the (reduced) values of natural forces calculated with Eqs. (34)–(37) and (56) for the same interaction p, T, x and y state parameters. Obviously, the calculations must be performed in this case with entropy and enthalpy functions of state having the same zero reference state.

The importance of the currents coupling is worth mentioning. Indeed, let us consider the mathematical form of the chemical interactions given in Section 3 and particularize it for processes involving separate or simultaneous, but non-coupled, mass and heat transfer, characterized by

$$
\begin{aligned}
& n' = n''; \\
& j'_{\mathrm{i}} = j''_{\mathrm{i}}, \quad i = 1, \ldots, n'; \\
& j_{\mathrm{q}} = 0; \\
& v'_{\mathrm{i}} = v''_{\mathrm{i}}, \quad A'_i = A''_i, \quad i = 1, \ldots, n'.
\end{aligned}
\tag{62}
$$



(a)

(b)

Fig. 4. The i.p.a. effect behaviour for the reduced mass (a) and heat current (b) as functions of solution mass fraction.

In this case, the non-equilibrium (natural) thermodynamical force of a non-coupled mass and heat transfer process is expressed with Eqs. (56) and (62) by:

$$-X = -\sum_{i=1}^{n'} j'_{i,\,r}\left[\left(s'_i - s''_i\right) + h'_i\left(\frac{1}{T'_i} - \frac{1}{T_e}\right)\right] \qquad (63)$$

For a system approaching an ideal point $T'_i \to T_e$, and therefore $s'_i \to s''_i$, $i = 1,\dots,n'$ and $-X \to 0$; this means that the i.p.a. effect is rather a coupling effect.

The specialized literature does not contain systematic theoretical or experimental accounts of the non-equilibrium interaction in the NH_3/H_2O system against which the results obtained here might be compared. The only confirmation of such results is given by their compliance with a few experimental works which are in agreement with the graphs shown in Figs. 3–10, proving the increase of the gaseous mass flow driven as a two-phase binary system is approaching a state of saturation. To this effect, some mention should be made of the experimental work of Hui and Thome [31] who investigated the boiling of binary azeotropic etha-

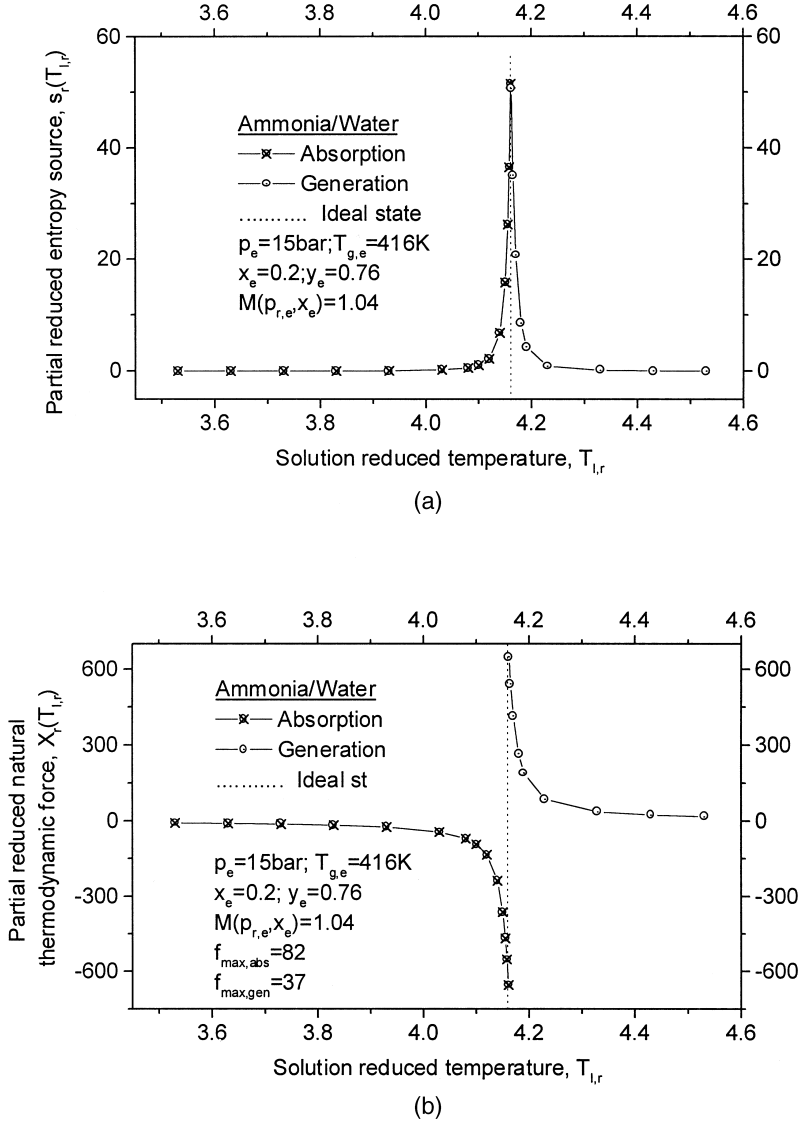


Fig. 5. The i.p.a. effect behaviour for the reduced entropy source (a) and natural thermodynamic force (b) as functions of solution temperature.

nol–water and ethanol–benzene mixtures and ascertained the increase in the number of vaporization points, until it became impossible for such points to be individually distinguished, as the molar fraction of the mixtures approached the saturation value.

At this point it is possible to give a satisfactory qualitative explanation to the problem of the ammonia bubble absorption, raised in the introduction of this paper. Indeed, during the *growth* phase the absorbed mass flow j_r increases continuously as the state of the interface approaches an equilibrium point, according to the diagram shown in Fig. 4a plotted with p, T, x and y values close to the experimental conditions. At a certain point of time, this increase exceeds the value of the feeding flow rate, causing the collapse of the bubble, and continues after the starting of the collapse at an even higher speed, up to the total absorption of the bubble. This further explains why the *collapse* duration is much shorter than the duration of the *growth*. Moreover, the non-equilibrium phenomenological

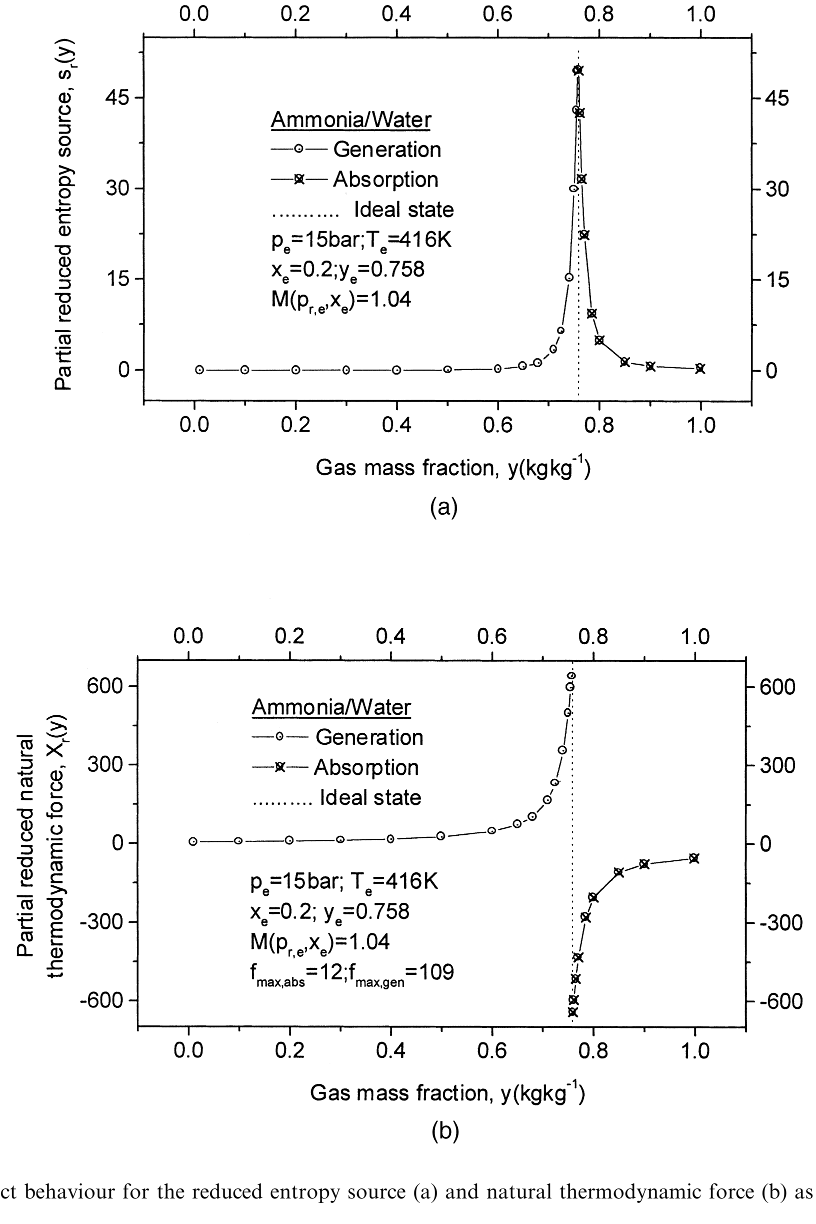
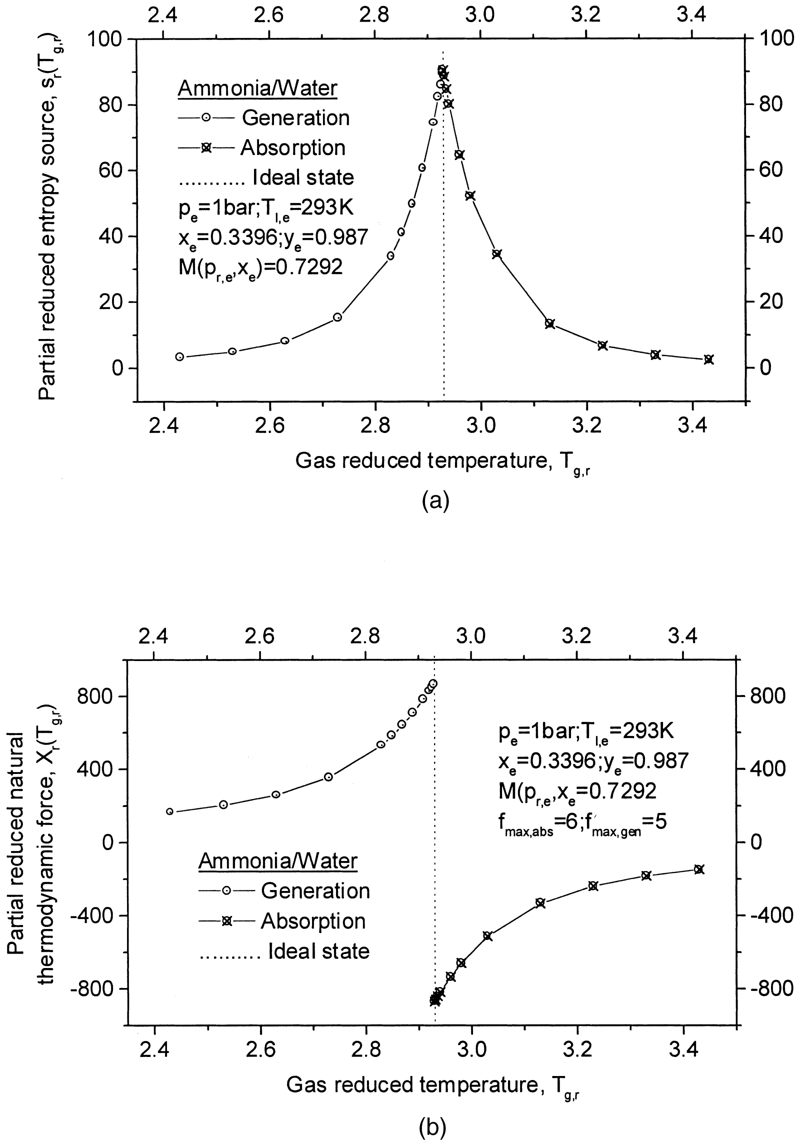


Fig. 6. The i.p.a. effect behaviour for the reduced entropy source (a) and natural thermodynamic force (b) as functions of gas mass fraction.

qualitative explanation of the bubble collapse leads to the conclusion that: (i) the currents depend directly on the interface variables only and not on the interface magnitude, therefore absorption in the NH_3/H_2O system should not be a surface process, as it is usually considered and consequently, (ii) the use of the mass transfer coefficients K_g and K_l as surface factors (Eq. (2)) is improper, at least in the case of the NH_3/H_2O system and (iii) estimation of the interface mass transfer by analogy with heat transfer is improper too, because the force in Eq. (2) tends to zero when approaching an ideal point, which, from the non-equilibrium point of view, is not true. A quantitative estimate of the evolution of the NH_3/H_2O gaseous mixture bubble in the NH_3/H_2O liquid absorber is given in a paper to follow [29].

5. Non-equilibrium (natural) and equilibrium (ideal) thermodynamical forces

Some readers may consider our results contradic-



(a)

(b)

Fig. 7. The i.p.a. effect behaviour for the reduced entropy source (a) and natural thermodynamic force (b) as functions of gas reduced temperature.

tory to the classic approach of the mass and heat transfer. This is because the known thermodynamical forces governing coupled heat and mass transfer in continuous or discontinuous (interface) media, like $\nabla T/T^2$ and $\nabla \mu/T$ or ΔT and Δx, respectively, are vanishing in an ideal point and the same applies to chemical forces, expressed with the help of the chemical affinity [19,22,23], but the natural forces, given by Eqs. (34) and (56), are not. In order to distinguish between the two types of forces, the classic ones, involved in coupled mass and heat transfer, will be referred to as equilibrium (ideal) thermodynamical forces. The difference between the natural and ideal forces is formal and comes from the different tools which they were obtained with, non-equilibrium and equilibrium, respectively. The natural forces describe the evolution of an interacting system, towards an ideal point, without knowing whether an equilibrium will be reached or not (this depends on the future external conditions of the interaction), while the ideal ones regard the same evolution assuming that equilibrium already exists. The two approaches, natural and ideal, lead to the same results and can be coupled in order to assess a mass and heat transfer process. The first successful example in this direction is shown in the paper to follow [29], where ammonia bubble absorption in ammonia/water mixtures is modeled and the model is proved by experiment.

The non-equilibrium thermodynamical forces of physical and chemical interactions enjoy several important properties. Some of them are given for the physical interactions in a previous work [30], but here they are given in a reworked and completed form. First, as already mentioned, force (Eq. (34)) applies also to physical interactions of solid–liquid, solid–gas or gas–gas, liquid–liquid type, provided that appropriate indexes be used (e.g., for a liquid–solid interaction with a solid final phase, the indices g and l change in l, and s, respectively). Unlike the ideal forces of Fourier and Fick type, which cannot be applied to discontinuous media because ∇ is not defined in points of discontinuity (such as those of an interface), the natural force is valid for both continuous or discontinuous media. Obviously, the currents assessment needs to analytically determine the right phenomenological coefficients, which is often a difficult task. The second property is related to the natural force behaviour close to an ideal point. This force being essentially new, the specialized literature does not point out this aspect and refers only to the total entropy increase to maximum values when the system approaches such a point, causing the source strictly confirming to the positive definition. This is not enough to describe its behaviour near such a point. According to previous works [22,23], the ideal forces are governing the evolution of systems involving coupled heat and mass transfer processes and the same is valid for the non-equilibrium (natural) thermodynamical forces, which quantify the natural tendency of such systems leading to an equilibrium and obey the following:

Postulate. *The non-equilibrium (natural) thermodynamical force of a closed or open evolution system, involving coupled mass and heat transfer, continuously increases in absolute value to maximal finite values approaching an ideal point.*

The phenomenological factors, proportional to the force (entropy source, currents), must have the same

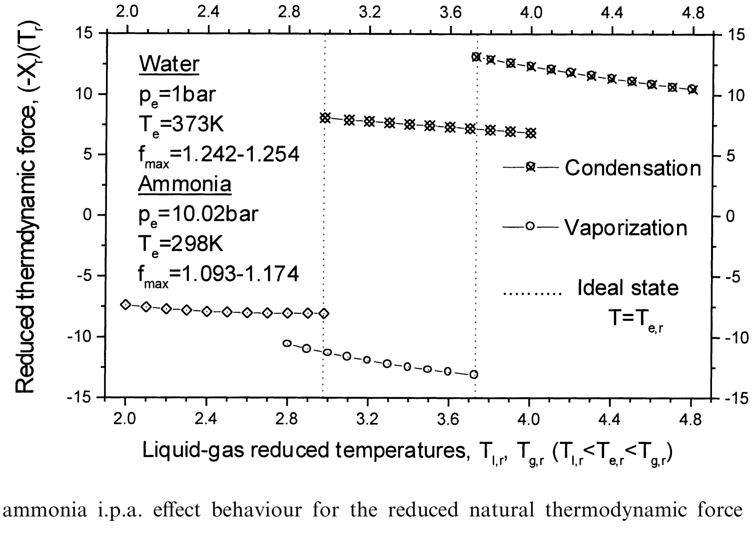


Fig. 8. The water and ammonia i.p.a. effect behaviour for the reduced natural thermodynamic force as function of liquid–gas reduced temperature.

force feature. The postulate and its consequence are verified by all study cases synthesized in Figs. 3–11, including physical interactions of pure components with ideal mixture, and binary with non-ideal mixture, as well as a chemical one. Third, we have the following:

Lemma. *A natural thermodynamical force is an odd function at least in close proximity of an ideal point,* $z_e = z_e(p_{l,e}, T_{l,e}, x_e, p_{g,e}, T_{g,e}, y_e)$:

$$(-X)(z_e+\delta) = -(-X)(z_e-\delta).$$

This property results by integrating the total force derivative in a closed path, symmetrical with respect to the ideal point. Because $(-X)$ is a function of state, the integral is zero and making $\delta \to 0$, the lemma is

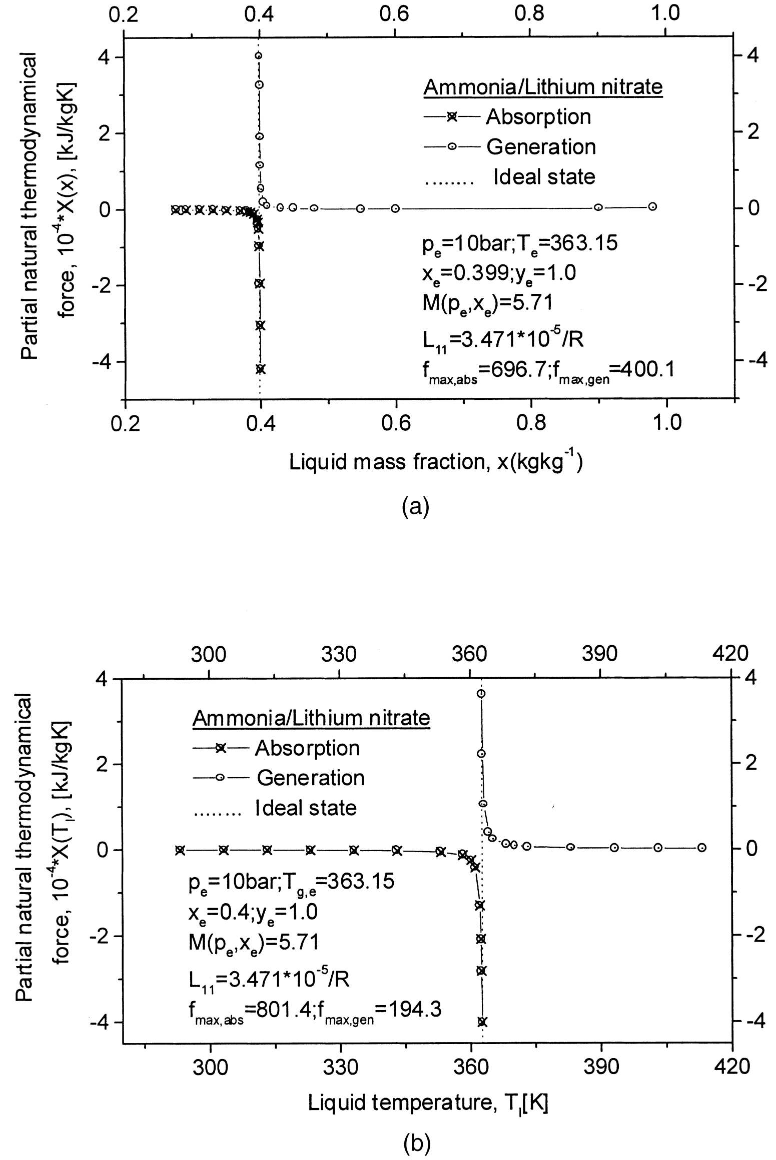


Fig. 9. The i.p.a. effect behaviour for partial natural thermodynamical forces of liquid mass fraction (a) and liquid temperature (b) in case of the $NH_3/LiNO_3$ system.

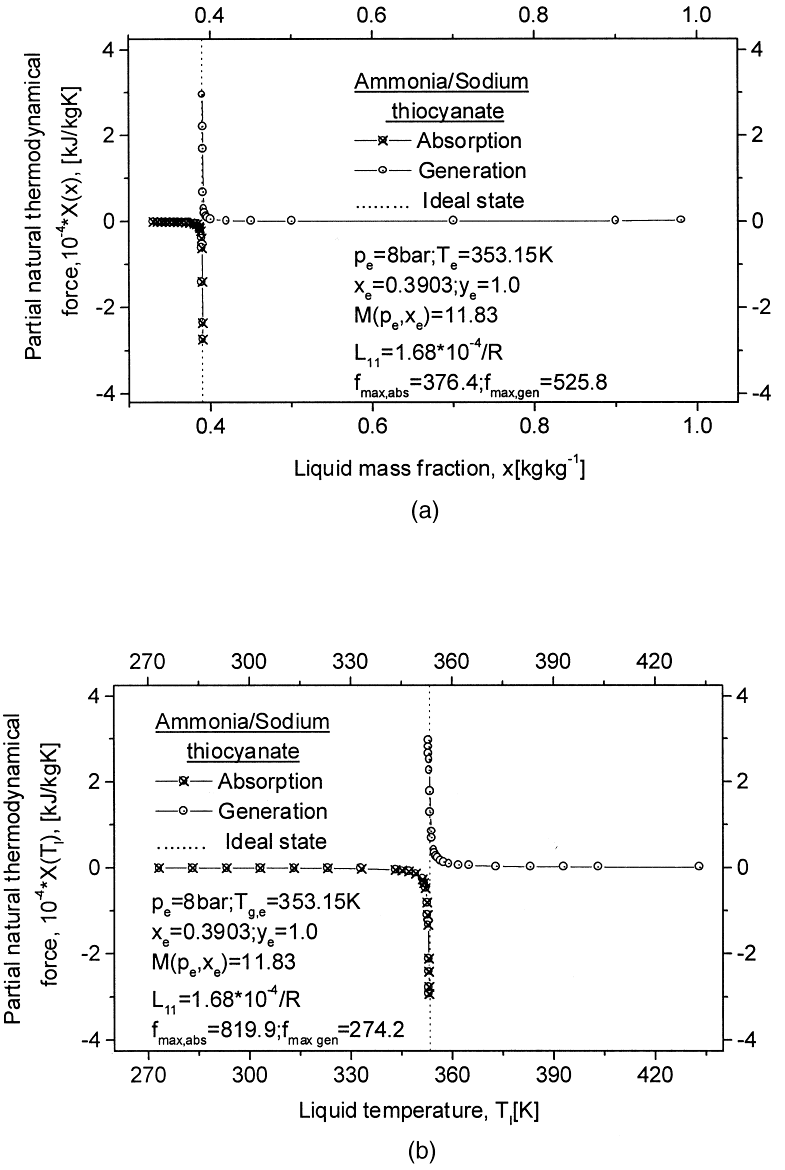


Fig. 10. The i.p.a. effect behaviour for partial natural thermodynamical forces of liquid mass fraction (a) and liquid temperature (b) in case of the NH_3/NaSCN system.

demonstrated. Fourth, the force must not be defined in an ideal point, because, according to the lemma, it should, at the same time and with same probability, take two opposite values, corresponding to the elementary processes adjacent to an ideal point with opposite signs of the homologues currents, which is impossible. Therefore we have the following:

Corollary. *A natural thermodynamical force of coupled mass and heat transfer processes is not defined in an ideal point.*

Here, both the double ideal points (e.g., absorption (condensation) and generation (vaporization)) and the triple ones are included. This property extends to the currents and to the entropy source, not defined in an ideal point as well.

6. Conclusions

The above leads to the following conclusions:

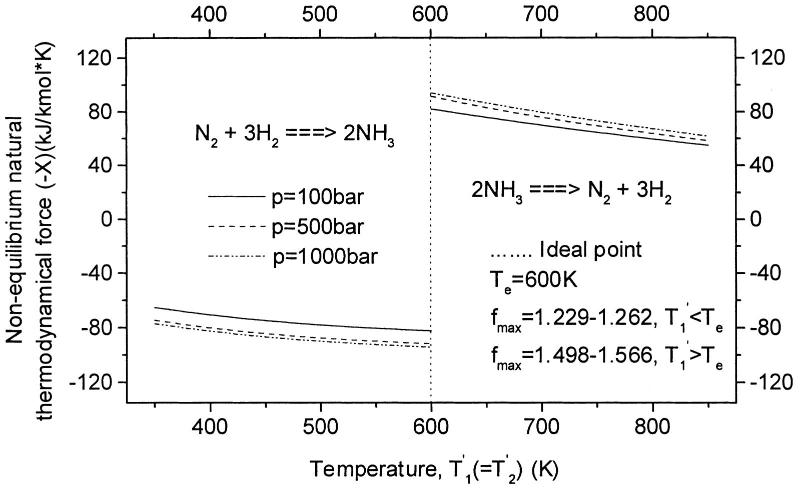


Fig. 11. The i.p.a. effect behaviour calculated in case of the natural chemical force for the ammonia synthesis, against the reactants same temperature.

1. The paper presents an original non-equilibrium phenomenological theory of mass and heat transfer. In the frame of it are introduced the non-equilibrium (natural) thermodynamical forces, which govern the mass and heat transfer in physical and chemical interactions.
2. The theory is particularized to a few case studies, including evolution of physical binary gas–liquid interactions in non-ideal mixture (working pairs NH_3/H_2O, NH_3/$LiNO_3$, NH_3/NaSCN), pure components (NH_3, H_2O), as well as an independent chemical interaction (ammonia synthesis). All applications emphasize an important feature of the mass and heat coupled currents, that of the i.p.a effect, not mentioned so far in the specialized literature. The i.p.a. effect consists of a continuous increase of the mass and heat currents of an interaction evolving towards an ideal point, by several percentages to several hundreds of times, as compared to the states which are far from the same ideal point. The smallest increase effect was observed in case of the physical (pure component) interactions in the ideal mixture, followed by that of the chemical reaction. The highest effect was exhibit by the physical (working pair) interactions in the non-ideal mixture. On the contrary, the forces of systems with non-coupled mass and heat currents tend to zero when evolved to equilibrium.
3. The existence of the i.p.a. effect satisfactorily explains from a qualitative point of view the problem of the ammonia bubble absorption, raised in the introduction of this paper. This explanation throws a new light on the absorption phenomenon encountered by the working pairs used in the thermal absorption technology: (i) absorption process is not a surface phenomenon, as it is usually considered and (ii) the actual estimation of the interface mass transfer by analogy with heat transfer is improper.
4. The non-equilibrium approach, outlined in this paper, is not contradictory to the classic equilibrium phenomenological theory. On the contrary, it may be an equivalent alternative or it may be combined with the classic approach in order to assess coupled mass and heat transfer processes. Its main investigation tool, the natural thermodynamical force, has specific important features in the neighbourhood of an ideal point, expressed by a postulate, a lemma and a corollary, given in the paper.

Appendix A

The natural thermodynamical force may also be given explicitly, solving the second degree algebraic equation in $-X_r$, obtained from Eq. (34)

$$d(-X_r)^2+(1-ad+c)(-X_r)-(a+b)=0 \qquad \text{(A1)}$$

where

$$a = X_{i,r} + h_{g,r}\left(\frac{1}{T_{g,r}} - \frac{1}{T_{l,r}}\right)$$

$$b = \frac{A_r h_{l,\,r}}{T_{l,\,r}}$$

$$c = \frac{A_r\left(h_{g,\,r} - h_{l,\,r}\right)M(p_{r,\,e}, x_e)}{T_{l,\,r}}$$

$$d = A_r L_{11,\,r} \tag{A2}$$

Absorption processes occur when $1 - ad + c < 0$ and $d < 0$ and the force is given by

$$(-X_r) = \frac{|1 - ad + c| - \sqrt{(1 - ad + c)^2 + 4|d|(a + b)}}{2d} \tag{A3}$$

Generation processes take place when $1 - ad + c > 0$ and $d > 0$ and the force is expressed by

$$(-X_r) = \frac{-|1 - ad + c| + \sqrt{(1 - ad + c)^2 + 4|d|(a + b)}}{2d} \tag{A4}$$

or by Eq. (A3), when $1 - ad + c > 0$, but $d < 0$. From the above it can be remarked that the use of the explicit form of the force is no simpler than that of the Eq. (34), which the author always preferred in computations although the values obtained with it are comparatively smaller up to a maximum 1.5%.

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