

# Exergy calculation of lithium bromide–water solution and its application in the exergetic evaluation of absorption refrigeration systems LiBr–H<sub>2</sub>O

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## SUMMARY

The aim of this study is to present a methodology to calculate the exergy of lithium bromide–water solution (LiBr/H<sub>2</sub>O) widely used in absorption refrigeration systems, absorption heat pumps and absorption heat transformers. As the LiBr/H<sub>2</sub>O solution is not ideal, it is necessary to take into account the activity of the constituents in the chemical exergy calculation. Adopting the reference environment proposed by Szargut *et al.*, the chemical exergy of pure LiBr was obtained as well as the chemical and physical exergy of the LiBr/H<sub>2</sub>O solution. Results are reported in the temperature range between 5 and 180°C. In the literature, exergy values for LiBr/H<sub>2</sub>O solution are widely varied. This fact is due to different reference systems adopted to calculate exergy. Some cases in the literature are compared with that obtained with the methodology proposed in this study and with the approaches of Koehler, Ibele, Soltes and Winter and Oliveira and Le Goff. Copyright © 2010 John Wiley & Sons, Ltd.

## KEY WORDS

absorption system; exergy; lithium bromide; chemical exergy; reference system

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## 1. INTRODUCTION

The bromide lithium–water (LiBr/H<sub>2</sub>O) solution is widely used as working fluid in absorption refrigeration systems because of its nonvolatile and non-toxic, besides being environmentally friendly by not contributing to ozone depletion. Employing this solution avoids the use of CFC refrigerants and its consequent environmental damage.

Low cost and easy handling are the advantages of using water as refrigerant (despite its high freezing point). On the other hand, low crystallization temperature, high absorption capacity and low viscosity are the advantages of LiBr/H<sub>2</sub>O solution as absorbent [1].

Absorption refrigeration systems are attractive and of increasing interest because they can be driven by low-temperature heat sources and provide an excellent

way for converting solar energy or waste heat into useful refrigeration [2,3]. They differ from compression systems due to the use of a heat source as energy input to operate; on the other hand, the refrigeration devices based on compression systems need mechanical energy to operate. This is the main advantage of absorption systems; which can run on burning fuel or using waste heat, recovered from other thermal systems.

In exergy studies, it is necessary to calculate the exergy of the working fluid at different points of the system. In some studies found in the literature [3–6], the exergy of the solution is calculated considering the thermal component only (physical exergy), without considering the chemical exergy.

In the literature there are some studies about exergetic evaluation of absorption systems considering explicitly the chemical exergy for the pair H<sub>2</sub>O/NH<sub>3</sub> [7,8], but not many studies on absorption

system considering the chemical exergy for LiBr/H<sub>2</sub>O solution.

In terms of exergy destruction calculation (irreversibilities), the balance of physical exergies gives correct results due to the Gouy Stodola equation being implicitly applied [3].

Moreover, the choice of reference species to obtain chemical exergy does not influence the values of internal exergy losses but influences distinctly the values of external losses, and hence also the calculated values of the degree of thermodynamic perfection or the exergetic efficiency [9].

On the other hand, in the analysis of components such as absorbers or desorbers (generators), where there are processes of separation and mixture, the consideration of the chemical exergy of LiBr/H<sub>2</sub>O solution would give differences in the results of exergetic ratio of inlet and outlet type due to its dependence on the numeric values of the exergy.

Moreover, values of exergy of the LiBr/H<sub>2</sub>O solution reported in the literature are widely varied; for this reason there is the need to standardize the procedure for exergy calculation of the LiBr/H<sub>2</sub>O solution adopting a unique and general environment reference system.

Thus, this study presents a methodological proposal for the exergy calculation of a LiBr/H<sub>2</sub>O solution adopting the reference environment proposed by Szargut *et al.* [10] considering their physical and chemical components. This methodology represents a useful tool for exergy analysis of mixture and separation process in absorption systems LiBr/H<sub>2</sub>O owing to permit expanding the control volume including other thermal systems such as direct-fired or cogeneration systems; hence, an integrated analysis based in a unique reference system can be performed.

## 2. PROPERTIES OF THE LITHIUM BROMIDE-WATER SOLUTION

For exergy calculation of the LiBr/H<sub>2</sub>O solution, the thermodynamic properties are essential. The specific enthalpy and entropy are indispensable to calculate physical exergy, while the consideration of the components activities is necessary to calculate the exergy of the mixture [10,11].

Some studies in the past intended to describe the properties of the lithium bromide solution. The most known study is probably the research by McNeely [12].

Chua *et al.* [13] published an interesting study correlating entropy and enthalpy of LiBr/H<sub>2</sub>O solutions. In that paper, tables with values for enthalpy and entropy were presented for a range of temperatures and concentrations (0°C < T < 190°C and 0% < x < 75%).

In a recent study, Kim and Infante Ferreira [14] presented correlations for the calculation of enthalpy, entropy, osmotic coefficient and Gibbs free energy of the LiBr/H<sub>2</sub>O solution (0°C < T < 210°C and 0% < x < 70%).

### 2.1. Solubility of pure LiBr in water

Figure 1 shows the solubility of pure LiBr in water as a function of the temperature. The values are from Boryta [15].

### 2.2. Enthalpy

The enthalpy of LiBr/H<sub>2</sub>O solution was evaluated following the procedure described by Kim and Infante Ferreira [14],

$$\bar{h} = y_{\text{LiBr}} \cdot \bar{h}_{\text{LiBr}(T,p)}^{\infty} + (1 - y_{\text{LiBr}}) \cdot \bar{h}_{\text{H}_2\text{O}(T,p)}^l + \bar{h}_{(T,p,m)}^E \quad (1)$$

where  $\bar{h}_{\text{LiBr}(T,p)}^{\infty}$  is the molar enthalpy of the *ideal LiBr fluid*,  $\bar{h}_{\text{H}_2\text{O}(T,p)}^l$  is the molar enthalpy of pure water and  $\bar{h}_{(T,p,m)}^E$  is the enthalpy excess. These terms can be calculated by Equations (2)–(4). Values of the constants employed are presented in Table I.

$$\begin{aligned} \bar{h}_{\text{LiBr}}^{\infty} &= \bar{h}_{\text{LiBr};0}^{\infty} + \int_{T_0}^T C_{p\text{LiBr}}^{\infty} dT \\ &- \left[ V_{\text{LiBr}}^{\infty} - T \left( \frac{\partial V_{\text{LiBr}}^{\infty}}{\partial T} \right) \right] (p - p_0^*) \quad (2) \end{aligned}$$

$$\begin{aligned} \bar{h}_{\text{H}_2\text{O}}^l &= \bar{h}_{\text{H}_2\text{O};0}^l + \int_{T_0}^T C_{p\text{H}_2\text{O}}^l dT \\ &- \int_{p_0^*}^p \left[ V_{\text{H}_2\text{O}}^l - T \cdot \left( \frac{\partial V_{\text{H}_2\text{O}}^l}{\partial T} \right) \right] \cdot dp \quad (3) \end{aligned}$$

$$\bar{h}^E = -y_{\text{LiBr}} \cdot v \cdot \bar{R} \cdot T^2 \sum_{j=1}^6 \frac{2}{i} \cdot \left( \frac{\partial a_i}{\partial T} + \frac{i}{2v} \frac{\partial b_i}{\partial T} p \right) \cdot m^{i/2} \quad (4)$$

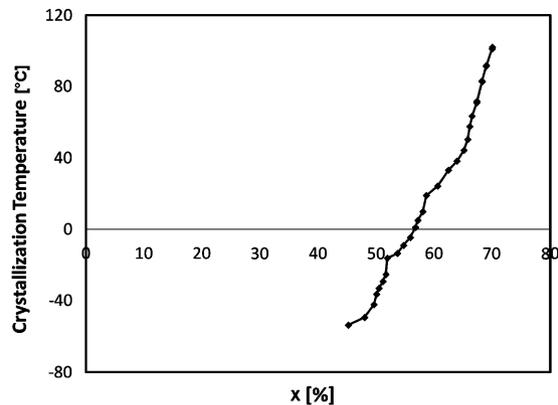
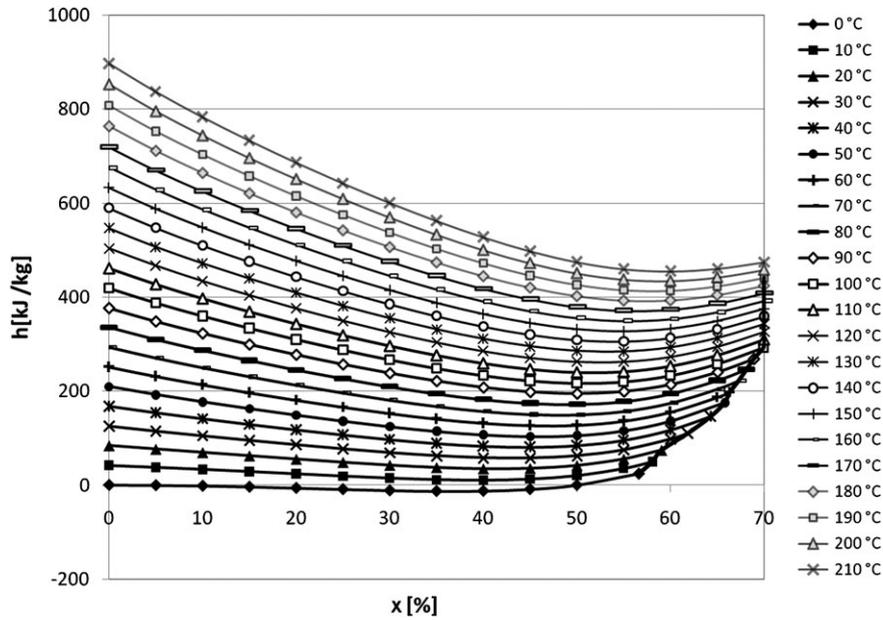


Figure 1. Solubility of pure LiBr in water.

**Table I.** Equation constants by Kim and Infante Ferreira [13].

	$j=0$	$j=1$	$j=2$
$a_{1j}$	$-2.19631610^1$	$+4.937232 \times 10^3$	$-6.5548406 \times 10^5$
$a_{2j}$	$-3.810475 \times 10^3$	$+2.611535 \times 10^6$	$-3.6699691 \times 10^8$
$a_{3j}$	$+1.228085 \times 10^5$	$-7.718792 \times 10^7$	$+1.039856 \times 10^{10}$
$a_{4j}$	$-1.47167410^6$	$+9.195285 \times 10^8$	$-1.189450 \times 10^{11}$
$a_{5j}$	$+7.765821 \times 10^6$	$-4.93756710^9$	$+6.317555 \times 10^{11}$
$a_{6j}$	$-1.511892 \times 10^7$	$+9.839974 \times 10^9$	$-1.27379 \times 10^{12}$
$b_{0j}$	$-4.417865 \times 10^{-5}$	$+3.114900^{-2}$	$-4.36112260$
$b_{1j}$	$+3.07410^{-4}$	$-1.86321 \times 10^{-1}$	$+2.738714 \times 10^1$
$b_{2j}$	$-4.080794 \times 10^{-4}$	$+2.160810^{-1}$	$-2.5175971 \times 10^1$
$c_j$	$-9.44013410^5$	$-5.84232610^8$	0
$d_j$	$+1.197193 \times 10^1$	$-1.83055 \times 10^{-2}$	$+2.87093810^{-5}$
$e_j$	$+2.66299 \times 10^{-3}$	$-3.865189 \times 10^{-6}$	$+7.464841 \times 10^{-9}$
$\bar{h}_{\text{LiBr};0}^{\infty}$	$-57.1521 \text{ (kJ kmol}^{-1}\text{)}$	$\bar{h}_{\text{H}_2\text{O};0}^{\infty}$	0
$\bar{s}_{\text{LiBr};0}^{\infty}$	$+47.5562 \text{ (kJ kmol}^{-1}\text{)}$	$\bar{s}_{\text{H}_2\text{O};0}^{\infty}$	0
$T_0$	273.15 K	$p_0^*$	0.6108 kPa

**Figure 2.** Enthalpy of lithium bromide–water solutions as a function of the concentration for different temperatures.

where  $\nu$  is the dissociation number for the solute ( $\nu = 2$ ).

$$\bar{C}_{\rho\text{LiBr}}^{\infty} = \bar{R} \cdot T^{-2} \sum_{j=0}^2 \frac{c_j}{T^j} \quad (5)$$

$$\bar{V}_{\text{LiBr}}^{\infty} = \bar{R} \cdot T \cdot b_0 \quad (6)$$

$$\bar{C}_{\rho\text{H}_2\text{O}}^l = \bar{R} \cdot \sum_{j=0}^2 d_j \cdot T^j \quad (7)$$

$$\bar{V}_{\text{H}_2\text{O}}^l = \bar{R} \cdot \sum_{j=0}^2 e_j \cdot T^j \quad (8)$$

$$a_i = \sum_{j=0}^2 a_{ij} \cdot T^{-j} \quad (9)$$

$$b_i = \sum_{j=0}^2 b_{ij} \cdot T^{-j} \quad (10)$$

As considered by different authors [12,13], the reference values herein used for enthalpy are: null values at 0°C for pure water and for the solution at 50 wt%. Enthalpy in mass basis is calculated using Equation (11). Results of the enthalpy, calculated with the previous equations, are presented in Figure 2.

$$h = \bar{h} / \bar{M}_{\text{sol}} \quad (11)$$

Where the Molar mass of the solution is calculated based on the molar fraction and molar mass of the components.

### 2.3. Entropy

For the entropy evaluation of the LiBr/H<sub>2</sub>O solution, the correlation proposed by Kim and Infante Ferreira [14] is used:

$$\bar{s} = y_{\text{LiBr}} \cdot \bar{s}_{\text{LiBr}(T,p)}^{\infty} + (1 - y_{\text{LiBr}}) \cdot \bar{s}_{\text{H}_2\text{O}(T,p)}^l - y_{\text{LiBr}} \cdot v \cdot \bar{R} \cdot \left[ \ln\left(\frac{m}{m_0}\right) - 1 \right] + \bar{s}_{(T,p,m)}^E \quad (12)$$

where the term  $\bar{s}_{\text{LiBr}(T,p)}^{\infty}$  is the molar entropy of the ideal LiBr fluid, and  $\bar{s}_{\text{H}_2\text{O}(T,p)}^l$  is the molar entropy of pure water.

The third term is the entropy generation in an ideal mixture ( $m_0$  is the standard molality:  $m_0 = 0,001 \text{ kmol kg}^{-1}$  of solvent) and the last term  $\bar{s}_{(T,p,m)}^E$  is the additional entropy generation for a real mixture process. These terms can be calculated by Equations (13), (14) and (15). Values of the constants employed are shown in Table I.

$$\bar{s}_{\text{LiBr}}^{\infty} = \bar{s}_{\text{LiBr};0}^{\infty} + \int_{T_0}^T \frac{C_{p\text{LiBr}}^{\infty}}{T} dT - \int_{p_0}^p \left( \frac{\partial V_{\text{LiBr}}^{\infty}}{\partial T} \right)_p dp \quad (13)$$

$$\bar{s}_{\text{H}_2\text{O}}^l = \bar{s}_{\text{H}_2\text{O};0}^l + \int_{T_0}^T \frac{C_{p\text{H}_2\text{O}}^l}{T} dT - \int_{p_0}^p \left( \frac{\partial V_{\text{H}_2\text{O}}^l}{\partial T} \right)_p dp \quad (14)$$

$$\bar{s}^E = y_{\text{LiBr}} \cdot v \cdot \bar{R} \cdot \sum_{j=1}^6 \left[ a_j + \frac{i \cdot b_j}{2 \cdot v} p + T \cdot \left( \frac{\partial a_j}{\partial T} + \frac{i}{2 \cdot v} \frac{\partial b_j}{\partial T} p \right) \right] \cdot m^{j/2} \quad (15)$$

Values of  $\bar{s}_{\text{LiBr};0}^{\infty}$  and  $\bar{s}_{\text{H}_2\text{O};0}^l$  are shown in Table I. The same reference values of enthalpy were used (0°C for pure water and solution at 50 wt%). The validity range for Equation (12) is: mass fraction of LiBr,  $x$ , from 0 to 70% and solution temperatures,  $T$ , from 0 to 210°C. Entropy in mass basis is calculated using Equation (16). The results of entropy are presented in Figure 3.

$$s = \bar{s} / \bar{M}_{\text{sol}} \quad (16)$$

### 2.4. Activities

Water activity in the solution can be calculated by the following expression [16]:

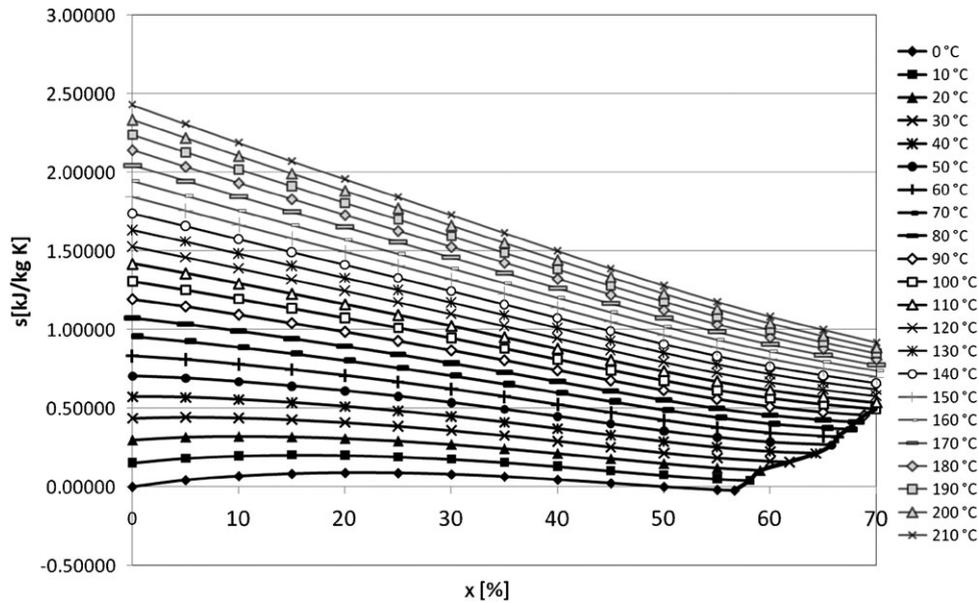
$$\ln(a_{\text{H}_2\text{O}}) = -\phi \cdot v \cdot m \cdot \bar{M}_{\text{H}_2\text{O}} \quad (17)$$

**2.4.1. Molality.** Molality is normally defined as the number of moles of solute per kilogram of solvent. In the calculation, following the procedure reported in [14], the molality is redefined as kilomole of solute per kilogram of solvent.

Then, the molality can be calculated from the LiBr mole fraction ( $y_{\text{LiBr}}$ ) or the LiBr mass fraction ( $x_{\text{LiBr}}$ ) as shown by the following equation:

$$m = \frac{x_{\text{LiBr}}}{(1 - x_{\text{LiBr}}) \cdot \bar{M}_{\text{LiBr}}} = \frac{y_{\text{LiBr}}}{(1 - y_{\text{LiBr}}) \cdot \bar{M}_{\text{H}_2\text{O}}} \quad (18)$$

**2.4.2. Osmotic coefficient.** Kim and Infante Ferreira [14] present the following expression to calculate the osmotic coefficient of the LiBr/H<sub>2</sub>O solution. The



**Figure 3.** Entropy of lithium bromide–water solutions as a function of the concentration for different temperatures.

terms  $a_i$  and  $b_i$  are obtained by Equations (9) and (10):

$$\phi = 1 + \sum_{i=1}^6 a_i \cdot m^{i/2} + \frac{p}{2 \cdot v} \sum_{i=1}^2 i \cdot b_i \cdot m^{i/2} \quad (19)$$

**2.4.3. Calculation of the LiBr activity in the solution.** The LiBr activity in the solution can be calculated from the water activity, applying the Gibbs–Duhem equation, Equation (20), following the method described in [17]. This method is utilized to calculate the activity of a non-volatile component when the activities of the other species are known:

$$\int_1^2 d(\ln a_{\text{LiBr}}) = - \int_1^2 \frac{y_{\text{H}_2\text{O}}}{y_{\text{LiBr}}} d(\ln a_{\text{H}_2\text{O}}) \quad (20)$$

The limits of integration are defined as follows [18]:

Point 1: General state,  $y_{\text{LiBr}}$

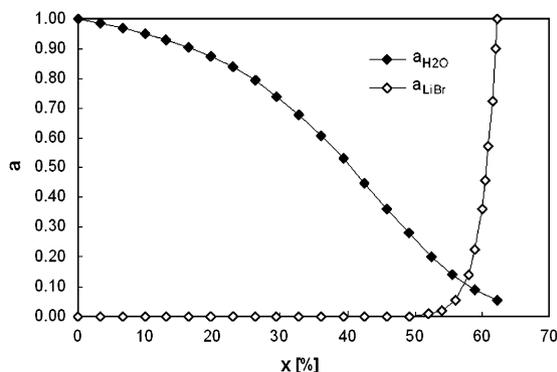
Point 2: Saturated state corresponding to the maximum solubility,  $y_{\text{LiBr:sat}}$

This upper limit of the integral was considered because the solution at this state is in equilibrium with pure lithium bromide, then the reference value for LiBr activity at this point (point 2) corresponds to the pure LiBr ( $a_{\text{LiBr}_2} = 1$ ).

Substituting Equations (17), (18) and (19) into Equation (20), after of operating and integrating, Equation (21) is obtained. The results are presented in Figure 4:

$$\ln(a_{\text{LiBr}}) = -v \cdot \left[ \ln \left( \frac{y_{\text{LiBr}}}{(1 - y_{\text{LiBr}}) \cdot \bar{M}_{\text{H}_2\text{O}}} \right) + \sum_{i=1}^6 \frac{(i+2)}{i} \cdot \left( a_i + i \cdot \frac{p \cdot b_i}{2 \cdot v} \right) \cdot \left( \frac{y_{\text{LiBr}}}{(1 - y_{\text{LiBr}}) \cdot \bar{M}_{\text{H}_2\text{O}}} \right)^{i/2} \right]^{y_{\text{LiBr:sat}}}_{y_{\text{LiBr}}} \quad (21)$$

where  $b_3 = b_4 = b_5 = b_6 = 0$ .



**Figure 4.** Activities of water and LiBr in the solution, at 25°C, as a function of the mass fraction of LiBr.

### 3. EXERGY CALCULATION OF LiBr/H<sub>2</sub>O SOLUTION

Exergy of the lithium bromide solution can be calculated as the sum of both physical and chemical exergy:

$$\text{ex} = \text{ex}_{\text{ph}} + \text{ex}_{\text{ch}} \quad (22)$$

#### 3.1. Physical exergy

Physical exergy is the maximum work available when the system is driven from its initial state ( $T, p$ ) up to the reference state ( $T_0, p_0$ ) by means of a reversible process, exchanging heat and work with the reference environment only. If kinetic and potential components of exergy are neglected, the physical exergy can be calculated through the following expression:

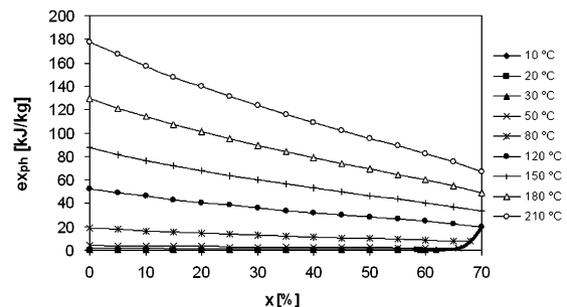
$$\text{ex}_{\text{ph}} = (h - h_0) - T_0 \cdot (s - s_0) \quad (23)$$

Figure 5 presents the physical exergy calculated by Equation (23) for mass fractions of LiBr,  $x$ , ranging from 0 to 70% and different  $T$  temperatures. The reference state considered was  $T_0 = 25^\circ\text{C}$  and  $p_0 = 101.325 \text{ kPa}$ . Enthalpies and entropies were calculated according to the procedure described in the previous section.

#### 3.2. Chemical exergy

Chemical exergy is the maximum work that can be achieved when a substance is driven from its equilibrium state at the environment pressure and temperature (dead restricted state) to the equilibrium state of equal chemical potentials (dead unrestricted state) by means of processes that involve heat, work and mass transfers with the environment. Because the LiBr/H<sub>2</sub>O solution is not ideal, the following expression [11] is used for chemical exergy calculation, as a function of the activities and standard exergies of pure species:

$$\text{ex}_{\text{ch}} = (1/\bar{M}_{\text{sol}}) \left[ \sum_{i=1}^n y_i \cdot \tilde{\epsilon}_i^0 + \bar{R} \cdot T_0 \sum_{i=1}^n y_i \cdot \ln a_i \right] \quad (24)$$



**Figure 5.** Physical exergy of LiBr/H<sub>2</sub>O solution as a function of the LiBr concentration.

For LiBr/H<sub>2</sub>O solution:

$$ex_{ch} = (1/\bar{M}_{sol})[y_{H_2O} \cdot \tilde{\epsilon}_{H_2O}^0 + y_{LiBr} \cdot \tilde{\epsilon}_{LiBr}^0 + \bar{R} \cdot T_0(y_{H_2O} \cdot \ln(a_{H_2O}) + y_{LiBr} \cdot \ln(a_{LiBr}))] \quad (25)$$

The chemical exergy equation above has two parts as follows:

*Standard chemical exergy of pure species:*

$$ex_{ch;0} = (1/\bar{M}_{sol})[y_{H_2O} \cdot \tilde{\epsilon}_{H_2O}^0 + y_{LiBr} \cdot \tilde{\epsilon}_{LiBr}^0] \quad (26)$$

*Exergy destruction due to dissolution process:*

$$ex_{ch;dis} = \frac{\bar{R} \cdot T_0}{\bar{M}_{sol}}(y_{H_2O} \cdot \ln(a_{H_2O}) + y_{LiBr} \cdot \ln(a_{LiBr})) \quad (27)$$

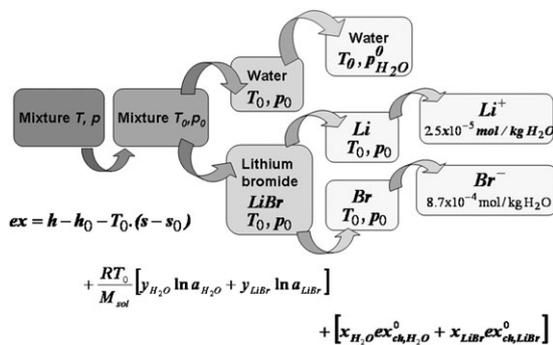
Figure 6 shows schematically the methodology to calculate the exergy components for LiBr/H<sub>2</sub>O solution. The path from initial solution at *x*, *p* and *T* to reach the dead state according to Kotas can be observed [11]. The values  $2.5 \times 10^{-5}$  and  $8.7 \times 10^{-4}$  mol kg<sup>-1</sup> H<sub>2</sub>O in Figure 6 are the conventional standard molarities of the reference species dissolved in sea water: Li<sup>+</sup> and Br<sup>-</sup>, respectively, according to [10].

**3.2.1. Standard chemical exergies.** The standard chemical exergies for water, lithium and bromide were found in [10]. Rivero and Garfias [19] accomplished a revision and re-calculation of the standard chemical exergies of elements but their results, for the substances *Li* and *Br*, do not present significant differences (deviations around -0.2%) in comparison with the values reported in [10].

$$\begin{aligned} \tilde{\epsilon}_{H_2O}^0 &= 0.9 \text{ kJ/mol} \\ \tilde{\epsilon}_{Li}^0 &= 393 \text{ kJ/mol} \\ \tilde{\epsilon}_{Br_2}^0 &= 101.2 \text{ kJ/mol} \end{aligned}$$

The standard chemical exergy for the LiBr compound can be calculated following Kotas's proposal [11]:

$$\tilde{\epsilon}^0 = \Delta \tilde{g}_f^0 + \sum_{i=1}^n \tilde{\epsilon}_{ci}^0 \quad (28)$$



**Figure 6.** Path from initial state at *x*, *T* and *p* to the dead state according to this study—Exergy components of LiBr/H<sub>2</sub>O solution.

In Equation (28), *n* indicates the number of elements, while subscript *el* indicates the element.



$$\tilde{\epsilon}_{LiBr}^0 = \Delta \tilde{g}_{LiBr}^0 + \tilde{\epsilon}_{Li}^0 + \frac{1}{2}\tilde{\epsilon}_{Br_2}^0 \quad (30)$$

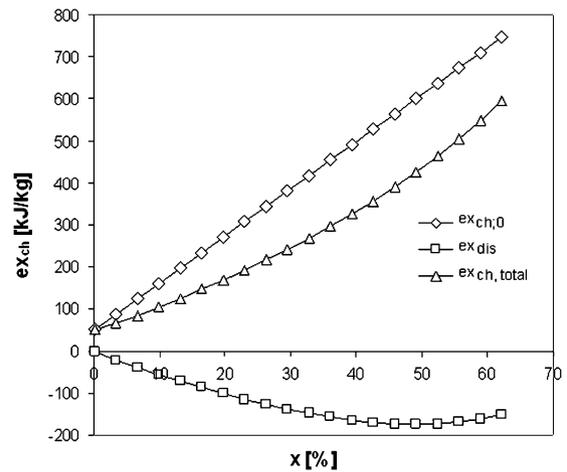
where

$$\Delta \tilde{g}_{LiBr}^0 = -342.0 \text{ kJ mol}^{-1} \quad [20]$$

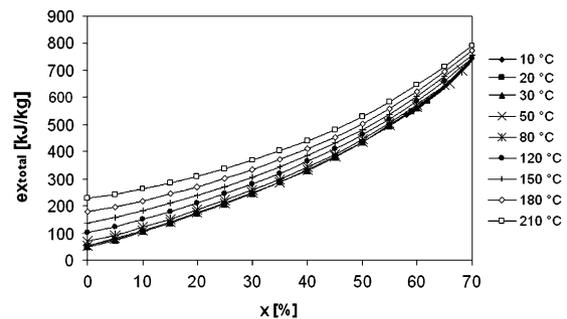
The result of Equation (28) is:  $\tilde{\epsilon}_{LiBr}^0 = 101.6$  kJ/mol. This value will be used later in Equation (25) for chemical exergy calculation of the LiBr/H<sub>2</sub>O solution.

Figure 7 presents the chemical exergy calculated as a function of standard chemical exergies of solution components (*ex<sub>ch;0</sub>*) as indicated in Equation (26), the variation of chemical exergy due to the dissolution process (*ex<sub>dis</sub>*), calculated according to Equation (27) and the total chemical exergy at 25°C calculated by the sum of previous terms according to Equation (25).

Figure 8 presents the total exergy by summing up both physical and chemical terms, calculated according to Equation (22).



**Figure 7.** Standard chemical exergy (*ex<sub>ch;0</sub>*), variation of chemical exergy due to the dissolution process (*ex<sub>dis</sub>*) and total chemical exergy at 25°C of LiBr/H<sub>2</sub>O solution as a function of LiBr concentration (mass basis).



**Figure 8.** Total exergy, chemical and physical of LiBr/H<sub>2</sub>O solution as a function of LiBr concentration (mass basis).

### 4. STUDY OF CASES— COMPARISON WITH OTHER APPROACHES

#### 4.1. Approach of Koehler *et al.* [1]

Koehler *et al.* [1] present an approach for exergy calculation of LiBr/H<sub>2</sub>O solution, which considers that the least potential of a solution for doing useful work is given when it is in a saturated state at  $T_0$  and  $p_0$  (*the minimum free energy state defines the zero exergy level at  $T$  and  $p$  defined*). Thus for a given environmental state, the exergy  $\psi$  can be treated as a state function and it can be chosen as a convenient path from any given state to the defined dead state. The path to the reference state is shown in Figure 9.

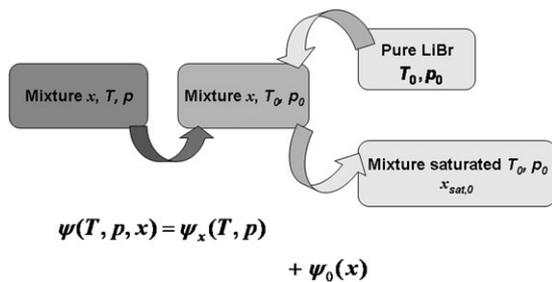
$$\psi(T, p, x) = \psi_x(T, p) + \psi_0(x) \quad (31)$$

The term  $\psi_x(T, p)$  is the temperature- and pressure-dependent part of the exergy (thermal term) while the term  $\psi_0(x)$  represents the exergy of dissolution. To find  $\psi_0(x)$ , these authors imagine a mixture at  $T_0$  and  $p_0$  undergoing a change of state from a given concentration  $x$  to the dead state  $x_{sat}$  by admitting an amount of solute at  $T_0$  and  $p_0$ . Applying the first and second law of thermodynamics to this process, the authors get an equation for exergy calculation of the LiBr/H<sub>2</sub>O solution.

Thus, the minimum level of exergy corresponds to the saturated solution  $x_{sat}$  while the highest value corresponds to pure water. In order to maintain the consistency in exergy balances, these authors should calculate the exergy of pure water according to their correlations, which consider the saturate state  $x_{sat}$  of LiBr/H<sub>2</sub>O solution as reference state.

#### 4.2. Approach of Oliveira and Le Goff [21]

Oliveira and Le Goff [21] also present an approach for exergy calculation of LiBr/H<sub>2</sub>O solutions. These authors consider a reference state at  $T_0$  and  $p_0$  and equilibrium compositions of the mixture at  $T_0$  and  $p_0$ . The reference conditions adopted for the LiBr/H<sub>2</sub>O solution were  $T_0 = 25^\circ\text{C}$ ,  $p_0 = 100\text{ kPa}$ , pure water ( $x = 0$ ) and a solution at  $x_0 = 20\text{ wt\%}$ . Hence, the



**Figure 9.** Path from initial state at  $x$ ,  $T$  and  $p$  to the reference state according to the approach of Koehler *et al.* [1]—Exergy components of LiBr/H<sub>2</sub>O solution.

exergy of mixture can be calculated from the properties of pure water and the reference solution at  $x_0$ . The path to the reference state is shown in Figure 10.

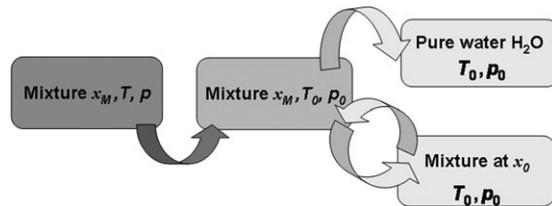
#### 4.3. Comparison of results with other approaches and studies

Three cases of the literature are studied and compared. The first is an absorption heat pump and the second and third are absorption refrigeration systems. Calculations were performed using equation engineering solver (EES) [22].

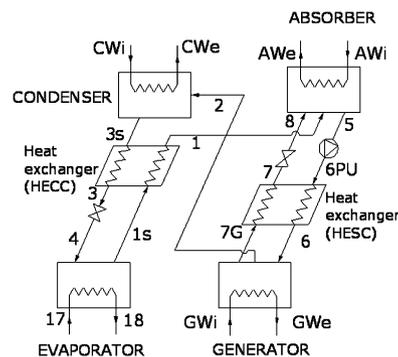
The absorption heat pump evaluated in Koehler’s study [1] is presented in Figure 11. The model considered by these authors consists of an internal and an external system. The external system represents the connection between the internal system and the surroundings. The internal system is a standard absorption cycle containing: evaporator, condenser, absorber, generator, pump, two expansion valves and two heat exchangers.

Table II shows the operational conditions of this system. Specific exergies reported by Koehler *et al.* [1] are compared with specific exergies calculated by Oliveira and Le Goff [21] approach and calculated by the procedure proposed in Section 3 of this study. Enthalpies and entropies were calculated using the procedure described in Section 2 according to Kim and Infante Ferreira [14].

The reference temperature adopted by Koehler *et al.* [1], in exergy calculation, was  $T_0 = 5^\circ\text{C}$ . On the other hand, the methodology proposed in this study as well



**Figure 10.** Path from initial state at  $x_M$ ,  $T$  and  $p$  to the reference state according to approach of Oliveira and Le Goff [21].



**Figure 11.** Absorption heat pump evaluated by Koehler *et al.* [1].

**Table II.** Operational conditions for absorption heat pump evaluated by Koehler *et al.* [1]—Comparison of specific exergy values with other approaches.

	<i>M</i> (kg/s)	<i>T</i> (K)	<i>P</i> (kPa)	<i>v</i> frac	<i>x</i> %	<i>h</i> * (kJ kg <sup>-1</sup> )	<i>s</i> (kJ kg <sup>-1</sup> K <sup>-1</sup> )	$\psi^*$ (kJ kg <sup>-1</sup> )	Oliveira and	
									Koehler <i>et al.</i> [1]	Le Goff [21]
1S	1	280.2	1	1	0	2513.76	8.9610	647.72	-157.6	-107.7
1	1	304.2	1	1	0	2558.96	9.1332	645.03	-158.6	-108.6
2	1	357	15.73	1	0	2656.09	8.1181	1024.51	229.4	279.4
3S	1	328.2	15.73	0	0	230.46	0.7686	643.15	5.834	55.79
3	1	317.4	15.73	0	0	185.26	0.6276	637.18	2.4	52.36
4	1	280.2	1	0.063	0	185.26	0.6597	628.22	-8.529	41.43
5	4.713	303.2	1	0	51.1	-174.05	0.2831	53.74	87.48	447.7
6PU	4.713	303.2	15.73	0	51.1	-174.04	0.2831	53.76	87.49	447.7
6	4.713	330.9	15.73	0	51.1	-113.92	0.4721	61.30	91	451.2
7G	3.713	388.2	15.73	0	64.9	-20.02	0.6848	9.87	214.5	658.6
7	3.713	345.7	15.73	0	64.9	-96.36	0.4680	-6.14	200.2	644.3
8	3.713	331.1	1	0.009	64.9	-96.33	0.4672	-5.92	199.8	643.8

\*Values of enthalpies, entropies and specific exergies reported by Koehler *et al.* [1].

†Enthalpies and entropies were calculated by equations of Kim and Infante Ferreira [14] according to item 2 of this study.

as Oliveira and Le Goff [21] approach adopt  $T_0 = 25^\circ\text{C}$  as reference temperature.

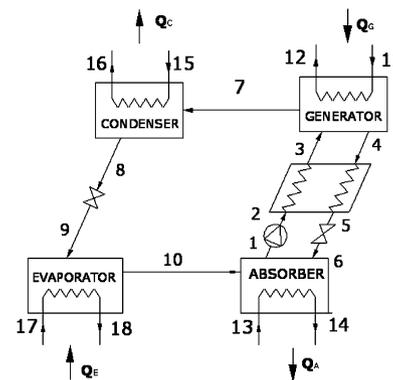
In Table II, negative values for enthalpies of LiBr/H<sub>2</sub>O solution (points 5, 6PU, 6, 7G, 7, 8) can be observed, which indicate that the references for enthalpy are different from that adopted by McNelly [12] and Kim and Infante Ferreira [14]. For the next cases some constants were adjusted in Koehler's exergy equation in order to get exergy values according to the graphics reported by these authors [1] using correlations of Kim and Infante Ferreira [14] to calculate properties.

It can be observed that specific exergies for pure water are negative in points: 1S and 1 for Oliveira and Le Goff approach [21] as well as this study approach due to these points are below the reference state. On the other hand, Koehler *et al.* [1] reported the highest values of exergy for pure water and lower exergies values of LiBr/H<sub>2</sub>O solution (negatives values in points 7 and 8). The approach of this study shows the highest values for LiBr/H<sub>2</sub>O solution.

It was not possible to compare irreversibilities and exergetic efficiencies reported by these authors, in this case, because they neither inform mass flows nor the pressure of the external points of the system (points EWI, EWE, CWI, CWE, AWI, AWE, GWI, GWE).

In the second case, the absorption refrigeration system of single effect evaluated by Sencan *et al.* [5] is shown in Figure 12. This system is composed of a condenser, generator, solution heat exchanger, absorber, evaporator, pump, solution expansion valve and refrigerant expansion valve.

Table III shows operation conditions for the system as well as specific exergies reported by the authors [5] and calculated by approaches described in the previous sections. For all approaches the reference temperature was adopted as  $T_0 = 25^\circ\text{C}$ .



**Figure 12.** Absorption refrigeration system evaluated by Sencan *et al.* [5].

Sencan *et al.* [5] also indicate  $25^\circ\text{C}$  as reference temperature but they do not indicate the reference pressure nor the chemical composition of reference state. The internal system pressures were calculated considering the temperature at condenser outlet and evaporator outlet. Thus, the lower and the higher pressures obtained for the system were 1.002 and 7.381 kPa, respectively. It was not possible to compare the results of irreversibilities or exergetic efficiencies reported by the authors [5] as they did not report values of pressure for points of the external circuit (11, 12, 13, 14, 15, 16, 17, 18).

From Table III it can be observed that specific exergies of LiBr/H<sub>2</sub>O solution in Sencan *et al.* [5] study are lower in comparison with the values obtained from approaches of this study and Oliveira and Le Goff [21]. In comparison with Koehler *et al.* [1] approach, specific exergies of LiBr/H<sub>2</sub>O solution of Sencan *et al.* [5] are lower than Koehler *et al.* values [1] for  $x = 57.59\%$  but they are higher for  $x = 58.15\%$ .

Regarding the exergy of pure water, Sencan *et al.* [5] report negative values at outlet of condenser, expansion valve of refrigerant and evaporator (points 8, 9 and 10).

In a recent study Arora and Kaushik [3] evaluated an absorption refrigeration system of single and double effect. The configuration of the absorption refrigeration system of single effect studied by these authors is the same as the configuration shown in Figure 12.

Table IV shows the operational conditions for this system. Specific exergies in each point of the cycle were calculated by the approaches described in previous sections. Arora and Kaushik [3] do not report values of exergy in each point of the cycle.

Unlike the previous cases, Arora and Kaushik [3] evaluate irreversibilities in each system component considering only the internal circuit, calculating the exergy of the heat flows.

In this study irreversibilities generated in each system component are calculated by means of exergy

balance.

$$I = \sum \dot{m}_{in} \cdot ex_{in} - \sum \dot{m}_{out} \cdot ex_{out} - \dot{Q} \cdot \left(1 - \frac{T_0}{T_r}\right) - \dot{W}_{vc} \quad (32)$$

In Equation (32)  $T_r$  is the temperature at the control surface where the heat transfer is taking place. Arora and Kaushik [3] define the temperature  $T_r$  for each component; thus, for the generator  $T_r = T_g = 87.8^\circ\text{C}$ , for the evaporator  $T_e = 7.2^\circ\text{C}$  and for the condenser and the absorber  $T_r = T_c = T_a = 37.8^\circ\text{C}$ .

To calculate exergetic efficiencies, the rational efficiency concept [11] is used:

$$\eta_{ex} = \frac{\text{product}}{\text{Fuel}} \quad (33)$$

This definition is applied to components where it is possible to define a *product*. This definition follows that recommended by Szargut *et al.* [10] and Kotas [11]. The latter one being named ‘rational efficiency’. On the

**Table III.** Operational conditions for absorption heat pump evaluated by Sencan *et al.* [5]—Comparison of specific exergy values with other approaches.

	$m$ (kg s <sup>-1</sup> )	$T$ (°C)	$x$ (%)	Secan <i>et al.</i> [5]	Koehler <i>et al.</i> [1]	Oliveira and Le Goff [21]	This study
				$\psi^*$ (kJ kg <sup>-1</sup> )	$\psi^\dagger$ (kJ kg <sup>-1</sup> )	$ex1^\dagger$ (kJ kg <sup>-1</sup> )	$ex2^\dagger$ (kJ kg <sup>-1</sup> )
1	0.5	40	57.59	12.95	20.87	130.8	530.4
2	0.5	40	57.59	12.95	20.87	130.8	530.4
3	0.5	67.6	57.59	22.09	25.67	135.6	535.2
4	0.495	80	58.15	29.73	26.29	143.3	546.3
5	0.495	52	58.15	21.52	19.59	136.6	539.6
6	0.495	52	58.15	21.52	19.59	136.6	539.6
7	0.005	80	0	99.07	745.7	124.6	174.5
8	0.005	40	0	-3.12	622.6	1.432	51.39
9	0.005	7	0	-3.12	614.5	-6.601	43.36
10	0.005	7	0	-161.7	463.8	-157.3	-107.4

\*Values reported by the authors.

†Values calculated in this study—Properties calculated according Kim and Infante Ferreira [14] procedure.

**Table IV.** Operational conditions for absorption refrigeration system evaluated by Arora and Kaushik [3]—Comparison of specific exergy values for different approaches.

	$m$ (kg s <sup>-1</sup> )	$T$ (°C)	$p$ (kPa)	Vfrac	$x$ (%)	$h$ (kJ kg <sup>-1</sup> )	$s$ (kJ kg <sup>-1</sup> K <sup>-1</sup> )	Koehler <i>et al.</i> [1]	Oliveira and Le Goff [21]	This study
								$\psi$ (kJ kg <sup>-1</sup> )	$ex1$ (kJ kg <sup>-1</sup> )	$ex2$ (kJ kg <sup>-1</sup> )
1	9.035	37.8	1.016	0	55.42	91.539	0.2288	32.56	114.9	501.4
2	9.035	37.8	6.558	0	55.42	91.543	0.2288	32.57	114.9	501.4
3	9.035	66.2	6.558	0	55.42	148.953	0.4054	37.35	119.7	506.2
4	8.035	87.8	6.558	0	62.32	221.19	0.4787	10.42	180.4	608.7
5	8.035	53.08	6.558	0	62.32	156.635	0.2905	1.882	171.8	600.2
6	8.035	53.08	1.016	0.002251	62.32	156.635	0.2906	1.881	171.8	600.2
7	1	87.8	6.558	0	0	2664.211	8.58	731.9	110.8	160.7
8	1	37.8	6.558	0	0	158.301	0.5428	622.2	1.021	50.98
9	1	7.2	1.016	0.05155	0	158.301	0.5661	615.2	-5.911	44.05
10	1	7.2	1.016	0	0	2513.751	8.968	465.7	-155.4	-105.5

other hand, for dissipative components, we used the ratio  $\zeta$  as 'exergetic effectiveness' of inlets and outlets. The inlet exergy, in this ratio, corresponds to the exergy of all the exergy carriers that get into the control volume considered. On the other hand, the outlet corresponds to the exergy of all the exergy carriers that go out the control volume.

The ratio  $\zeta$  is defined in Equation (34).

$$\zeta_{\text{ex}} = \frac{\sum \dot{m}_{\text{out}} \cdot \text{ex}_{\text{out}} + \dot{W}_{\text{out}} + \dot{Q}_{\text{out}} \cdot \eta_{\text{carnot}}}{\sum \dot{m}_{\text{in}} \cdot \text{ex}_{\text{in}} + \dot{W}_{\text{in}} + \dot{Q}_{\text{in}} \cdot \eta_{\text{carnot}}} \quad (34)$$

For instance, in the absorber, it is defined as:

$$\zeta_{\text{ex;a}} = \frac{\dot{m}_1 \cdot \text{ex}_1 + \dot{Q}_a \cdot (1 - T_0/T_a)}{\dot{m}_{10} \cdot \text{ex}_{10} + \dot{m}_6 \cdot \text{ex}_6} \quad (35)$$

Table V shows irreversibilities calculated by Arora and Kaushik [3] and by exergy balances according to the methodology proposed in Section 3 and according to the approaches of Koehler *et al.* [1] and Oliveira and Le Goff [21]. Furthermore, irreversibilities are calculated by Gouy Stodola equation (Equation (36)) using the correlations reported in item 2 of this study. Table VI shows the ratio,  $\zeta$ , calculated by each approach.

From Table V it can be observed small differences between irreversibilities reported by [3] and re-evaluated using the procedure of Kim and Infante Ferreira [14] for property calculations. The highest difference is in absorber (5.68%). Regarding irreversibilities calculated considering the different approaches, it can be observed that differences are not significant; owing to the fact that exergy balances the references

values cancel. Moreover, the irreversibility calculation can be performed without calculating exergies, considering the Gouy Stodola equation:

$$I = T_0 \left[ \sum_{\text{OUT}} \dot{m}_{\text{out}} \cdot S_{\text{out}} - \sum_{\text{IN}} \dot{m}_{\text{in}} \cdot S_{\text{in}} - \sum_r \frac{\dot{Q}_r}{T_r} \right] \quad (36)$$

Rational exergetic efficiency ( $\eta_{\text{ex}}$ ) resulted in the same value for all the approaches. It was calculated in generator, evaporator and heat exchanger of solution resulting in 89.3, 42.3 and 63%, respectively.

The ratio of inlet and outlet ( $\zeta$ ) resulted high in all the cases. There were little differences due to the different values of the different approaches. In Table VI it can be observed that this study presents the highest values of  $\zeta$  in system components where LiBr/H<sub>2</sub>O solution is involved. This a consequence of the high value of the standard chemical exergy considered. Exergetic efficiencies calculated by the approach of Oliveira and Le Goff [21] present intermediate values between this study and the Koehler approach [1].

Thus, it can be observed that, in the literature, the values of exergy for LiBr/H<sub>2</sub>O solution are widely varied because the reference conditions and chemical composition of the reference environment are unlike in the different approaches. There are also some differences in property values such as enthalpy or entropy of the LiBr/H<sub>2</sub>O solution.

For instance, Sencan *et al.* [5] report  $\text{ex} = \psi = 19.95 \text{ kJ kg}^{-1}$  for  $x = 57.59\%$  and  $T = 40^\circ\text{C}$ ; and  $\text{ex} = \psi = 21.52 \text{ kJ kg}^{-1}$  for  $x = 58.15\%$  and  $T = 52^\circ\text{C}$ . In [4], Talbi and Agnew report  $\text{ex} = \psi = 227.817 \text{ kJ kg}^{-1}$

**Table V.** Irreversibilities in kW for each component of the system—Comparison of results in system evaluated by Arora and Kaushik [3].

	Gouy Stodola equation	Arora and Kaushik [3]		Koehler <i>et al.</i> [1]	Oliveira and Le Goff [21]	This study
	(1)	(2)	(3)			
Absorber	66.24	70.48	67.24	66	66.28	66.47
Condenser	6.60	6.61	6.60	6.60	6.60	6.60
Evaporator	86.25	86.28	86.25	86.25	86.25	86.25
Generator	57.15	55.57	57.15	57.39	57.12	56.93
Heat exchanger of solution	27.69	25.08	25.36	25.36	25.36	25.36

(1) Values calculated in this study—Entropy calculated according Kim and Infante Ferreira [14] procedure. (2) Values reported by Arora and Kaushik [3]—Properties calculated according to Pátek and Klomfar [23] (3) Values calculated in this study—Properties calculated to according Kim and Infante Ferreira [14] procedure.

**Table VI.** Exergetic ratio of inlets and outlets  $\zeta$ —Comparison with approaches of Koehler *et al.* [1] and Oliveira and Le Goff [21].

	Koehler <i>et al.</i> [1]	Oliveira and Le Goff [21]	This study
Absorber	86.27	94.59	98.59
Condenser	99.10	94.04	95.89
Evaporator	85.98	—	—
Generator	93.43	96.47	98.89
Heat exchanger of solution	93.29	98.98	99.73

for  $x = 59.5\%$  and  $T = 47^\circ\text{C}$ ; although there are slight differences in temperatures and concentrations the value reported by Talbi and Agnew [4] is quite big in comparison with that reported by Sencan *et al.* [5].

Misra *et al.* [6] consider the physical exergy and the chemical exergy of the pure water contained in the solution. They report  $ex = 33.91 \text{ kJ kg}^{-1}$  for  $x = 56.43\%$  and  $T = 34^\circ\text{C}$  which is almost two times the value reported by Sencan *et al.* [5] under similar conditions.

Consequently, there is the need to standardize the procedure for exergy calculation of LiBr/H<sub>2</sub>O solution and this study intends to contribute to this objective proposing a methodology of exergy calculation considering the reference environment of Szargut *et al.* [10].

Furthermore, this proposal permits an integrated analysis considering the external losses of exergy or considering a control volume that includes more pieces of equipment as the direct-fired system. For instance, Figure 13 shows an absorption refrigeration system of single effect together with a cooling tower. The heat duty in the condenser and absorber is removed by the water flow of the cooling tower. The local temperature considered is  $29^\circ\text{C}$  but for exergetic analysis standard conditions are considered:  $T_0 = 25^\circ\text{C}$  and  $p_0 = 101.325 \text{ kPa}$ . The temperature  $T_7$  is calculated considering the boiling temperature of the solution at concentration  $x_3$ , on the other hand, the temperature  $T_4$  is the equilibrium temperature at concentration  $x_4$  according to Herold and Radermacher [24].

Furthermore, the exergetic evaluation of a direct fired system can be accomplished. In this case streams of natural gas, air and exhaust gases should be considered according to Figure 14 (25, 26 and 27). In order to take into account heat losses to the environment, an efficiency of heat transfer  $\eta_{ht,g}$  in the generator is adopted as 0.84 [25]:

$$\dot{Q}_g = \eta_{ht,g} \cdot \dot{v}_{gas} \cdot LHV_{gas} \quad (37)$$

The temperature of exhaust gases is calculated by a balance of enthalpies using JANAF tables of EES,

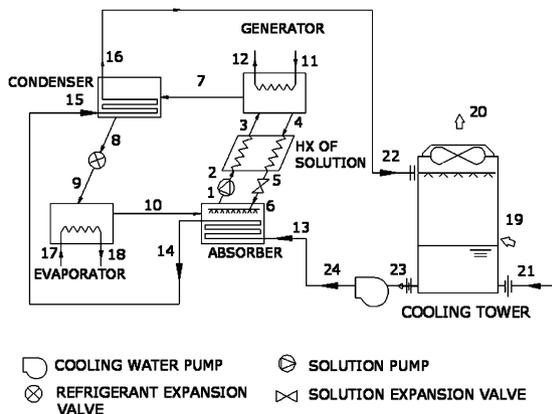


Figure 13. Absorption refrigeration system of single effect with cooling tower.

considering heat losses to environment of 5%. Thus, the temperature of exhaust gases resulted as  $202.5^\circ\text{C}$ .

Table VII shows the results of the exergy calculation with the proposed methodology in each point of this system. Table VIII shows the heat exchanged, irreversibilities and exergetic efficiencies. It can be observed the low value of the exergetic efficiency for the direct-fired system (2.5%), which indicates that the absorption refrigeration systems are more appropriate to operate together with cogeneration systems or utilizing of some waste heat. The values of  $\zeta_{ex}$  are very high owing to the high numerical values of input and output exergy and the consideration of adiabatic devices. In the case of a hot-water-driven system, the element with higher irreversibility is the cooling tower, due to the high loss of mass that occurs in this element. The irreversibility of cooling tower represents 20.97% of the total irreversibility of the system.

Still in this analysis there are some values of negative exergy for water streams because the pressure of these streams is below the reference pressure  $p_0$ . This effect can be observed in rows 9 and 10 of Table VII.

In relation to the reference states chosen by other authors for exergy calculation of LiBr-H<sub>2</sub>O solution, there are some issues that deserve mention. Koehler *et al.* [1] approach considers the minimum exergy level for the maximum solubility state of the solution while the highest values of exergy correspond to pure water. Hence, the minimum exergy level corresponds to the minimum of free energy at the reference temperature and pressure adopted. These authors preferred to adopt the local environmental conditions as reference state. In order to obtain consistent results, the exergy of pure water should be calculated with an appropriate equation reported by [1]; this equation takes into account the properties of the solution at saturated state, of pure water and pure LiBr, at the reference temperature. Exergy negatives values can be obtained depending on the solution temperature and concentration compared with the reference conditions. This effect can be observed in Table II, points 7 and 8.

Different from Koehler, the Oliveira and Le Goff [21] approach adopts as reference conditions fixed values of temperature and pressure:  $T_0 = 25^\circ\text{C}$ ,  $p_0 = 100 \text{ kPa}$ , and also pure water and a solution concentration of 20%.

Adopting variable reference conditions of temperature and pressure to calculate exergy has positive and

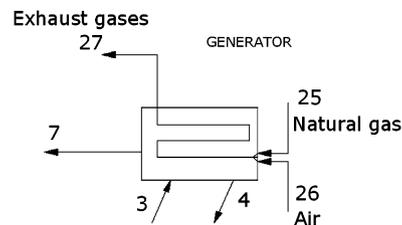


Figure 14. Generator of the direct-fired absorption refrigeration system.

**Table VII.** Operational conditions at each point of the single-effect system.

Pto.	$m$ (kg s <sup>-1</sup> )	$P$ (kPa)	$T$ (°C)	$X$ (%LiBr)	$h$ (kJ kg <sup>-1</sup> )	$S$ (kJ kg <sup>-1</sup> K <sup>-1</sup> )	exph (kJ kg <sup>-1</sup> )	exch (kJ kg <sup>-1</sup> )	exto (kJ kg <sup>-1</sup> )
1	1.177	0.84	32.9	54.9	80.6	0.205	0.117	494.2	494.3
2	1.177	7.5	32.9	54.9	80.7	0.205	0.123	494.2	494.3
3	1.177	7.5	62.1	54.9	140.4	0.391	4.3	494.2	498.4
4	1.042	7.5	89	62	221.1	0.489	11.2	593.2	604.4
5	1.042	7.5	53.1	62	153.7	0.293	2.2	593.2	595.4
6	1.042	0.8	47.3	62	153.7	0.300	0.1	593.2	593.3
7	0.135	7.50	73.5	0	2637	8.441	124.9	49.96	174.9
8	0.135	7.50	40.3	0	168.8	0.576	1.5	49.96	51.45
9	0.135	0.84	4.5	0	168.8	0.608	-8.1	49.96	41.86
10	0.135	0.84	4.5	0	2508.7	9.038	-181.3	49.96	-131.3
11	16.55	424.7	95		398.2	1.250	30.2	49.96	80.13
12	16.55	145.2	89		372.8	1.181	25.3	49.96	75.22
13	20.46	424.7	29		121.9	0.423	0.4	49.96	50.39
14	20.46	274.05	33.8		141.6	0.488	0.7	49.96	50.66
15	20.46	274.05	33.8		141.6	0.488	0.7	49.96	50.66
16	20.46	145.2	37.7		157.9	0.541	1.1	49.96	51.1
17	13.58	424.7	12		50.8	0.180	1.5	49.96	51.5
18	13.58	145.2	6.5		27.5	0.099	2.5	49.96	52.51
19	14.37	101.3	29		74.4	5.870	0.1	0	0.09224
20	14.64	101.3	35		128.9	6.050	1.9	0	1.897
21	0.266	101.325	29		121.6	0.423	0.1	49.96	50.07
22	20.46	101.325	37.7		157.9	0.541	1.1	49.96	51.09
23	20.46	101.325	29		121.6	0.423	0.1	49.96	50.07
24	20.46	424.7	29		121.9	0.423	0.4	49.96	50.39
25	0.0097	101.325	29		8.3	10.840	0.057	51254	51254
26	0.1894	101.325	29		74.4	5.870	0.092	0	0.09224
27	0.1983	101.325	202.5		197.5	7.701	42.76	65.4	108.2

**Table VIII.** Heat transfer, irreversibilities, exergetic efficiency ( $\eta_{ex}$ ) and exergetic ratio ( $\zeta_{ex}$ ) for the absorption refrigeration system of single effect shown in Figure 13.

Component	$Q$ (kW)	$I$ (kW)	$\eta_{ex}$ (%)	$\zeta_{ex}$ (%)
Heat exchanger solution	70.29	4.46	52.35	99.63
Condenser	333.25	7.67	—	99.28
Evaporator	315.93	9.764	58.24	98.62
Absorber	403.92	13.3	—	99.18
Refrigerant expansion valve	—	1.29	—	81.37
Solution expansion valve	—	2.242	—	99.64
Cooling water pump	—	3.126	60.44	99.70
Solution pump	—	0.0053	47.45	99.99
Cooling tower	737.17	14.95	—	96.08
Generator: hot-water-driven system	421.23	14.45	82.22	99.25
Generator: direct fired system	421.23	410.7	13.38	60.2
Global system: hot water driven system	—	71.26	14.29	97.28
Global system: direct fired system	—	467.50	2.65	60.99

negative aspects. In some cases, to analyze an isolated refrigeration system adopting the local temperature and pressure can be useful. But this selection will be difficult for any comparison between system performances working in different conditions.

## 5. CONCLUSIONS

In this paper, a methodology for the exergy calculation of the lithium bromide–water solution, used in absorption refrigeration systems, was presented. The

methodology encompasses the calculation of the currently called physical and chemical exergy, taking into account the dissolution exergy [10,11].

The thermodynamic properties of the solution, enthalpy and entropy, were obtained from the bibliography. Owing to the fact that the LiBr/H<sub>2</sub>O solution is not ideal, to calculate chemical exergy the concept of activity must be applied. Water activity was obtained through the osmotic coefficient, while for LiBr activity in the solution, a correlation was developed from water activity by using the Gibbs–Duhem equation. The results show that LiBr activity in the solution is almost null for low concentrations, but increases abruptly close to the solubility limit.

In relation to chemical exergy, the term calculated with standard chemical exergies is the highest and presents a great increase with LiBr concentration. The term of chemical exergy related to the dissolution process was negative due to the exergy destruction, inherent to this process, following the trend of the Gibbs free energy reduction for the solution. This indicates that the work input is necessary to separate the dissolution components.

Regarding total exergy, which is the sum of physical and chemical exergies, it increases with LiBr concentration.

The lack of a pre-established methodology has led several authors to perform exergy calculations reporting widely varied exergy values for the LiBr/H<sub>2</sub>O solution. Some of these studies are limited to the calculation of irreversibilities and exergetic efficiency of the overall system considering only pure water properties. Thus, there is the need to adopt a unique methodology for exergy calculation of LiBr/H<sub>2</sub>O solution. Koehler *et al.* [1] and Oliveira and Le Goff [21] deal with this topic proposing different reference systems. This study proposes the adoption of a universal reference system, which permits extending the control volume to more complex systems, including the hot source, doing a unique integrated analysis based in a unique reference system for exergy calculations.

Thus, it is possible to compare on the same basis a direct-fired absorption system, burning some fuel, or a cogeneration system that could operate jointly with the absorption system.

## APPENDIX A: NUMERICAL EXAMPLE OF EXERGY CALCULATION FOR A SPECIFIC POINT

It considered the general point:  $T = 37.8^\circ\text{C}$ ,  $p = 1.016\text{ kPa}$ ,  $x_{\text{LiBr}} = 55.42\%$

$$\bar{M}_{\text{LiBr}} = 86.85\text{ kg kmol}^{-1}$$

$$\bar{M}_{\text{H}_2\text{O}} = 18.02\text{ kg kmol}^{-1}$$

$$x_{1w} = x_{\text{LiBr}}/100 = 0.5542$$

Molar fraction

$$y_{\text{H}_2\text{O}} = (1 - x_{1w}) \cdot \bar{M}_{\text{LiBr}} / [(1 - x_{1w}) \cdot$$

$$\bar{M}_{\text{LiBr}} + x_{1w} \cdot \bar{M}_{\text{H}_2\text{O}}] = 0.795$$

$$y_{\text{LiBr}} = 1 - y_{\text{H}_2\text{O}} = 0.205$$

Molar mass of solution

$$\bar{M}_{\text{sol}} = y_{\text{H}_2\text{O}} \cdot \bar{M}_{\text{H}_2\text{O}} + y_{\text{LiBr}} \cdot \bar{M}_{\text{LiBr}} = 32.13\text{ kg kmol}^{-1}$$

Molality

$$m = x_{1w} / [(1 - x_{1w}) \cdot M_{\text{LiBr}}] = 0.01431$$

### A.1. Enthalpy calculation

$$T_0 = 273.15\text{ K}, R = 8.314\text{ kJ kmol}^{-1}\text{ K}^{-1}$$

$$\bar{h}_{\text{LiBr}}^\infty = \bar{h}_{\text{LiBr};0}^\infty$$

$$\begin{aligned} & - R \cdot \left[ c_0 \cdot \left( \frac{1}{T} - \frac{1}{T_0} \right) + \frac{c_1}{2} \cdot \left( \frac{1}{T^2} - \frac{1}{T_0^2} \right) \right. \\ & \left. + \frac{c_2}{3} \cdot \left( \frac{1}{T^3} - \frac{1}{T_0^3} \right) \right] + R \cdot \left( b_{01} + 2 \cdot \frac{b_{02}}{T} \right) \cdot (p - p_0^*) \\ & = -10\,983\text{ kJ kmol}^{-1} \end{aligned}$$

$$\bar{h}_{\text{H}_2\text{O}}^1 = \bar{h}_{\text{H}_2\text{O};0}^1 + R$$

$$\begin{aligned} & \cdot \left[ d_0 \cdot (T - T_0) + \frac{d_1}{2} \cdot (T^2 - T_0^2) + \frac{d_2}{3} \cdot (T^3 - T_0^3) \right] + R \\ & \cdot (e_0 - 2 \cdot e_2 \cdot T + e_2 \cdot T^2) \cdot (p - p_0^*) \\ & = 2853\text{ kJ kmol}^{-1} \end{aligned}$$

$$\bar{h}^E = -y_{\text{LiBr}} \cdot v \cdot \bar{R} \cdot T^2 \sum_{j=1}^6 \frac{2}{j} \cdot \left( \frac{\partial a_i}{\partial T} + \frac{i}{2 \cdot v} \frac{\partial b_i}{\partial T} \right) \cdot m^{i/2}$$

$$= 2950\text{ kJ kmol}^{-1}$$

$$\begin{aligned} \bar{h} & = y_{\text{LiBr}} \cdot \bar{h}_{\text{LiBr}(T,p)}^\infty + (1 - y_{\text{LiBr}}) \cdot \bar{h}_{\text{H}_2\text{O}(T,p)}^1 + \bar{h}_{(T,p,m)}^E \\ & = 2966\text{ kJ kmol}^{-1} \end{aligned}$$

$$h = \bar{h} / \bar{M}_{\text{sol}} = 92.31\text{ kJ kg}^{-1}$$

### A.2. Entropy calculation

$$\bar{s}_{\text{LiBr}}^\infty = \bar{s}_{\text{LiBr};0}^\infty - R$$

$$\begin{aligned} & \cdot \left[ \frac{c_0}{2} \cdot \left( \frac{1}{T^2} - \frac{1}{T_0^2} \right) + \frac{c_1}{3} \cdot \left( \frac{1}{T^3} - \frac{1}{T_0^3} \right) + \frac{c_2}{4} \cdot \left( \frac{1}{T^4} - \frac{1}{T_0^4} \right) \right] \\ & - R \cdot \left( b_{00} - \frac{b_{02}}{T^2} \right) \cdot (p - p_0^*) \\ & = 9.952\text{ kJ kmol}^{-1}\text{ K}^{-1} \end{aligned}$$

$$\bar{s}_{\text{H}_2\text{O}}^1 = \bar{s}_{\text{H}_2\text{O};0}^1 + R$$

$$\begin{aligned} & \cdot \left( d_0 \cdot \ln \left( \frac{T}{T_0} \right) + d_1 \cdot (T - T_0) + \frac{d_2}{2} \cdot (T^2 - T_0^2) \right) - R \\ & \cdot (e_1 + 2e_2 \cdot T) \cdot (p - p_0^*) \\ & = 9.783\text{ kJ kmol}^{-1}\text{ K}^{-1} \end{aligned}$$

$$\begin{aligned} \bar{s}^E &= y_{\text{LiBr}} \cdot v \cdot \bar{R} \cdot \sum_{j=1}^6 \left[ a_j + \frac{i \cdot b_j}{2 \cdot v} p + T \cdot \left( \frac{\partial a_j}{\partial T} + \frac{i}{2 \cdot v} \frac{\partial b_j}{\partial T} p \right) \right] \\ &\quad \cdot m^{i/2} \\ &= 3.35 \text{ kJ kmol}^{-1} \text{ K}^{-1} \end{aligned}$$

$$\begin{aligned} \bar{s} &= y_{\text{LiBr}} \cdot \bar{s}_{\text{LiBr}(T,p)}^\infty + (1 - y_{\text{LiBr}}) \cdot \bar{s}_{\text{H}_2\text{O}(T,p)}^\infty - y_{\text{LiBr}} \cdot v \cdot \bar{R} \\ &\quad \cdot \left[ \ln \left( \frac{m}{m_0} \right) - 1 \right] + \bar{s}_{(T,p,m)}^E = 7.503 \text{ kJ kmol}^{-1} \text{ K}^{-1} \end{aligned}$$

$$s = \bar{s} / \bar{M}_{\text{sol}} = 0.2335 \text{ kJ Kg}^{-1} \text{ K}^{-1}$$

### A.3. Physical exergy

Enthalpy and entropy of reference for LiBr-H<sub>2</sub>O solution considered:  $T_{0,r} = 25^\circ\text{C}$ ,  $p_{0,r} = 101.325 \text{ kPa}$  and  $x_{\text{LiBr}} = 55.42\%$

$$\begin{aligned} h_{0,r} &= 66.83 \text{ kJ kg}^{-1} \\ s_{0,r} &= 0.1495 \text{ kJ kg}^{-1} \text{ K}^{-1} \\ \text{ex}_{\text{ph}} &= (h - h_{0,r}) - T_{0,\text{ref}} \cdot (s - s_{0,r}) \\ &= 92.31 - 66.83 - (25 + 273.15) \times (0.2335 - 0.1495) \\ &= 0.44 \text{ kJ kg}^{-1} \end{aligned}$$

### A.4. Chemical exergy calculation

Osmotic coefficient

$$\phi = 1 + \sum_{i=1}^6 a_i \cdot m^{i/2} + \frac{p}{2 \cdot v} \sum_{i=1}^2 i \cdot b_i \cdot m^{i/2} = 3.762$$

Activity H<sub>2</sub>O

$$\begin{aligned} \ln(a_{\text{H}_2\text{O}}) &= -\phi \cdot v \cdot m \cdot \bar{M}_{\text{H}_2\text{O}} \\ &= -3.762 \times 2 \times 0.01431 \times 18.02 \\ &= -1.9402 \\ a_{\text{H}_2\text{O}} &= 0.1437 \end{aligned}$$

Molality in saturated state  $x_{\text{LiBr,sat}} = 62.23\%$

$$m_{\text{sat}} = \frac{x_{\text{LiBr,sat}}}{(1 - x_{\text{LiBr,sat}}) \cdot \bar{M}_{\text{LiBr}}} = 0.01897 \text{ kmol kg}^{-1}$$

Activity LiBr

Substituting  $m$  in Equation (21)

$$\begin{aligned} \ln(a_{\text{LiBr}}) &= -v \cdot \left[ \ln(m) + \sum_{i=1}^6 \frac{(i+2)}{i} \right. \\ &\quad \cdot \left. \left( a_i + i \cdot \frac{p \cdot b_i}{2 \cdot v} \right) \cdot (m)^{i/2} \right]_{m_{\text{sat}}} = -3.204 \\ a_{\text{LiBr}} &= 0.04062 \end{aligned}$$

Standard chemical exergy of pure species

$$\begin{aligned} \text{ex}_{\text{ch},0} &= 1 / \bar{M}_{\text{sol}} [y_{\text{H}_2\text{O}} \cdot \bar{\epsilon}_{\text{H}_2\text{O}}^0 + y_{\text{LiBr}} \cdot \bar{\epsilon}_{\text{LiBr}}^0] \\ &= 1/32.13 \times (0.795 \times 900 + 0.205 \times 101\,600) \\ &= 670.6 \text{ kJ kg}^{-1} \end{aligned}$$

Exergy destruction due to dissolution process

$$\begin{aligned} \text{ex}_{\text{ch,dis}} &= \frac{\bar{R} \cdot T_0}{\bar{M}_{\text{sol}}} (y_{\text{H}_2\text{O}} \cdot \ln(a_{\text{H}_2\text{O}}) + y_{\text{LiBr}} \cdot \ln(a_{\text{LiBr}})) \\ &= 8.314 \times 298.15 / 32.13 \times (0.795 \\ &\quad \times -1.9402 + 0.205 \times -3.204) \\ &= -169.67 \text{ kJ kg}^{-1} \end{aligned}$$

Chemical exergy

$$\text{ex}_{\text{ch}} = 670.6 + (-169.67) = 500.9 \text{ kJ kg}^{-1}$$

Total exergy

$$\text{ex}_{\text{to}} = 0.44 + 500.9 = 501.3 \text{ kJ kg}^{-1}$$

## NOMENCLATURE

$a$	= activity
$C_p$	= specific heat at constant pressure (kJ kg <sup>-1</sup> K <sup>-1</sup> )
$\bar{C}_p$	= molar specific heat at constant pressure (kJ kmol <sup>-1</sup> K <sup>-1</sup> )
$\text{ex}$	= specific exergy (kJ kg <sup>-1</sup> )
$h$	= enthalpy (kJ kg <sup>-1</sup> )
$\bar{h}$	= molar enthalpy (kJ kmol <sup>-1</sup> )
$I$	= irreversibility (kW)
LHV	= lowing heating value (kJ m <sup>-3</sup> )
$m$	= molality (mol kg <sup>-1</sup> of solvent)
$\bar{m}$	= molecular mass (kg kmol <sup>-1</sup> )
$p$	= pressure (kPa)
$\dot{Q}$	= heat flow rate (kW)
$\bar{R}$	= universal gas constant (kJ kmol <sup>-1</sup> K <sup>-1</sup> )
$s$	= entropy (kJ kg <sup>-1</sup> K <sup>-1</sup> )
$\bar{s}$	= molar entropy (kJ kmol <sup>-1</sup> K <sup>-1</sup> )
$T$	= temperature (K)
$v$	= dissociation number (= 2 for LiBr)
$\dot{v}_{\text{gas}}$	= volumetric flow of natural gas
$\dot{W}$	= power (kW)
$\bar{V}$	= molar specific volume (m <sup>3</sup> kmol <sup>-1</sup> )
vfrac	= vapour fraction
$x$	= concentration of solute in mass
$y$	= mole fraction

Greek letters

$\bar{\epsilon}^0$	= standard chemical exergy (kJ kmol <sup>-1</sup> )
$\Delta$	= difference
$\eta$	= efficiency
$v$	= dissociation number for the solute
$\rho$	= density

$\phi$	= osmotic coefficient
$\Delta\bar{g}_f^0$	= standard molar Gibbs free energy of formation (kJ kmol <sup>-1</sup> )
$\psi$	= specific exergy calculated by Koehler <i>et al.</i> [1] and Sencan <i>et al.</i> [5]
$\xi$	= exergetic ratio of inlet and outlet

#### Subscripts

0	= reference state
1,2...	= points of the cycle
a	= absorber
Br <sub>2</sub>	= molecular bromide
c	= condenser
ch	= chemical
dis	= dissolution
e	= evaporator
ex	= exergetic
g	= generator
gas	= natural gas
H <sub>2</sub> O	= water
ht,g	= heat transfer in the generator
in	= inlet
Li	= lithium
LiBr	= lithium bromide
M	= mixture
out	= outlet
ph	= physical
sat	= saturation
sol	= solution
to	= total
vc	= control volume

#### Superscripts

*	= saturate state of pure solvent
∞	= ideal fluid for solute species
E	= excess property
l	= liquid phase

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