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On Exergy Calculations of Seawater with Applications in Desalination Systems

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Abstract

Exergy analysis is a powerful diagnostic tool in thermal systems performance evaluation. The use of such an analysis in seawater desalination processes is of growing importance to determine the sites of the highest irreversible losses. In the literature, exergy analyses of seawater desalination systems have sometimes modeled seawater as sodium chloride solutions of equivalent salt content or salinity; however, such matching does not bring all important properties of the two solutions into agreement. Furthermore, a common model that represents seawater as an ideal mixture of liquid water and solid sodium chloride may have serious shortcomings. Therefore, in this paper, the most up-to-date thermodynamic properties of seawater, as needed to conduct an exergy analysis, are given as correlations and tabulated data. The effect of the system properties as well as the environment dead state on the exergy and flow exergy variation is investigated. In addition, an exergy analysis for a large MSF distillation plant is performed using plant operating data and results previously published using the above-mentioned ideal mixture model. It is demonstrated that this ideal mixture model gives flow exergy values that are far from the correct ones. Moreover, the second law efficiency differs by about 80% for some cases.

Keywords

Exergy, Flow exergy, Exergy analysis, Seawater, Desalination

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1. Introduction

Increasing attention is being given to energy conservation, and this has resulted in increasing use of the exergy analysis concept for thermal systems analysis and performance evaluation. This concept is widely recognized as a necessary tool to quantify the thermodynamic losses in a given system or process. One important application of exergy analysis is seawater desalination because there is a large difference between the theoretical minimum energy required for seawater desalination and the practical requirements, owing to the irreversible losses in real systems. Therefore, a number of exergy analysis studies have been carried out to determine these inefficiencies and to give relevant recommendations for improvement of desalination systems.

It is important to emphasize that determination of the exergy requires knowledge of the reliable thermodynamic properties of the working fluid involved in a given process. These properties are available for many pure substances and some aqueous solutions. However, for seawater, relatively little data is available in the literature. Many researchers have performed exergy analysis of seawater desalination systems [1-13] including multistage flash (MSF), multi-effect distillation (MED), reverse osmosis (RO), mechanical vapor compression (MVC) and thermal vapor compression (TVC). In these analyses, different models have been adopted to estimate the thermodynamic properties of seawater. Frequently, seawater has been represented by aqueous sodium chloride solutions of equivalent salt content or salinity [1-3].

Although sodium chloride is the major constituent in seawater, such matching does not bring all important properties of the two solutions into agreement [4]. Some researchers have further represented seawater as an ideal mixture of pure water and solid sodium chloride salt [5-13]. In this model, the thermodynamic properties of pure water were determined from steam tables and those of the salt were calculated by using the thermodynamic relations for solids. It is, however, important to note that aqueous sodium chloride solution and seawater are strong electrolytes that can not be represented by an ideal mixture model. This may result in significant deviations in the thermodynamic properties [4].

On the other hand, some researchers oversimplify the problem by using the thermodynamic properties of pure water instead of seawater when performing energy and exergy analyses for seawater desalination systems [14]. Differences between pure water and seawater thermodynamic properties, even if only in the range of 5 to 10%, can have important effects in design of thermal desalination systems such as MSF and MED. For instance, density, specific heat capacity, vapor pressure and boiling point elevation are all examples of properties whose variation has a significant effect on seawater system performance [15].

The objective of this paper is to provide the most up-to-date correlations for seawater thermodynamic properties [16] that are required to calculate the exergy of seawater. The variation of the exergy and flow exergy with the system and environment state conditions is investigated mathematically using an ideal mixture model. Further, this exergy

variation is verified using the actual thermodynamic data of seawater. In addition, an exergy analysis is performed on a large MSF plant for which data was previously presented by Kahraman and Cengel [9], and which they analyzed using the ideal mixture model mentioned above.

2. Exergy

Exergy is the maximum amount of work obtainable when a system is brought into equilibrium from its initial state to the environmental (dead) state. In this regard, the state of the environment must be specified. The system is considered to be at zero exergy when it reaches the environment state, which is called the dead state. The equilibrium can be divided into thermal, mechanical and chemical equilibrium. These equilibriums can be achieved when the temperature (T), pressure (p) and concentration (w) of the system reaches the ones of the environment (T_0, p_0, w_0), respectively. Therefore, exergy consists of a thermomechanical exergy and a chemical exergy. The thermomechanical exergy is the maximum work obtained when the temperature and pressure of the system changes to the environment temperature and pressure (T_0, p_0) with no change in the concentration. Consequently, we say that thermomechanical equilibrium with the environment occurs. The chemical exergy is the maximum work obtained when the concentration of each substance in the system changes to its concentration in the environment at the environment pressure and temperature (T_0, p_0). Consequently, chemical equilibrium occurs.

For a control mass (closed system), the exergy, e, can be mathematically expressed as [17, 18],

$$e = u - u^* + p_0\left(v - v^*\right) - T_0\left(s - s^*\right) + \sum_{i=1}^{n} w_i\left(\mu_i^* - \mu_i^0\right) \tag{1}$$

where u, s, v, μ, and w are the specific internal energy, specific volume, specific entropy, chemical potential and mass fraction, respectively. Properties with "$*$" in the above equation are determined at the temperature and pressure of the environment (T_0, p_0) but at the same composition or concentration of the initial state. This is referred to as the *restricted* dead state, in which only the temperature and pressure are changed to the environmental values. However, the properties with "0" in the above equation (i.e., μ^0) are determined at the temperature, pressure and concentration of the environment (T_0, P_0, w_0), which is called the *global* dead state.

For a control volume (open system), the flow exergy, e_f, can be calculated by adding the flow work to the exergy in Eq. (1) which mathematically can be expressed as [17, 18],

$$e_f = e + v\left(p - p_0\right) \tag{2}$$

Knowing that $h = u + pv$, and eliminating e in Eq. (2) using Eq. (1), the flow exergy can be rewritten as

$$e_f = h - h^* - T_0\left(s - s^*\right) + \sum_{i=1}^{n} w_i\left(\mu_i^* - \mu_i^0\right) \tag{3}$$

It is important to note that if the system and the environment are both pure substances (e.g. pure water), the chemical exergy (last term in Eqs. (1) and (3)) will vanish. However, for a multi-component system (e.g. seawater, exhaust gases) the chemical

exergy must be considered. Ignoring it may lead to unrealistic and illogical results for the exergy variation with the concentration [4].

2.1 Exergy Variation

The exergy of a control mass system (given by Eq. (1)) and the exergy of a control volume system (flow exergy given by Eq. (3)), are intensive thermodynamic properties which are the maximum obtainable work per unit mass of the system. They are functions in the initial state as well as the environment state. However, if the environmental state is specified (T_0, p_0, w_0), the exergy is a function only in the system initial state (T, p, w).

In this section we examine how the exergy (for control mass system) and flow exergy (for control volume system) change with the temperature, pressure, and mass concentration of the initial state with respect to the environment dead state. Assuming the environmental dead state is at $T = T_0$, $p = p_0$ and $w = w_0$, and assuming an ideal gas mixture with equivalent mixture properties, R, c_p, c_v that satisfies the ideal gas relation $(pv=RT)$.

Case 1: $p = p_0$, $w = w_0$ but $T \neq T_0$

In this case, the chemical exergy (last term in Eq. (1)) vanishes and the exergy can be written for an ideal gas mixture as

$$e \quad c_v T \quad T_0 \quad p_0 \quad \frac{RT}{p} \quad \frac{RT_0}{p_0} \quad T_0 c_p \ln \frac{T}{T_0} \quad R \ln \frac{p}{p_0} \tag{4}$$

For $p = p_0$

$$e = c_v(T - T_0) - R(T - T_0) + T_0 c_p \ln \frac{T}{T_0} \qquad (5)$$

Using $c_p = c_v + R$, the exergy will be

$$e = c_p T_0 \left[\frac{T}{T_0} - \ln \frac{T}{T_0} - 1 \right] \qquad (6)$$

Equation (6) for the case when the pressure and concentration are equal to the dead state shows that the exergy is always positive at any temperature (see Fig. 1). If the system has a temperature equal to the dead state ($T/T_0 = 1$), the exergy is zero. However if the temperature is higher or lower than the dead state temperature, the exergy is always positive. The positive exergy is due to the heat that can be transferred between the system temperature and the dead state temperature, in one direction or the other as appropriate, to operate a heat engine cycle that can produce positive work. The same result (Eq. (6)) can be obtained for a control volume system using the flow exergy equation (Eq. (3)). Therefore, as long as $p = p_0$, $w = w_0$, any temperature difference between the system state and the dead state will result in positive exergy and positive flow exergy.

Case 2: $T = T_0$, $w = w_0$ but $p \neq p_0$

In this case, the chemical exergy (last term in Eq. (1)) vanishes and the exergy of a control mass can be written for an ideal gas mixture as

$$e = c_v(T - T_0) + p_0 \left(\frac{RT}{p} - \frac{RT_0}{p_0} \right) - T_0 \left(c_p \ln \frac{T}{T_0} - R \ln \frac{p}{p_0} \right) \qquad (7)$$

For $T = T_0$ the exergy will be

$$e \quad RT_0 \frac{p_0}{p} \quad \ln \frac{p}{p_0} \quad 1 \tag{8}$$

Equation (8) for the case when the temperature and concentration are equal to the dead state, shows that the exergy of the "control mass system" is always positive at any pressure (see Fig. 2). If the system has a pressure equal to the dead state pressure ($p/p_0 = 1$), the exergy is zero. However if the pressure is higher or lower than the dead state pressure, the exergy of the control mass system is always positive. The positive exergy is due to the mechanical work that can be obtained by expansion (if $p > p_0$) or compression (if $p < p_0$) of the system to reach the environment pressure.

However, for a control volume system (open system), the flow exergy (given by Eq. (3)) can be written for an ideal gas mixture as (with $w = w_0$)

$$e_f \quad c_p \quad T \quad T_0 \quad T_0 \quad c_p \ln \frac{T}{T_0} \quad R \ln \frac{p}{p_0} \tag{9}$$

For $T = T_0$ the flow exergy will be

$$e_f \quad RT_0 \ln \frac{p}{p_0} \tag{10}$$

It is clear from Eq. (10) that the flow exergy of a control volume system may be positive or negative depending on the pressure of the system. If the pressure of the control volume system is higher than the dead state pressure (i.e. $p > p_0$), a flow stream can be expanded reversibly (e.g., using a turbine) to the environment pressure and produce work resulting in a positive flow exergy. However, if the pressure is lower than the dead state pressure (i.e. $p < p_0$), an external work should be applied to compress the flow stream (e.g., using a

compressor) to the environment pressure resulting in a negative flow exergy (see Fig. 3). Therefore, the exergy of the control mass is always positive at any pressure; however the exergy of the control volume (flow exergy) can be negative at pressures lower than the dead state pressure.

Case 3: $T = T_0$, $p = p_0$ but $w \neq w_0$

In this case, when $T = T_0$ and $p = p_0$, the first two terms in the exergy equation (Eq. (1)) and flow exergy equation (Eq. (3)) vanish. The only remaining term is the last term which is the chemical exergy. The exergy or flow exergy in this case can be written as follows

$$e = e_f = \sum_{i=1}^{n} w_i \left(\mu_i^* - \mu_i^0 \right) \tag{11}$$

For an ideal mixture model, the chemical potential differences are given as

$$\mu_i - \mu_i = R_i T \ln x_i \tag{12}$$

where x_i is the mole fraction, μ_i is evaluated at a hypothetical standard state for the component i, and it is not equal to μ_i^0. Therefore, the chemical potential differences in Eq. (11) can be written as

$$\mu_i^* - \mu_i^0 = \left(\mu_i^* - \mu_i \right) - \left(\mu_i^0 - \mu_i \right) = R_i T \ln \frac{x_i}{x_{i,0}} \tag{13}$$

Substituting equation (13) into Eq. (11) yields

$$e = e_f = \sum_{i=1}^{n} w_i R_i T \ln \frac{x_i}{x_{i,0}} \tag{14}$$

Assuming for simplicity the mixture consists of two substances (1 and 2) and using $T = T_0$ yields,

$$e = e_f = w_1 R_1 T_0 \ln \frac{x_1}{x_{1,0}} + w_2 R_2 T_0 \ln \frac{x_2}{x_{2,0}} \tag{15}$$

Using the following two relationships

$$w_1 R_1 = x_1 R \tag{16}$$

$$w_2 R_2 = x_2 R \tag{17}$$

where R is the gas constant for the mixture. We also know that;

$$x_1 = 1 - x_2 \tag{18}$$

$$x_{1,0} = 1 - x_{2,0} \tag{19}$$

Substituting equations (16) – (19) into Eq. (15) and dropping the subscript 2 yields

$$e = e_f = RT_0 \left[(1 - x) \ln \frac{1 - x}{1 - x_0} + x \ln \frac{x}{x_0} \right] \tag{20}$$

Now, we can prove mathematically that Eq. (20) is always positive at any mole fraction (concentration) by taking the first and second derivatives with respect to x:

$$\frac{\partial e}{\partial x} = RT_0 \left[\ln \frac{x}{x_0} - \ln \frac{1 - x}{1 - x_0} \right] \tag{21}$$

$$\frac{\partial^2 e}{\partial x^2} = RT_0 \left[\frac{1}{x} + \frac{1}{1 - x} \right] \tag{22}$$

From Eq. (20), at $x = x_0$ the exergy (and flow exergy) is zero. From Eq. (21) at $x < x_0$ the first derivative (slope) is negative, meaning that the exergy is decreasing. And at $x > x_0$ the first derivative (slope) is positive, meaning that the exergy is increasing. Finally, from

Eq. (22), the second derivative is always positive, which together with the previous findings means that the point $x = x_0$ is a minimum. This mathematical proof is shown graphically in Fig. 4 where the flow exergy is always positive and zero at the dead state concentration.

The positive exergy is due to mass transfer process that can be used to produce work. For instance, if the concentration of a solute in a mixture at the system state is higher than the concentration of this solute at the dead state, the solvent in the environment can flow through a semi-permeable membrane to the system due to the chemical potential difference. This will increase the static head of the system and can produce positive work (exergy) though a hydropower turbine. This fact has been discussed since 1970s [19] and recently was applied in a pilot osmotic power plant in Norway [20]. The same thing will happen if the solute concentration in the system is lower than that at the environment dead state, but the flow of solvent in this case will be from the system to the environment. This is clearly illustrated in Fig. 4, which is applicable at any selected dead state.

From the above discussion, we conclude that the exergy of the control mass system is always positive at any temperature, pressure, and mass concentration. However, the exergy of a control volume system (flow exergy) may have negative values if the pressure of the system is lower than the dead state pressure. It is important to note that this fact was proved mathematically for an ideal gas mixture; however, the same conclusion can be obtained for real systems using actual thermodynamic data. Therefore, the most up-to-date correlations for seawater thermodynamic properties are given in the

Appendix for exergy calculation. In the following section the exergy and flow exergy of seawater are calculated to show the various trends with respect to important parameters.

3. Seawater Exergy

The correlations given in the Appendix for the thermodynamic properties of seawater are used to calculate the flow exergy of seawater. In this regard, the (environment) dead state should be specified. However it is important to mention that the choice of the dead state does not affect the exergy analysis results. In seawater desalination systems, usually the intake seawater condition of the desalination plant is taken as the environment dead state condition. This condition varies from place to place depending on the geographical location of the desalination plant (ambient temperature, altitude, salinity of the seawater source). In addition, the pressure of the intake seawater depends on the depth of the intake system which varies from 5-50 m [21]. Therefore, the dead state pressure may change from 1 to 5 atmospheres.

The effect of changing the environmental dead state as well as the initial state on seawater flow exergy is shown in Figures 5 – 8. Figure 5 shows the specific flow exergy of seawater as it changes with the initial state temperature when the pressure and salt concentration are equal to the dead state values. As shown in this figure, the flow exergy is zero at the dead state temperature. It is *always positive* at any temperature other than the dead state temperature. This is true for any selected dead state temperature, therefore whenever there is a difference in temperature between the system and environment, there will be a thermal potential difference that makes the flow exergy positive.

Figure 6 shows the specific flow exergy of seawater as it changes with the salt concentration of the initial state temperature when the pressure and temperature are equal to the dead state values. As shown in this figure, the flow exergy is *always positive* at any concentration other than the dead state concentration. This fact is true for any selected dead state salt concentration, therefore whenever there is a difference in concentration between the system and environment, there will be a chemical potential difference that makes the flow exergy positive. For instance, if the salt concentration of the flow stream is higher than the salt concentration at the dead state, pure water can flow from the environment to the flow stream through a semi-permeable membrane. This will increase the static head of the flow stream and can produce positive work (exergy) though a hydropower turbine [4]. The same thing will happen if the salt concentration of the flow stream is lower than that of the environment dead state, but the flow of water in this case will be from the flow stream to the environment. This is clearly illustrated in Fig, 6, which is applicable for any selected dead state.

The effect of changing the dead state pressure is shown in Fig. 7. As shown in this figure, the flow exergy is zero at the dead state pressure. It is *positive* at pressures higher than the dead state pressure and *negative* at pressures lower than the dead state pressure. However, the exergy of a control mass system (closed system) is always positive whenever, the pressure is higher or lower than the dead state pressure as shown in Fig. 8. This has been proved mathematically in section 2.1 assuming an ideal gas mixture model.

Tabulated data for seawater thermodynamic properties are given in Table 1 using the equations presented in section 2 and the appendix. The properties include specific volume, specific internal energy, specific enthalpy, specific entropy, specific exergy and specific flow exergy. These are given at temperature of 10 – 90 $^{\circ}$C, salt concentration of 0.035 kg/kg (absolute salinity 35 g/kg) and pressure of 101.325 kPa. However, the equations presented in the appendix can be used up to temperature of 120 $^{\circ}$C. In this case for temperatures higher than the normal boiling temperature, the pressure is the saturated pressure and the state of the seawater is the saturated liquid state. For the exergy and flow exergy values given in Table 1, the environment dead state is selected at $T_0 = 25$ $^{\circ}$C, $p_0 = 101.325$ and $w_{s,0} = 0.035$ kg/kg.

4. Exergy Analysis

A comparison between the ideal and actual energy required in desalination processes shows that the actual energy consumption is much greater than the ideal operation [3]. This is due to the large irreversible losses involved in the desalination systems which need some improvements. The first step in any improvement or enhancement process is diagnostics, and exergy analysis is a powerful diagnostic tool. The use of such an analysis in desalination processes is of growing importance to determine the sites of the highest irreversible losses (or exergy destruction). In addition, it identifies the components responsible for the greatest thermodynamic losses in the system. Therefore, in this section, an exergy analysis is performed for a large multi-stage flash (MSF) desalination plant which was presented previously by Kahraman and Cengel [9].

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Figure 9 shows a schematic diagram of a dual purpose MSF plant in Saudi Arabia [9]. The water production capacity of the plant is 230 MGD (0.871 million m^3/day), having an installed power generation capacity of 1295 MW. The plant is located near the city of Al-Jubail at the Arabian Gulf coast. The MSF plant consists of 40 distillation units, and each unit consists of 22 flashing stages and is capable of producing distilled water at a rate of 272 kg/s. The intake seawater has a salt concentration of 0.0465 kg/kg (salinity of 46,500 ppm) enters the plant at 35 ^{o}C at atmospheric pressure (101.325 kPa) and at a rate of 2397 kg/s. The properties at various points throughout the plant are given in Fig. 9. The given properties are also listed in Table 2, together with the flow exergy values calculated by Kahraman and Cengel [9], and calculated using the seawater correlations presented in the present paper. The environmental dead state is selected at $T_0 = 35$ ^{o}C, p_0 = 101.325 kPa and $w_{s,0} = 0.0465$ kg/kg (which is the intake seawater conditions).

It is important to emphasize that Kahraman and Cengel [9] used an ideal mixture model of pure water and sodium chloride salt to present and calculate the thermodynamic properties of seawater. This model was initially suggested by Cerci [5] and has been discussed by Sharqawy et al [4]. As shown in Table 2, some flow exergy values calculated by that ideal mixture model have negative values at pressure equal to or higher than the dead state pressure. In addition, the flow exergy of that model always decreases with salt concentration and has negative values at salinities higher than the dead state salinity. This is due to the chemical exergy part which was neglected in this ideal mixture model [5, 9]. However, by using the formulation presented in the present paper for the flow exergy together with the seawater thermodynamic properties correlations, correct

trends for the flow exergy are obtained, as shown in Table 2. The deviation of the ideal mixture model values are also shown in Table 2 (last column).

After determining the flow exergy at each state in the desalination plant, this MSF desalination plant is analyzed assuming steady state operation and a combined pump-motor efficiency of 75% [9]. Neglecting the kinetic and potential energies of the fluid streams, the exergy balance is similar to the energy balance performed using the first law of thermodynamics. However, the exergy is not a conserved quantity due to the irreversibilities (or exergy destruction). Thus, the exergy balance is expressed as

$$Inlet\ Exergy \quad Outlet\ Exergy \quad Exergy\ destroyed \tag{23}$$

The second law efficiency is defined as the ratio of the minimum work required for the desalination process to the total exergy input. The minimum work required is equivalent to the minimum work of separation which can be calculated using the flow exergy of the inlet and outlet streams from the equivalent system (see Sharqawy et al. [4]), while the total exergy input is the sum of the flow exergy of the heating stream (steam) and exergy input to the driving pumps. This can be written as,

$$_{II} \quad \frac{W_{\min}}{E_{input}} \tag{24}$$

where

$$W_{\min} \quad E_{f,16} \quad E_{f,15} \quad E_{f,0} \tag{25}$$

$$E_{input} \quad E_{f,11} \quad E_{f,12} \quad \frac{1}{_{pump}} \quad E_{f,1} \quad E_{f,0} \quad E_{f,13} \quad E_{f,5} \quad E_{f,14} \quad E_{f,6} \quad E_{f,8} \quad E_{f,7} \tag{26}$$

The fraction of exergy destruction within a component is determined by dividing the exergy destruction of that component by the total exergy destruction in the plant. Table 3 shows this fraction for each component in the MSF desalination plant calculated using the values of the flow exergy in Table 2. As shown in Table 3, there is a difference between the fraction of exergy destruction calculated by Kahraman and Cengel [9] and by the present work. This difference reaches 25% for the exergy destroyed in the heat exchangers. In addition the value of the second law efficiency calculated from the present work is 7.65% while from Kahraman and Cengel [9] it is 4.2%, a difference of about 80%. This shows that the exergy analysis and the second law efficiency calculations performed using the ideal mixture model of Kahraman and Cengel [9] are comparatively far from the correct values.

5. Concluding Remarks

The variation of the exergy and flow exergy with the system and environment properties is critically examined both for a previously published model for seawater properties and actual sea water properties. It is demonstrated mathematically, using an ideal gas mixture model, that the flow exergy can only have negative value at pressures lower than the dead state pressure; otherwise this quantity is positive for any system temperature and concentration. Correlations for the thermodynamic properties of seawater are given and the exergy of seawater is calculated. The variation of the seawater exergy with temperature, pressure and salt concentration using the actual thermodynamic properties is consistent with results that are presented here in a closed-form for an ideal gas mixture.. In addition, an exergy analysis is performed for a large MSF desalination

plant that was presented earlier in the literature using the previously published model for seawater flow exergy. This model attempted to treat seawater as an ideal mixture of pure water and solid sodium chloride salt. It is found that this ideal mixture model gives unrealistic flow exergy values and a second law efficiency that differs by as much as 80% from the correct value. This shows that exergy calculations and analyses performed using that model are comparatively far from the correct values.

Acknowledgments

Nomenclature

c_p	specific heat at constant pressure	J kg^{-1} K^{-1}
c_v	specific heat at constant volume	J kg^{-1} K^{-1}
E_f	flow exergy	W
e	specific exergy	J kg^{-1}
e_f	specific flow exergy	J kg^{-1}
G	Gibbs energy	J
g	specific Gibbs energy	J kg^{-1}
h	specific enthalpy	J kg^{-1}
m	mass	kg
n	number of species in mixture	
p	pressure	Pa
R	gas constant	J kg^{-1} K^{-1}
s	specific entropy	J kg^{-1} K^{-1}
T	temperature	$^{\circ}$C
u	specific internal energy	J kg^{-1}
v	specific volume	m^3 kg^{-1}
W_{min}	minimum work of separation	W
w	mass fraction	kg kg^{-1}
x	mole fraction	

Greek Symbols

η_{II}	second law efficiency	
μ	chemical potential	J kg^{-1}
ρ	density	kg m^{-3}

Subscripts

0	environmental dead state
1, 2	substances 1 and 2
s	salt
sw	seawater
w	pure water

Superscripts

*	restricted dead state
•	standard state

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Appendix: Seawater Thermodynamic Properties

Seawater is a complex electrolyte solution of water and salts. The salt concentration, w_s, is the total amount of solids present in a unit mass of seawater. It is usually expressed by the salinity (on reference-composition salinity scale) as defined by Millero et al. [22] which is currently the best estimate for the absolute salinity of seawater. In this appendix, correlations of seawater thermodynamic properties namely specific volume, specific enthalpy, specific entropy and chemical potentials to be used in exergy analysis calculations are given. In this regard, a fundamental equation for the Gibbs energy as a function of temperature, pressure and salinity is used to calculate the thermodynamic properties of seawater. Details of this fundamental equation can be found in a recent release issued by the International Association of Properties of Water and Steam, IAPWS 2008 [23].

The thermodynamic properties of seawater are calculated using the correlations provided by Sharqawy et al. [16]. These correlations fit the data extracted from the seawater Gibbs energy function of IAPWS 2008 [23]. They are polynomial equations given as functions of temperature and salt concentration at atmospheric pressure (or saturation pressure for temperatures over normal boiling temperature). In these correlations, the reference state for the enthalpy and entropy values is taken to be the triple point of pure water (0.01 ^{o}C) and at zero salt concentration. The temperature is defined by the International Temperature Scale ITS-1990 [24]. For other correlations of

seawater thermophysical properties, the equations recommended by Sharqawy et al. [16] are used.

A.1. Specific volume

The specific volume is the inverse of the density as given by Eq. (A.1). Both are intensive properties however in thermodynamics literature it is preferred to use the specific volume instead of the density because it is directly related to the flow work. The density of seawater is higher than that of pure water due to the salts; consequently the specific volume is lower. The seawater density can be calculated by using Eq. (A.2) given by Sharqawy et al. [16] which fits the data of Isdale and Morris [25] and that of Millero and Poisson [26] for a temperature range of $0 - 180$ ^{o}C and salt concentration of $0 - 0.16$ kg/kg and has an accuracy of ± 0.1 %. The pure water density is given by Eq. (A.3) which fits the data extracted from the IAPWS [27] with an accuracy of ± 0.01%.

$$v_{sw} = 1/\rho_{sw} \tag{A.1}$$

$$\rho_{sw} = \rho_w + w_s \left(a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 w_s T^2 \right) \tag{A.2}$$

$$\rho_w = 9.999 \times 10^2 + 2.034 \times 10^{-2} T - 6.162 \times 10^{-3} T^2 + 2.261 \times 10^{-5} T^3 - 4.657 \times 10^{-8} T^4 \tag{A.3}$$

where v_{sw} is the specific volume of seawater in m^3/kg, ρ_{sw} and ρ_w are the density of seawater and pure water respectively in kg/m^3, T is the temperature in ^{o}C, w_s is the salt concentration in kg$_s$/kg$_{sw}$ and

$$a_1 = 8.020 \times 10^2, a_2 = -2.001, a_3 = 1.677 \times 10^{-2}, a_4 = -3.060 \times 10^{-5}, a_5 = -1.613 \times 10^{-5}$$

Figure A.1 shows the specific volume of seawater calculated from Eq. (A.1) as it changes with temperature and salt concentration. It is shown that the specific volume of

seawater is less than that of pure water by about 8.6% at 0.12 kg/kg salt concentration and 120 ^{o}C. It is important to mention that for incompressible fluids (e.g. seawater) the variation of the specific volume with pressure is very small and can be neglected in most desalination practical problems. The error in calculating the specific volume is less than 1% when the pressure is varying from the saturation pressure to the critical pressure in the compressed liquid region. Therefore, Eq. (A.1) can be used at pressures higher than the atmospheric pressure (up to the critical pressure) and at pressure lower than the atmospheric pressure (up to the saturation pressure) with a negligible error (less than 1%).

A.2. Specific enthalpy

The specific enthalpy of seawater is lower than that of pure water since the heat capacity of seawater is less than that of pure water. It can be calculated using Eq. (A.4) given by Sharqawy et al. [16] which fits the data extracted from the seawater Gibbs energy function of IAPWS [23] for a temperature range of 10 – 120 ^{o}C and salinity range of 0 – 0.12 kg/kg and has an accuracy of ±0.5 %. The pure water specific enthalpy is given by Eq. (A.5) which fits the data extracted from the IAPWS [27] with an accuracy of ±0.02%. It is valid for temperature range of 5 – 200 ^{o}C.

$$h_{sw} \quad h_w \quad w_s \; b_1 \quad b_2 w_s \quad b_3 w_s^2 \quad b_4 w_s^3 \quad b_5 T \quad b_6 T^2 \quad b_7 T^3 \quad b_8 w_s T \quad b_9 w_s^2 T \quad b_{10} w_s T^2 \qquad (A.4)$$

$$h_w \quad 141.355 \quad 4202.070 \; T \quad 0.535 \; T^2 \quad 0.004 \; T^3 \qquad (A.5)$$

where h_{sw} and h_w are the specific enthalpy of seawater and pure water respectively in (J/kg), $10 \le T \le 120$ ^{o}C, $0 \le w_s \le 0.12$ kg/kg and

$b_1 = 2.348 \times 10^4, b_2 = 3.152 \times 10^5, b_3 = 2.803 \times 10^6, b_4 = 1.446 \times 10^7, b_5 = 7.826 \times 10^3$

$b_6 = 4.417 \times 10^1, b_7 = 2.139 \times 10^{-1}, b_8 = 1.991 \times 10^4, b_9 = 2.778 \times 10^4, b_{10} = 9.728 \times 10^1$

Figure A.2 shows the specific enthalpy of seawater calculated from Eq. (A.4) as it changes with temperature and salt concentration. It is shown that the specific enthalpy of seawater is less than that of pure water by about 14% at 0.12 kg/kg salt concentration and 120 °C. It is important here to add the effect of pressure on the specific enthalpy. The seawater is an incompressible fluid and hence the following approximation can be used to determine the specific enthalpy at different pressure [17],

$$h_{sw}(T, p, w_s) = h_{sw}(T, p_0, w_s) + v(p - p_0) \tag{A.6}$$

where $h_{sw}(T, p_0, w_s)$ is the specific enthalpy of seawater at atmospheric pressure calculated from Eq. (A.4) and v is the specific volume of seawater calculated from Eq. (A.1).

A.3. Specific entropy

The specific entropy of seawater is lower than that of pure water. It can be calculated using Eq. (A.7) given by Sharqawy et al. [16] which fits the data extracted from the seawater Gibbs energy function of IAPWS [23] for a temperature range of 10 – 120 °C and salt concentration of 0 – 0.12 kg/kg and has an accuracy of ±0.5 %. The pure water specific entropy is given by Eq. (A.8) which fits the data extracted from the IAPWS [27] with an accuracy of ±0.1%. It is valid for $T = 5 - 200$ °C.

$$s_{sw} = s_w - w_s(c_1 + c_2 w_s + c_3 w_s^2 + c_4 w_s^3 + c_5 T + c_6 T^2 + c_7 T^3 + c_8 w_s T + c_9 w_s^2 T + c_{10} w_s T^2) \tag{A.7}$$

$$s_w = 0.1543 + 15.383 T - 2.996 \times 10^{-2} T^2 + 8.193 \times 10^{-5} T^3 - 1.370 \times 10^{-7} T^4 \tag{A.8}$$

where s_{sw} and s_w are the specific entropy of seawater and pure water respectively in (J/kg K), $10 \leq T \leq 120\ ^\circ C$, $0 \leq w_s \leq 0.12$ kg/kg and

$$c_1 = 4.231 \times 10^2, c_2 = -1.463 \times 10^4, c_3 = 9.880 \times 10^4, c_4 = -3.095 \times 10^5, c_5 = 2.562 \times 10^1$$
$$c_6 = -1.443 \times 10^{-1}, c_7 = 5.879 \times 10^{-4}, c_8 = 6.111 \times 10^1, c_9 = 8.041 \times 10^1, c_{10} = 3.035 \times 10^{-1}$$

Figure A.3 shows the specific entropy of seawater calculated from Eq. (A.7) as it changes with temperature and salt concentration. It is shown that the specific entropy of seawater is less than that of fresh water by about 18% at 0.12 kg/kg salt concentration and 120 $^\circ C$. It is important to mention that for incompressible fluids (e.g. seawater) the variation of specific entropy with pressure is very small and can be neglected in most practical cases [17]. Therefore, Eq. (A.7) can be used at pressures different than the atmospheric pressure.

A.4. Chemical potential

The chemical potentials of water in seawater and salts in seawater are determined by differentiating the total Gibbs energy function with respect to the composition:

$$\mu_w = \frac{\partial G_{sw}}{\partial m_w} = g_{sw} - w_s \frac{\partial g_{sw}}{\partial w_s} \tag{A.9}$$

$$\mu_s = \frac{\partial G_{sw}}{\partial m_s} = g_{sw} + (1 - w_s) \frac{\partial g_{sw}}{\partial w_s} \tag{A.10}$$

where g_{sw} is the specific Gibbs energy of seawater defined as

$$g_{sw} = h_{sw} - (T + 273.15) s_{sw} \tag{A.11}$$

The specific Gibbs energy function can be calculated using the enthalpy and entropy correlations given by Eq. (A.6) and (A.7) above. The differentiation of the specific Gibbs

energy with respect to salt concentration is carried out using the enthalpy and entropy correlations as follows,

$$\frac{g_{sw}}{w_s} \quad \frac{h_{sw}}{w_s} \quad T \quad 273.15 \frac{s_{sw}}{w_s} \tag{A.12}$$

Note that the differentiation of the pure water part in Eq. (A.5) and (A.8) with respect to the salt concentration is zero, the differentiation of the enthalpy and entropy with respect to the salt concentration will be

$$\frac{h_{sw}}{w_s} \quad b_1 \quad 2b_2 w_s \quad 3b_3 w_s^2 \quad 4b_4 w_s^3 \quad b_5 T \quad b_6 T^2 \quad b_7 T^3 \quad 2b_8 w_s T \quad 3b_9 w_s^2 T \quad 2b_{10} w_s T^2 \tag{A.13}$$

$$\frac{s_{sw}}{w_s} \quad c_1 \quad 2c_2 w_s \quad 3c_3 w_s^2 \quad 4c_4 w_s^3 \quad c_5 T \quad c_6 T^2 \quad c_7 T^3 \quad 2c_8 w_s T \quad 3c_9 w_s^2 T \quad 2c_{10} w_s T^2 \tag{A.14}$$

Figure A.4 shows the chemical potential of water in seawater calculated from Eq. (A.9) as it changes with temperature and salt concentration. Figure A.5 shows the chemical potential of salts in seawater calculated from Eq. (A.10) as it changes with temperature and salt concentration. It is shown in Fig. A.4 that the chemical potential of water in seawater decreases with both temperature and salt concentration, while the chemical potential of salts in seawater increases with both temperature and salt concentration as shown in Fig. A.5.

LIST OF FIGURES
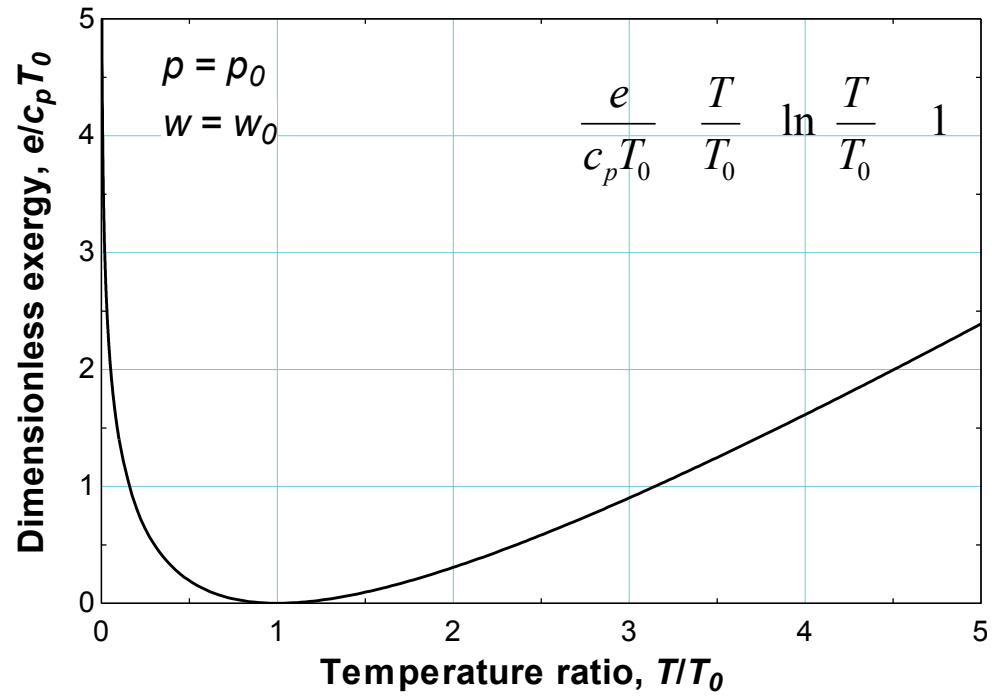
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Fig. 1

Fig. 1 Dimensionless exergy as a function of temperature ratio
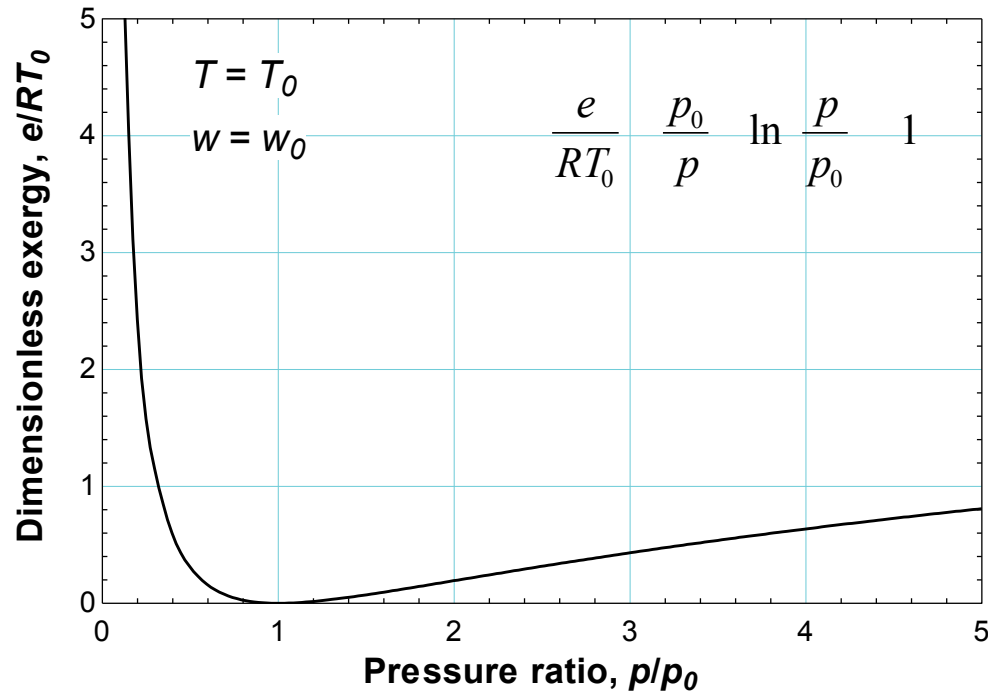
Fig. 2

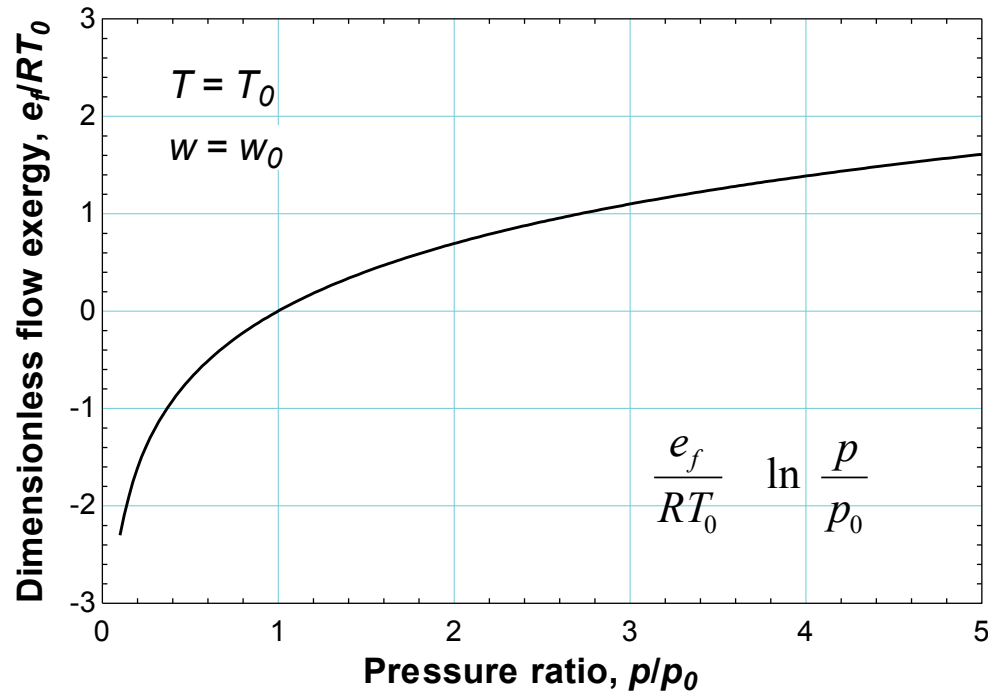**Fig. 2 Dimensionless exergy of control mass system as a function of pressure ratio**

Fig. 3

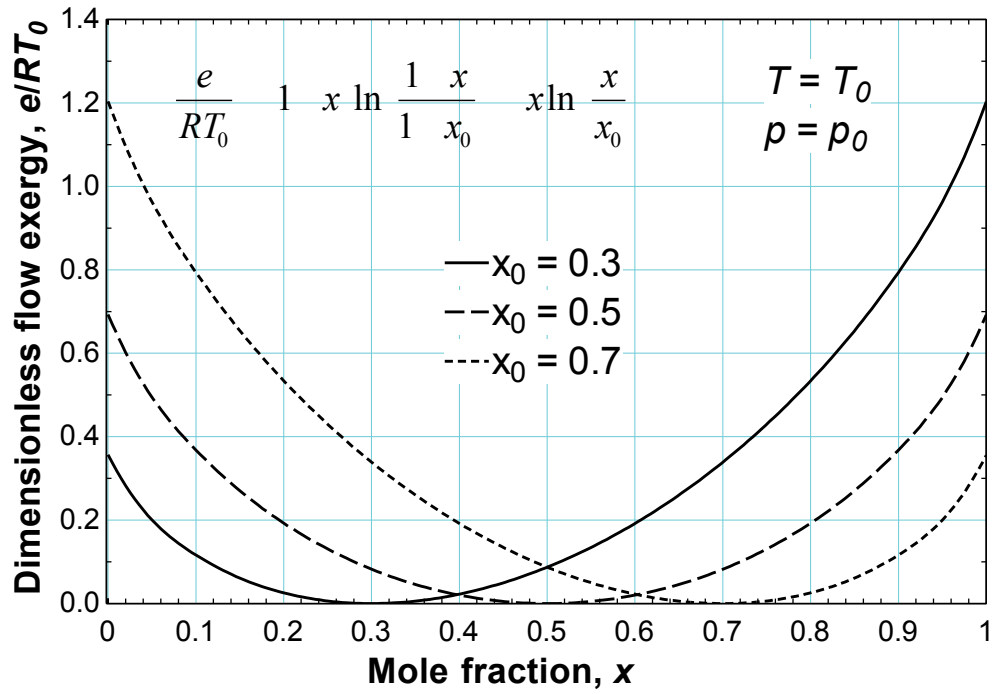**Fig. 3 Dimensionless flow exergy as a function of pressure ratio**

Fig. 4

The plot's axes and embedded labels:

- Y-axis: **Dimensionless flow exergy, e/RT_0**, ranging from 0.0 to 1.4
- X-axis: **Mole fraction, x**, ranging from 0 to 1

$$\frac{e}{RT_0} = \left(1-x\right)\ln\frac{1-x}{1-x_0} + x\ln\frac{x}{x_0}$$

$$T = T_0$$
$$p = p_0$$

Legend:
- —— $x_0 = 0.3$
- – – $x_0 = 0.5$
- ···· $x_0 = 0.7$

Fig. 4 Dimensionless exergy as a function of concentration

Fig. 5
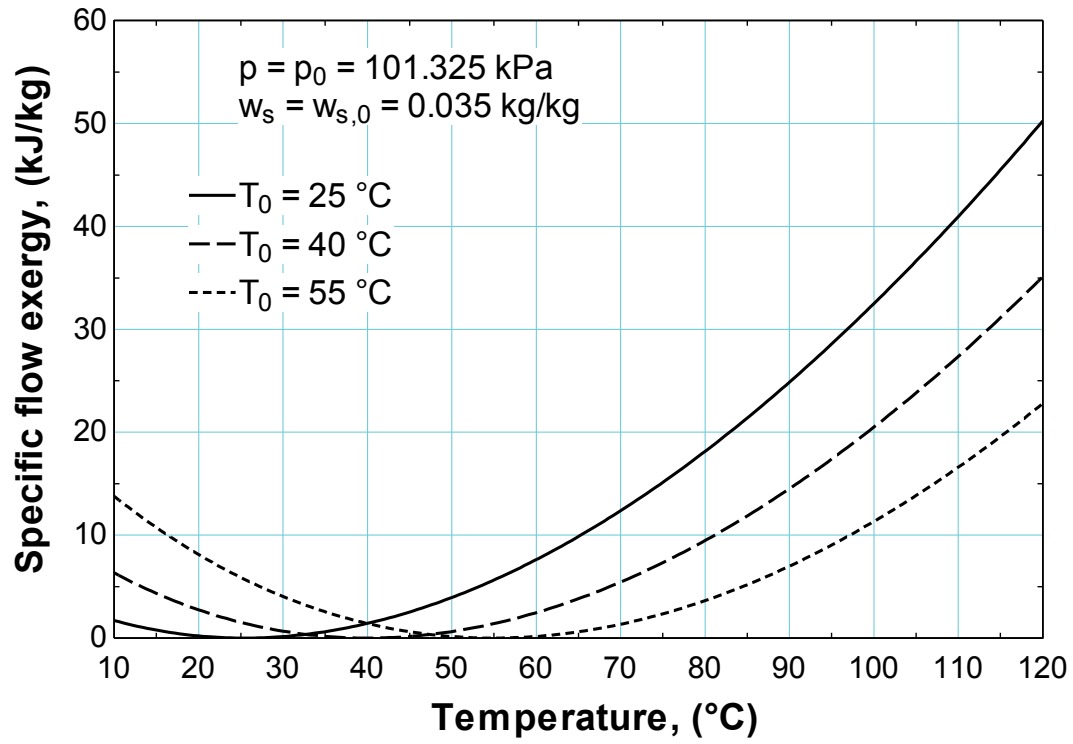
Fig. 5 Specific flow exergy of seawater as a function of temperature
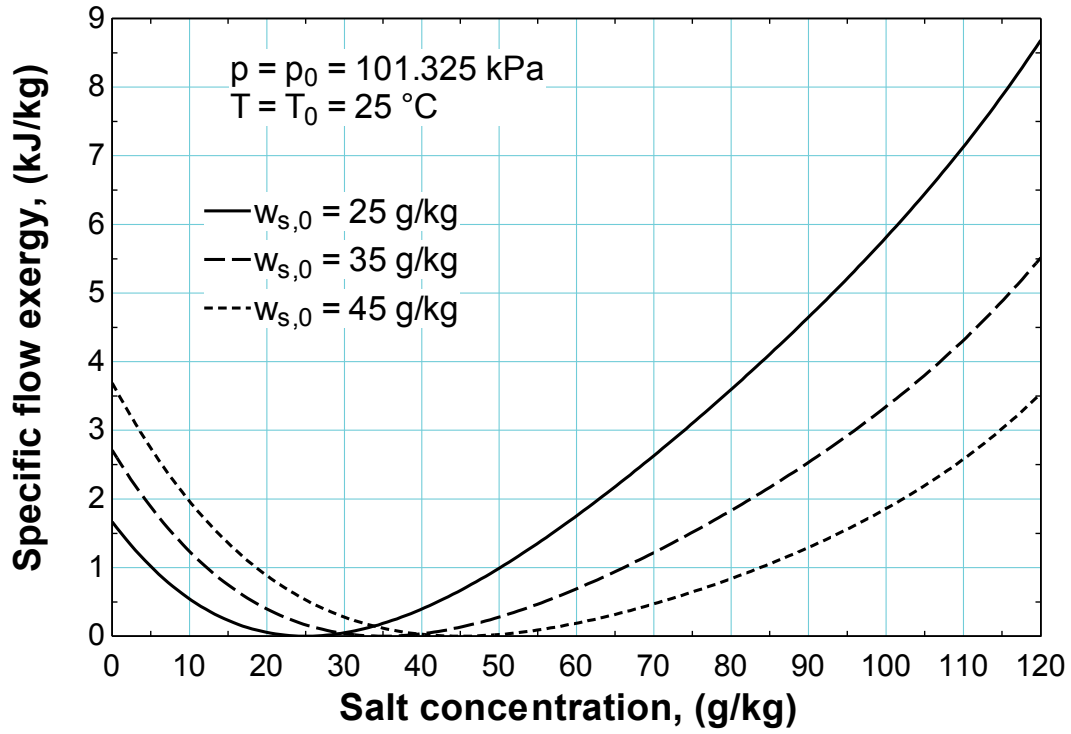
Fig. 6

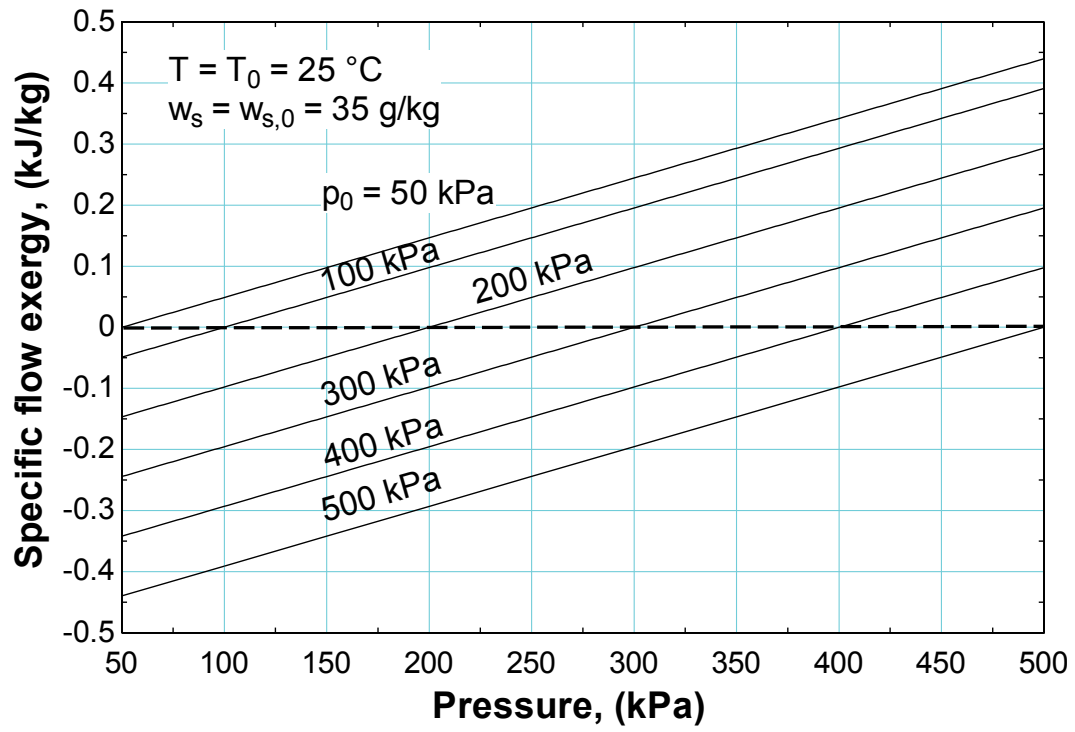Fig. 6 Specific flow exergy of seawater as a function of salt concentration

Fig. 7

Fig. 7 Specific flow exergy of seawater as a function of pressure
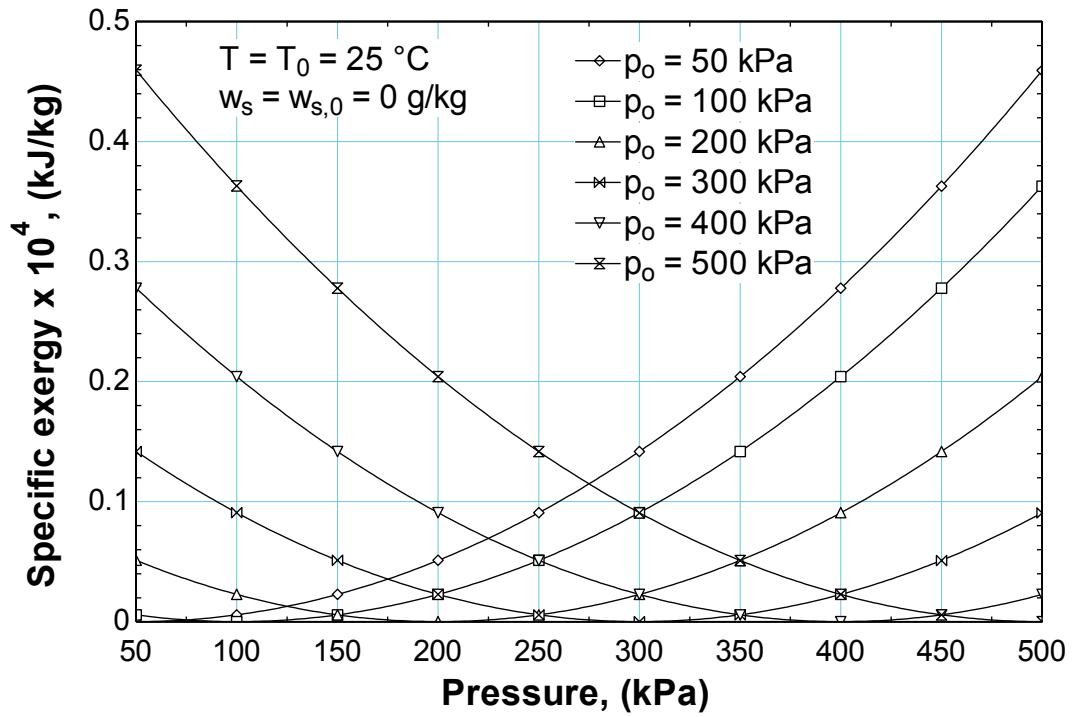
Fig. 8

Fig. 8 Specific exergy of water as a function of pressure

Fig. 9
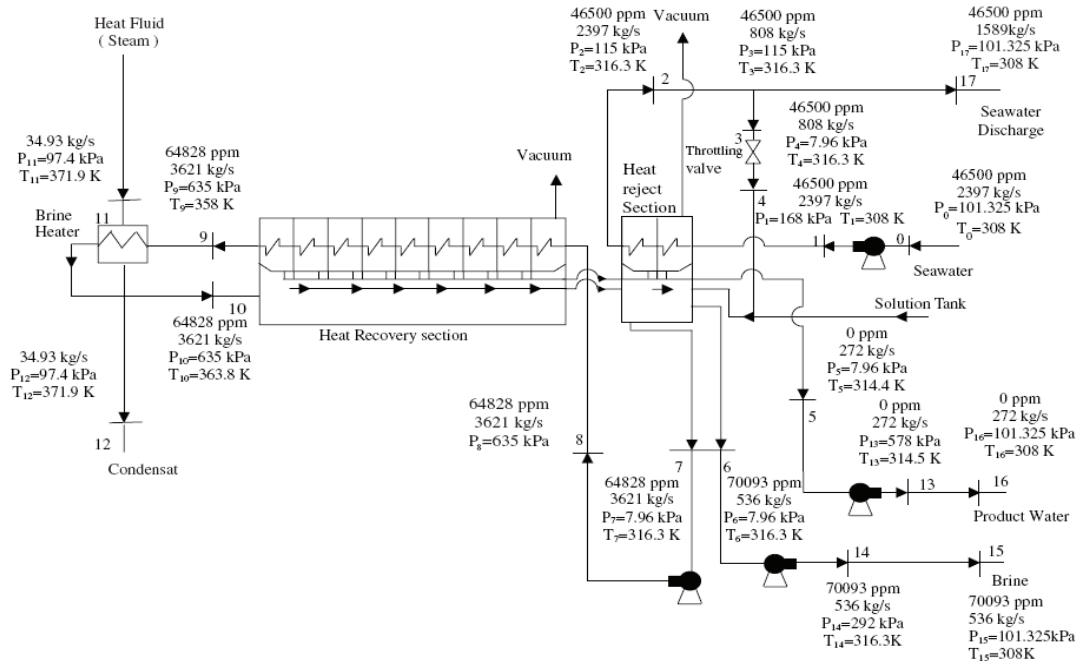

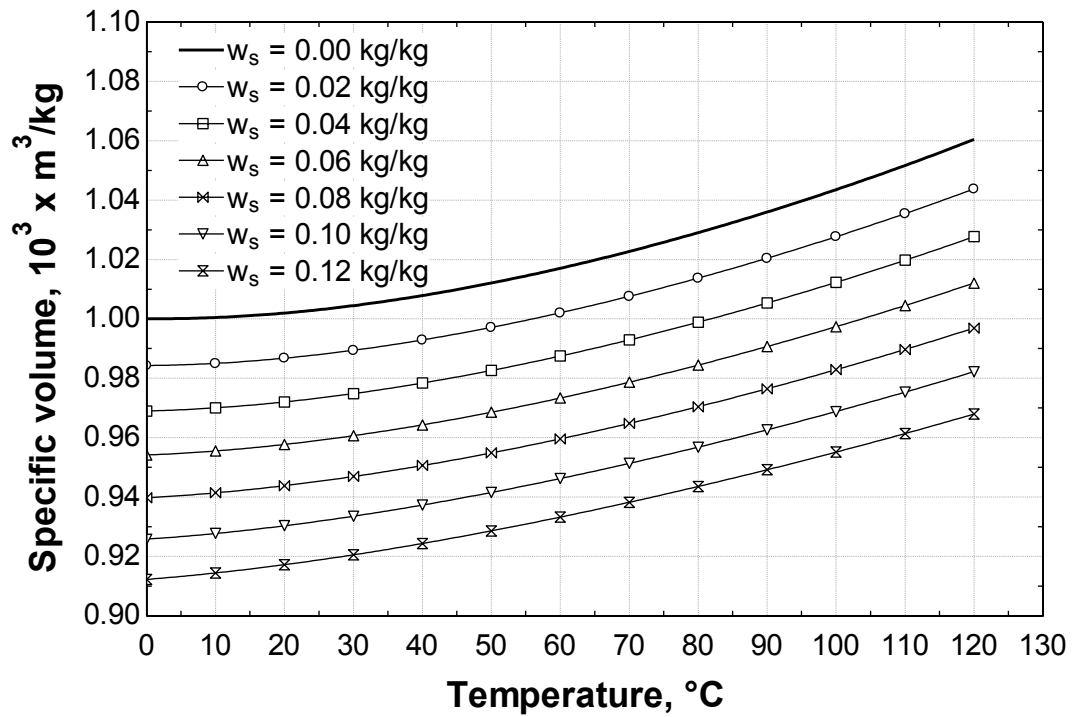Fig. 9 MSF desalination plant [9]

Fig. A.1

Fig. A.1 Seawater specific volume variations with temperature and salt concentration

Fig. A.2

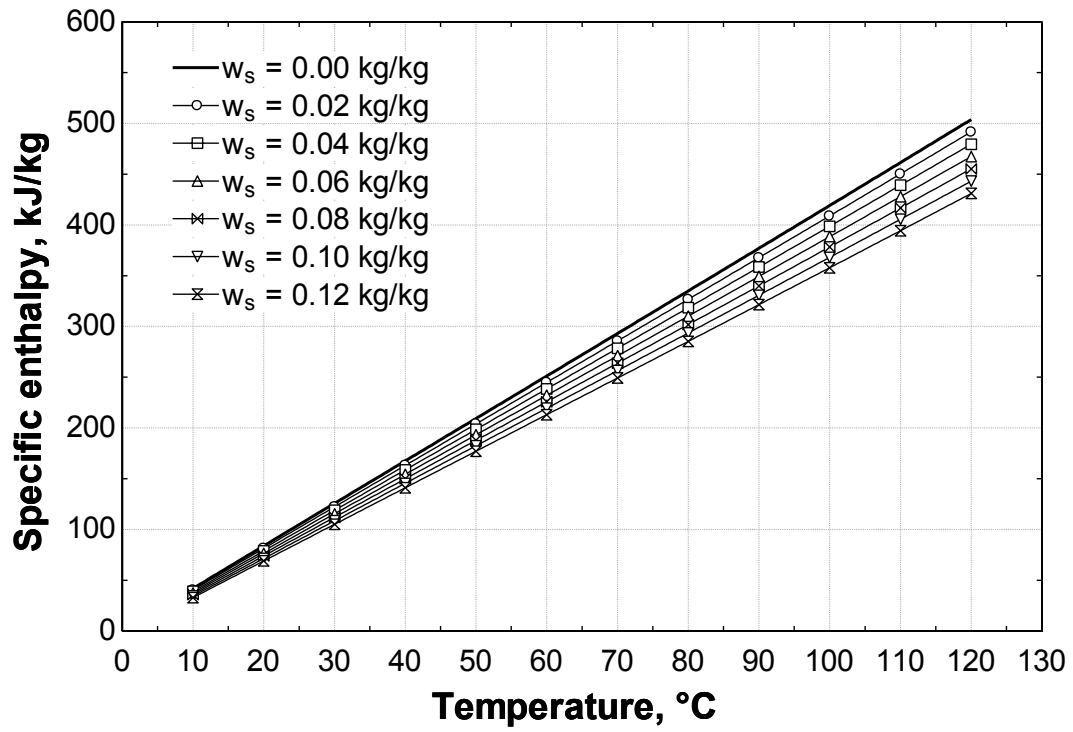**Fig. A.2 Seawater specific enthalpy variations with temperature and salt concentration**
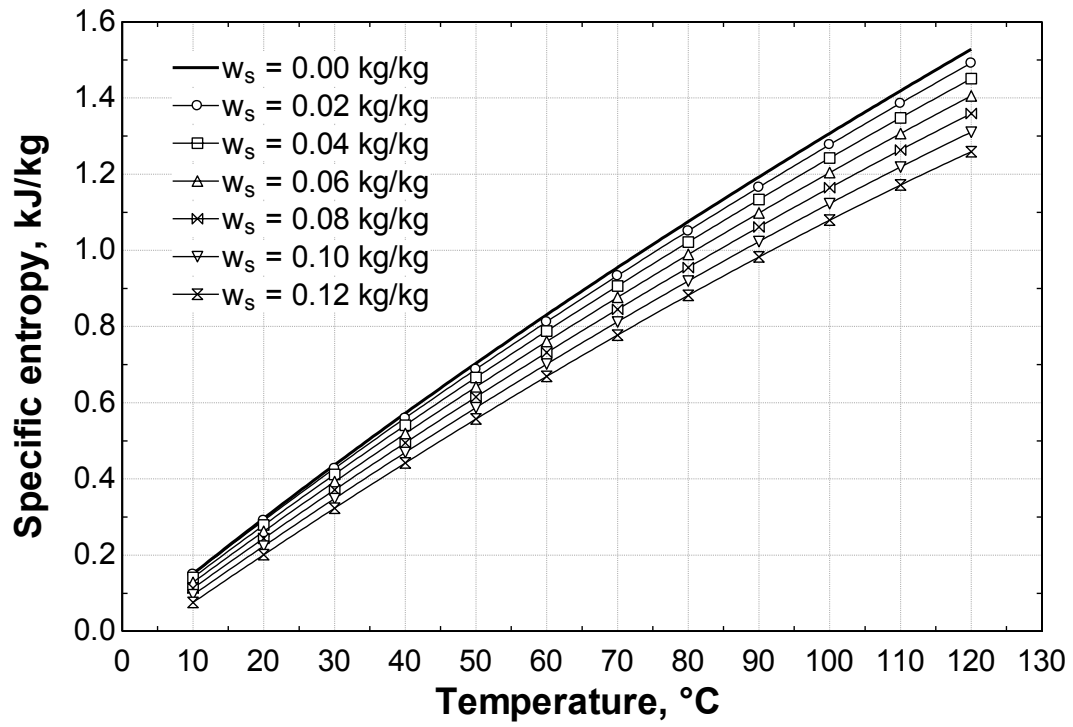
Fig. A.3 Seawater specific entropy variations with temperature and salt concentration
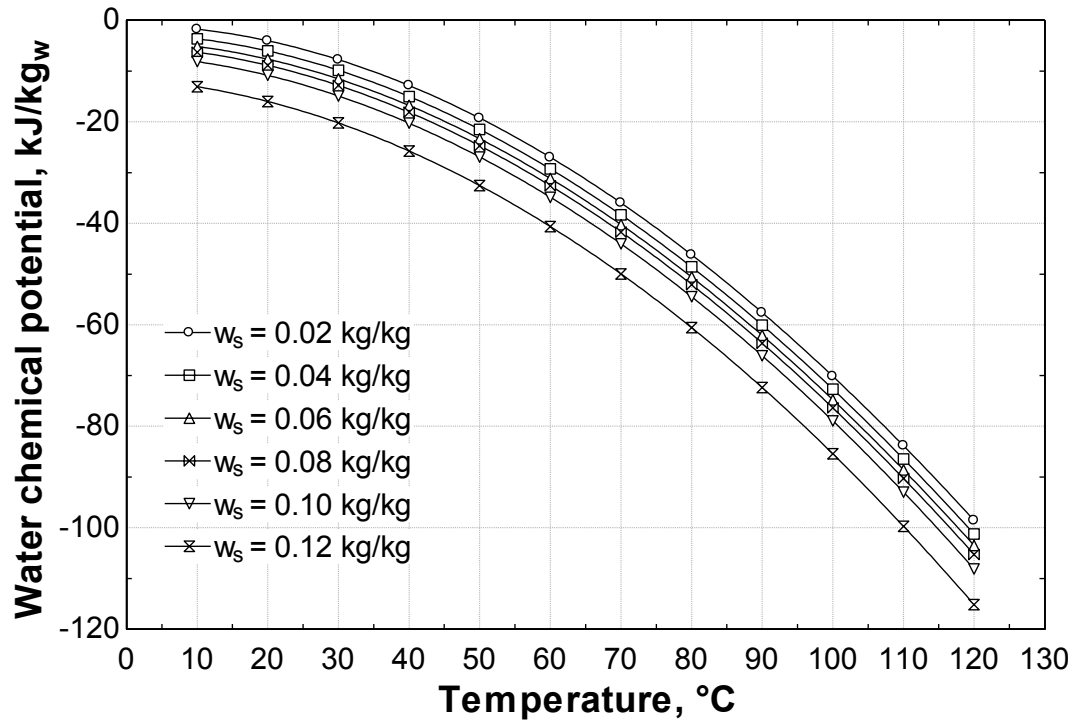
Fig. A.4

Fig. A.4 Chemical potential of water in seawater
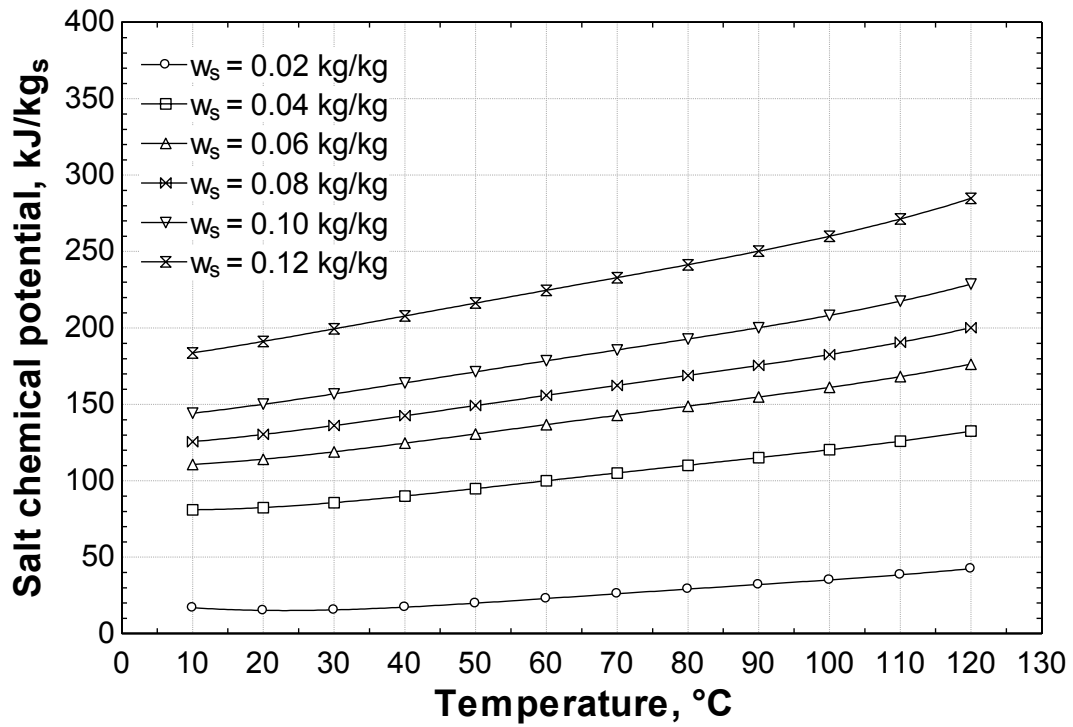
Fig. A.5

Fig. A.5 Chemical potential of salts in seawater

Table 1 Seawater Thermodynamic Properties

T °C	v m^3/kg	u kJ/kg	h kJ/kg	s kJ/kg K	μ_w kJ/kg	μ_s kJ/kg	e_f kJ/kg
10	0.000974	40.0	40.1	0.144	-3.2	68.95	1.71
15	0.000975	59.8	59.9	0.214	-4.2	69.07	0.77
20	0.000976	79.7	79.8	0.282	-5.56	69.74	0.20
25	0.000977	99.7	99.8	0.350	-7.28	70.87	0.00
30	0.000978	119.6	119.7	0.416	-9.34	72.36	0.14
35	0.000980	139.6	139.7	0.482	-11.74	74.16	0.62
40	0.000982	159.6	159.7	0.546	-14.49	76.17	1.42
45	0.000984	179.7	179.8	0.610	-17.56	78.35	2.53
50	0.000986	199.7	199.8	0.672	-20.96	80.63	3.94
55	0.000989	219.8	219.9	0.734	-24.69	82.98	5.64
60	0.000991	239.9	240.0	0.795	-28.73	85.36	7.62
65	0.000994	260.0	260.1	0.855	-33.09	87.74	9.87
70	0.000997	280.1	280.2	0.914	-37.76	90.11	12.37
75	0.000999	300.3	300.4	0.972	-42.73	92.45	15.13
80	0.001003	320.4	320.5	1.029	-48.01	94.76	18.14
85	0.001006	340.5	340.6	1.086	-53.59	97.06	21.39
90	0.001009	360.7	360.8	1.142	-59.46	99.36	24.86

$T_0 = 25$ °C, $p = p_0 = 101.325$ kPa, $w_s = w_{s,0} = 0.035$ kg/kg

Table 2 Thermodynamic properties at various locations throughout the MSF plant

#	p, kPa	T, ⁰C	w_s, g/kg	m^o, kg/s	e_f, kJ/kg*	e_f, kJ/kg**	% deviation
0	101.3	35.0	46.5	2397	0.000	0.000	0.0
1	168.0	35.0	46.5	2397	0.065	0.064	1.3
2	115.0	43.3	46.5	2397	0.442	0.493	-11.4
3	115.0	43.3	46.5	808	0.442	0.493	-11.4
4	9.0	43.3	46.5	808	0.339	0.392	-15.6
5	9.0	41.4	0.0	272	4.152	10.489	-152.6
6	9.0	43.3	70.1	536	0.752	-3.502	565.9
7	9.0	43.3	64.8	3621	0.601	-2.672	544.4
8	635.0	43.3	64.8	3621	1.204	-2.082	272.9
9	635.0	85.0	64.8	3621	15.070	-12.123	180.4
10	635.0	90.8	64.8	3621	18.350	15.495	15.6
11	97.4	98.9	0.0	34.9	411.200	388.177	5.6
12	97.4	98.9	0.0	34.9	23.120	0.000	100.0
13	578.0	41.5	0.0	272	4.735	11.062	-133.6
14	292.0	43.3	70.1	536	1.023	-3.238	416.5
15	101.3	35.0	70.1	536	0.420	-3.887	1025.1
16	101.3	35.0	0.0	272	3.972	10.268	-158.5
17	101.3	35.0	46.5	1589	0.000	0.000	0.0

* Present work calculations;
** Kahraman and Cengel [9]

Table 3 Exergy analysis results for the MSF plant

	Present work	Kahraman and Cengel [9]	% deviation
Exergy destroyed in flash chambers, %	75.54	77.80	2.90
Exergy destroyed in heat exchangers, %	10.53	8.30	-26.87
Exergy destroyed in pumps, %	5.58	5.30	-5.30
Exergy destroyed in cooling processes, %	4.46	4.80	7.17
Exergy destroyed in brine disposal, %	2.05	2.10	2.38
Exergy destroyed in product, %	1.32	1.30	-1.15
Exergy destroyed in throttling valves, %	0.53	0.50	-5.92
Minimum separation work, kW	1306	710	-82.05
Second law efficiency, %	7.65	4.20	-83.94