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Comparative study on the methods of calculating theoretical minimum energy requirement for desalination

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ABSTRACT

Theoretical calculations to estimate the minimum required energy for desalination are compared. In order to calculate the reversible energy to produce purified water from saline water, three different theoretical methods are applied, which are the second law of thermodynamics, the osmotic pressure theory and the vapor compression theory. For each method, the derivation of the equations to calculate the theoretical minimum energy is reviewed in detail from the background and assumptions, and the equations are summarized for an infinitesimal and a finite recovery cases. Various temperatures, recoveries and the salinities of feed and product water are considered for case studies to analyze the quantitative difference between the methods. For 25°C and 35,000 ppm feed saline water, the minimum required energy to produce a unit product water of 0 ppm is calculated as 0.762, 0.742 and 0.761 kWh/ton for an infinitesimal recovery and 1.068, 1.071 and 1.098 kWh/ton for a 50% recovery from the second law of thermodynamics, the osmotic pressure theory with the van't Hoff equation and the vapor compression theory with the boiling point elevation Eq. (33), respectively. In general, it is supposed that the calculation of theoretical minimum energy could include 5%–10% uncertainty, depending on the conditions of the concerned case and the applied equation. It is believed that for the same conditions the theoretical minimum energy for desalination should be identical in nature, regardless of the type of desalination, for example, membrane, thermal or any other way of desalination.

Keywords: Desalination; Theoretical minimum energy; Minimum separation work; Second law of thermodynamics; Osmotic pressure theory; Vapor compression theory

1. Introduction

Desalination is known to be an energy intensive technology, thus the energy consumption of desalination has gained much interest from academic and industrial societies. Current seawater reverse osmosis (SWRO) consumes around 3.6–4.0 kWh of electricity per ton of freshwater production [1]. To understand how large this energy for desalination is, it is better to understand the typical household electricity consumption, which is 2.90 kWh/d/person in Korea, and 12.45 kWh/d/person in UAE [2]. The residential water consumption of 280 L/d/person in Korea [3] and 550 L/d/person in UAE [4] can be interpreted as 1.12 and 2.20 kWh_{eq}/d/person electricity consumption, respectively, if all consuming water is assumed from a SWRO desalination plant at 4 kWh/m^3. Thus, desalination could add up 17.7%–38.6% to the household electricity consumption if there is no other freshwater source than desalination. Because of such a huge energy consumption, there have been a lot of efforts to reduce the energy cost of desalination, and the first step would be understanding the final goal which is the theoretical minimum energy requirement for desalination.

The theoretical minimum energy required for desalination has been well known since 1960s [5,6]. A typical approach of the second law of thermodynamics assumes seawater or saline water as a NaCl solution, and the Gibbs function and the ideal gas law are applied. Once the Gibbs function including chemical potential for a mixture is defined,

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a simplified equation can be driven by assuming the solution as ideal and then by comparing the difference between the chemical potential of both the ideal mixture and the pure substances. From this simplified equation in terms of chemical potential, the entropy increase from the pure substances to the ideal solution is obtained, thus the reversible work for mixing, which is the minimum separation work, can be calculated [7]. The second approach is based on the osmotic pressure theory. Once a proper equation for osmotic pressure, for example, the van't Hoff equation, is given, the work by the osmotic pressure can be easily calculated, which is the minimum separation work [1]. The last approach is based on the vapor compression theory. Two isolated containers, one with feed saline water and the other with purified water at the same temperature, both at vapor saturated, can be considered. Though the water temperature is the same, the saturated pressure of the two containers is different due to the boiling point elevation (BPE) difference from different salinity. If an ideal compressor could transfer the steam vapor at lower pressure in the feed saline water container to the higher pressure container with the purified water, the energy required for this isentropic compressor is the minimum energy for desalination [8]. Most of the researchers have introduced the theoretical minimum energy for desalination using one of the aforementioned methods, which numbers are reported in the range of 0.7–0.76 kWh/m^3 for an infinitesimal recovery to produce pure water from 25°C and 35,000 ppm saline water. In case of a 50% recovery, the minimum work increases to about 1.06 kWh/m^3 [9,10]. Unfortunately, however, a comprehensive comparative study between the theories has been limited, from which the quantitative uncertainty could be understood from the assumptions made for each theoretical methods.

In this paper, the three known theoretical methods are reviewed with their background and assumptions. For the approach by the second law of thermodynamics, the correspondent simplified equations for some limiting conditions are provided. For the approaches by the osmotic pressure theory and by the vapor compression theory, a hypothesis to obtain the generalized equation for an arbitrary recovery from the simpler equation for an infinitesimal recovery is proposed. Calculation results from three theoretical methods are compared for various temperatures, recoveries and the feed/product water salinities. Though the minimum work for desalination shall be the same in nature for the same conditions, the quantitative comparison of the results from each theory is the purpose of this paper to understand the magnitude of uncertainties laying in the theoretical approaches for calculating the minimum work for desalination.

2. Schematic of desalination process

Desalination is a salt reject process to produce less saline water from more saline water. This process is entropy increasing, thus energy (or work) is required for desalination. In nature, solar energy is the main source for desalination, that is, part of seawater evaporates from the surface of oceans with solar energy and the released water vapor condenses in the cool air, becoming freshwater. In general, a desalination process can be described as in Fig. 1 [7].

In Fig. 1, N is the number of moles, and for subscripts, feed saline water is denoted as "f", product water "p", brine reject/blowdown "b", salt "s" and water "w", respectively.

From the mass conservation of each species:

$$N_{s,f} = N_{s,b} + N_{s,p} \tag{1}$$

$$N_{w,f} = N_{w,b} + N_{w,p} \tag{2}$$

In order to calculate the number of moles in a solution, it is important to understand the dissociation level of each species. In case of a NaCl solution, the degree of dissociation is studied as a function of molality, which is shown in Fig. 2 [11].

From Fig. 2, the degree of dissociation α is 0.797 for a 35,000 ppm (0.60 mol/kg) and 0.793 for a 45,000 ppm (0.77 mol/kg) NaCl solution at 25°C. It is noted that the degree of dissociation varies rapidly at a lower molality, which approaches to 1.000 for pure water (0.00 mol/kg). The following equation shows that the total number of moles in a solution is $(1 + \alpha)N$, where $(1 + \alpha)$ is called a dissociation constant.

$$\begin{array}{cccc} \mathrm{NaCl} & \leftrightarrow & \mathrm{Na^+} & \mathrm{Cl^-} \\ (1-\alpha)N & & \alpha N & \alpha N \end{array} \tag{3}$$

Though the seawater, which is the interested solution in this paper, contains various dissolved solids,

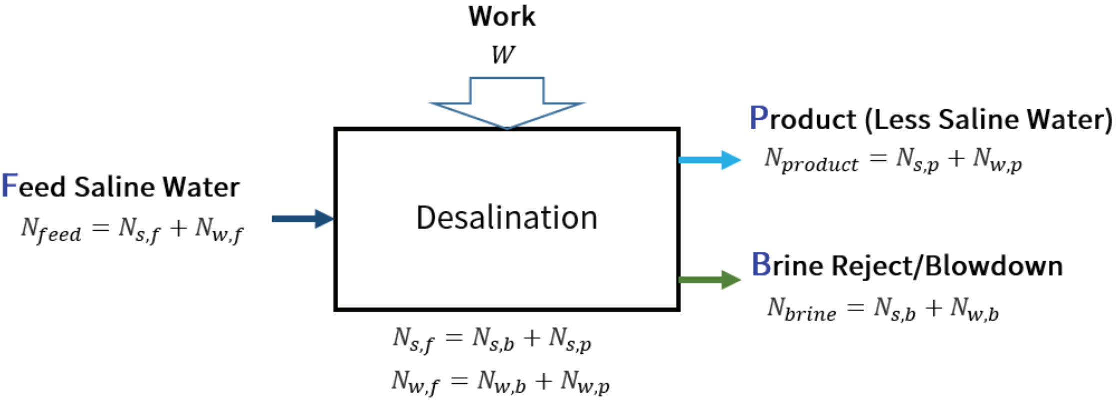

Fig. 1. Schematic diagram of desalination process [7].

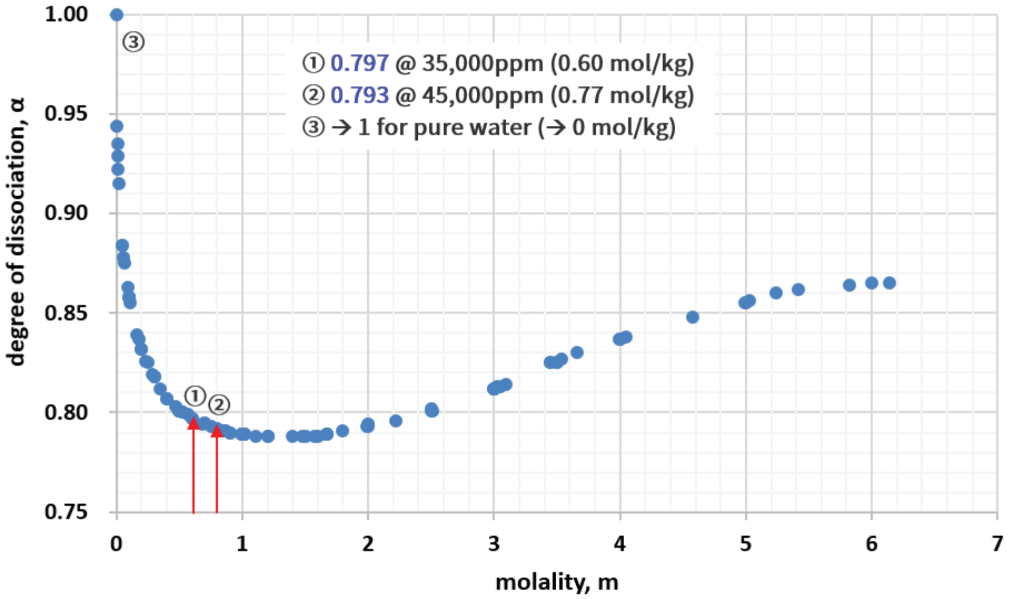

Fig. 2. Degree of dissociation α as a function of molality m (mol/kg) for NaCl(aq) at 25°C [11].

only NaCl is considered with the dissociation constant of 1.8 when the colligative properties of seawater are required. This kind of simplification, typically applied for the second law of thermodynamics and the osmotic pressure theory, could generate a certain uncertainty in calculating the theoretical minimum energy for desalting seawater.

3. Theories to calculate minimum work for desalination

Theoretical minimum work for desalination can be calculated via three different approaches. In this chapter, the background and assumptions of each approach are explained in detail.

3.1. Minimum separation work by the second law of thermodynamics

The first method to calculate the theoretical minimum work for desalination is based on the second law of thermodynamics. If seawater can be assumed as an ideal solution (or ideal mixture), each component follows the ideal gas law, and the entropy change during mixing can be calculated as follows:

$$\Delta S_{\text{mixing,ideal}} = -R_u \sum_i N_i \ln x_i \tag{4}$$

where R_u (=8.31446 J/mol/K) is the universal gas constant, N_i is the mole number and x_i is the mole fraction of the i-th component. The derivation of Eq. (4) is summarized in Appendix A (details can be found in reference [7]).

As the minimum work of separation is the reversible work, which is the same to the exergy destruction during mixing:

$$W_{\text{rev}} = W_{\text{min,separation}} = T_0\,\Delta S_{\text{mixing,ideal}} = -R_u T_0 \sum_i N_i \ln x_i \tag{5}$$

where T_0 is the reference temperature in K, that is, large enough reservoirs are assumed for each feed water, product water and brine discharge at T_0.

For a desalination system in Fig. 1, where the substances are salt and water, the minimum required work will be:

$$W_{\text{min}} = W_{\text{min,feed}} - (W_{\text{min,brine}} + W_{\text{min,product}}) \tag{6}$$

where

$$W_{\text{min,feed}} = -R_u T_0 (N_{s,f} \ln x_{s,f} + N_{w,f} \ln x_{w,f}) \tag{6a}$$

$$W_{\text{min,brine}} = -R_u T_0 (N_{s,b} \ln x_{s,b} + N_{w,b} \ln x_{w,b}) \tag{6b}$$

$$W_{\text{min,product}} = -R_u T_0 (N_{s,p} \ln x_{s,p} + N_{w,p} \ln x_{w,p}) \tag{6c}$$

Then, Eq. (6) becomes:

$$\begin{aligned} W_{\text{min}} = R_u T_0 \big(&N_{s,b} \ln(x_{s,b}/x_{s,f}) + N_{s,p} \ln(x_{s,p}/x_{s,f}) \\ &+ N_{w,b} \ln(x_{w,b}/x_{w,f}) + N_{w,p} \ln(x_{w,p}/x_{w,f})\big) \end{aligned} \tag{7}$$

Though Eq. (7) is derived from the ideal solution (ideal mixture) assumption, which is valid for sufficiently low saline water, Eq. (7) itself is valid for an arbitrary feed water salinity, recovery, and product water quality.

It is important to notice that Eq. (7) can be further simplified at each limiting conditions as follows:

- Condition 1. Infinitesimal recovery ($R = 0+$)

$$\begin{gathered} W_{\text{min}} \cong R_u T_0 \big(N_{s,p} \ln(x_{s,p}/x_{s,f}) + N_{w,p} \ln(x_{w,p}/x_{w,f})\big) \\ \because \ln(x_{s,b}/x_{s,f}) \to 0,\ \ln(x_{w,b}/x_{w,f}) \to 0 \end{gathered} \tag{8}$$

- Condition 2. Pure product water (product water salinity $X_p = 0$ ppm)

$$W_{\min} \cong R_u T_0 \left(N_{s,b} \ln(x_{s,b}/x_{s,f}) + N_{w,b} \ln(x_{w,b}/x_{w,f}) + N_{w,p} \ln(1/x_{w,f})\right) \qquad (9)$$

$$\because N_{s,p} \to 0,\ x_{w,p} \to 1$$

- Condition 3. C1 + C2 (R = 0+ and X_p = 0 ppm)

$$W_{\min} \cong R_u T_0 N_{w,p} \ln(1/x_{w,f}) \qquad (10)$$

- Condition 4. C1 + C2 and sufficiently low feed water salinity (small enough X_f)

$$W_{\min} \cong R_u T_0 N_{w,p} x_{s,f} \qquad (11)$$

$$\because x_{w,f} \to 1 \text{ leads to } \ln(1/x_{w,f}) = -\ln x_{w,f} \cong 1 - x_{w,f} = x_{s,f}$$

It is noted that Eq. (10) is identical to the equation in Elimelech and Phillip [10], while Eq. (11) is identical to the equation in Spiegler and El-Sayed [9].

3.2. Minimum separation work by osmotic pressure theory – principle of membrane desalination

When pure liquid water is separated from an aqueous solution by a wall which is permeable to water and impermeable to the solute in the solution, it is known that water will pass from the pure water side to the solution side, and there is an equilibrium state when the pressure π (osmotic pressure) is exerted on the wall from the solution side [12]. The schematic diagram of osmotic pressure is given in Fig. 3.

Because the osmotic pressure of a solution is defined as the applied pressure to maintain the solution in equilibrium with pure solvent (net flux = 0 through the semi-permeable membrane), the minimum separation work for an infinitesimal recovery (R = 0+) can be calculated by multiplying the osmotic pressure by a unit volumetric flow of the product water. Though there are various methods for the calculation of osmotic pressure since van't Hoff [12], including [13], two representative methods are used in this paper.

The first method starts from the chemical potential equilibrium at a semi-permeable membrane. At an equilibrium state, the chemical potential μ of the water must be the same on the both sides of the semi-permeable membrane [14].

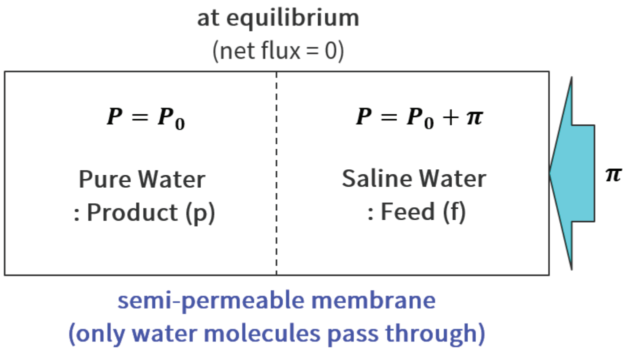

Fig. 3. Schematic diagram of osmotic pressure.

$$\mu_w(P_0) = \mu_w(P_0 + \pi)\big|_{\text{solution}} \qquad (12)$$

For the chemical potential at the solution side (RHS), Eq. (A22) in Appendix A is applicable by assuming the solution as ideal.

$$\mu_w(P_0 + \pi)\big|_{\text{solution}} = \mu_w(P_0 + \pi) + R_u T_0 \ln x_{w,f} \qquad (13)$$

The change in the chemical potential with pressure may be included.

$$\mu_w(P_0 + \pi) = \mu_w(P_0) + \int_{P_0}^{P_0+\pi} V_m dP = \mu_w(P_0) + V_m \pi \qquad (14)$$

where $V_m = V/N$ is the molar volume of water, which is assumed constant during the integration for the pressure change.

From Eqs. (12)–(14):

$$\pi = -\frac{R_u T_0}{V_m\big|_{w,p}} \ln x_{w,f} = -\frac{N_{w,p} R_u T_0}{V_{w,p}} \ln x_{w,f} \qquad (15)$$

and thus:

$$W_{\min} = \pi V_p \cong \pi V_{w,p} = -R_u T_0 N_{w,p} \ln x_{w,f} \qquad (16)$$

Eq. (16) is identical to Eq. (10), which is obtained for R = 0+ and X_p = 0 ppm from the second law of thermodynamics.

The second method is to use the van't Hoff equation for estimating an osmotic pressure. It is well known that the van't Hoff equation is obtained from the analogy between solutions and gases, and is valid only for sufficiently diluted solutions.

$$\pi = \frac{N_{s,f}}{V} R_u T_0 \qquad (17)$$

$$W_{\min} = R_u T_0 N_{s,f} \qquad (18)$$

It should be noted that Eq. (18) is different to Eq. (11), even though the same limiting conditions of R = 0+, X_p = 0 ppm and $x_{w,f} \to 1$ are assumed. Actually, as $x_{w,f} \to 1$:

$$\frac{\text{Eq. (18)}}{\text{Eq. (11)}} = \frac{N_{w,f} + N_{s,f}}{N_{w,p}} \cong 1 \qquad (19)$$

$$\frac{\text{Eq. (11)}}{\text{Eq. (10)} = \text{Eq. (16)}} = \frac{x_{s,f}}{-\ln\left(1 - x_{s,f}\right)} \cong 1 \qquad (20)$$

$$\frac{\text{Eq. (18)}}{\text{Eq. (10)} = \text{Eq. (16)}} = \frac{N_{s,f}}{N_{w,p} \ln(1/x_{w,f})} \cong 1 \qquad (21)$$

Therefore, both Eqs. (11) and (18) are valid for the sufficiently low feed water salinity with R = 0+ and X_p = 0 ppm. However, it is very important to note that Eq. (20) becomes

0.9901 and Eq. (21) becomes 0.9757 when the feed water is a 35,000 ppm NaCl solution, and the numbers become 0.9881 and 0.9706, respectively, for a 42,000 ppm NaCl solution. This shows that Eq. (18) loses its accuracy more rapidly than Eq. (11) when the feed salinity increases, and the quantitative error could be in the range of 1.0%–1.2% for Eq. (11) while the error could be 2.4%–2.9% for Eq. (18) when the equations are applied for the typical seawater salinity.

Though Eqs. (16) and (18) are derived for a pure water production (X_p = 0 ppm), it is not difficult to apply these equations for a finite salinity product water as follows:

$$W_{\min} = (\pi_f - \pi_p) \times V \tag{22}$$

$$W_{\min} = R_u T_0 N_{w,p} \ln(x_{w,p} / x_{w,f}) \text{ from Eq. (16)} \tag{23}$$

$$W_{\min} = R_u T_0 (N_{s,f} - N_{s,p}) \text{ from Eq. (18)} \tag{24}$$

Note that Eq. (23) does not have the full information of Eq. (8), though Eq. (16) was identical to Eq. (10) from the second law of thermodynamics. Eq. (24) could be rewritten as $W_{\min} = R_u T_0 N_{s,b}$, but this expression will not be used here to avoid any misunderstanding of the relation between $W_{\min}$ and $N_{s,b}$, that is, $W_{\min}$ should be understood from the feed and permeate conditions, not from the brine reject/blowdown condition.

Now, the only assumption for Eqs. (23) and (24) is the infinitesimal recovery (R = 0+). In order to obtain the generalized equations for an arbitrary recovery, Eq. (24) will be examined first, which can be rewritten as follows using $N_s = (1 + \alpha)X/M_s$:

$$W_{\min} = R_u T_0 \left(1 + \alpha\right) / M_s \times (X_f - X_p) = k_1 (X_f - X_p) \tag{25}$$

where $k_1 = R_u T_0 (1 + \alpha)/M_s$ = const.

For a finite recovery case, the feed water salinity varies from X_f to X_p while the permeate salinity could be assumed the same (X_p = const). For the averaging purpose of the minimum work from the feed water side to the brine reject/blowdown side, an integration path z should be taken along the same infinitesimal product amount, and the minimum work at z is:

$$W_{\min}(\mathrm{z}) = k_1 (X(z) - X_p) \tag{26}$$

where z is from the point A where $X(A) = X_f$ to the point B where $X(B) = X_b$.

Now, the following equation is valid through the same product amount path z:

$$\frac{d(\mathrm{X(z)} - \mathrm{X}_p)}{\mathrm{dz}} = k_2 (\mathrm{X(z)} - \mathrm{X}_p) \tag{27}$$

where k_2 is another constant.

Then, the average minimum work from A to B is:

$$\begin{aligned} W_{\min,\text{avg}} &= k_1 \frac{\int_A^B \left(X(z) - X_p\right) dz}{\int_A^B dz} \\ &= k_1 \frac{\int_{X(A)-\mathrm{X}_p}^{X(B)-\mathrm{X}_p} 1/\mathrm{k}_2 \, d(X(z) - \mathrm{X}_p)}{\int_{X(A)-\mathrm{X}_p}^{X(B)-\mathrm{X}_p} 1/\{k_2(X(\mathrm{z}) - \mathrm{X}_p)\} d(X(z) - X_p)} \\ &= k_1 \frac{(X(B) - X_p) - (X(A) - X_p)}{\ln(X(B) - X_p) - \ln(X(B) - X_p)} \\ &= R_u T_0 \frac{N_{s,b} - N_{s,f}}{\ln\{(N_{s,b} - N_{s,p}) / (N_{s,f} - \mathrm{N}_{s,p})\}} \\ &\equiv R_u T_0 \left(\mathrm{N}_{s,f\,\mathrm{to}\,b} - \mathrm{N}_{s,p}\right)_{\text{log mean}} \end{aligned} \tag{28}$$

Alternatively, the average minimum work could be obtained by calculating $W_{\text{min, avg}}|_{f\text{ to }b}$ at the feed water to the brine reject side while assuming the pure water production and calculating $W_{\text{min, avg}}|_p$ at the product water side with its finite salinity while assuming the pure water production, and then by observing the difference of $W_{\text{min, avg}}|_{f\text{ to }b}$ and $W_{\text{min, avg}}|_p$.

$$W_{\min,\text{avg}} \cong R_u T_0 \left(\mathrm{N}_{s,f\,\mathrm{to}\,b}\Big|_{\text{log mean}} - \mathrm{N}_{s,p}\right) \tag{29}$$

Eq. (29) cannot be obtained from Eq. (28), while the difference between the two equations is not significant when the product water salinity is sufficiently low. The approach deriving Eqs. (28) and (29) inspires the following hypothesis:

Hypothesis A. If an equation $f_{R=0+,X_p=0}(X_f, T_0)$ for calculating theoretical minimum work at R = 0+ and X_p = 0 ppm shows a linear behavior on the salinity of feed water X_f for the interested regime, a generalized equation can be approximately obtained for an arbitrary recovery and product water quality by using the logarithmic average of salinity difference or salinity as follows:

$$\begin{aligned} f_{R,Xp}(X_f, X_b, X_p, T_0) &\cong f_{R=0+,X_p=0} \\ &\quad (\text{log mean}(X_f - X_p, X_b - X_p), T_0) \\ &\cong f_{R=0+,X_p}(X_f, X_p, T_0)/(X_f - X_p) \times \\ &\qquad \text{log mean}(X_f - X_p, X_b - X_p) \end{aligned} \tag{30a}$$

or

$$\begin{aligned} f_{R,Xp}(X_f, X_b, X_p, T_0) &\cong f_{R=0+,X_p=0}(\text{log mean}(X_f, X_b), T_0) \\ &\qquad - f_{R=0+,X_p=0}(X_p, T_0) \end{aligned} \tag{30b}$$

Eq. (30) is quite useful, because there are many cases where $f_{R=0+,X_p=0}(X_f, T_0)$ is difficult to integrate analytically to obtain $f_{R,Xp}(X_f, X_b, X_p, T_0)$. For example, Eq. (16) or Eq. (23) from the chemical potential equilibrium is difficult to derive a generalized minimum energy equation for an arbitrary recovery (and product water quality), while it is easier to show the linearity of Eq. (16) on the feed water salinity numerically as in Fig. 4.

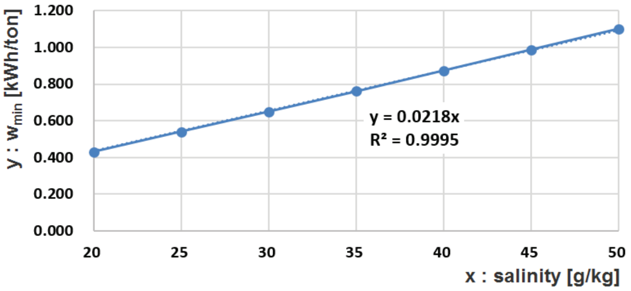

Fig. 4. $w_{\min}$ (kWh/ton) by osmotic pressure theory (chemical potential equilibrium) on salinity (g/kg) at 25°C.

Note that Fig. 4 is prepared by assuming the seawater as a NaCl solution with the dissociation constant of 1.8, while more precise calculation is possible if other dissolved solids are considered with proper dissociation constants.

Now, as per Hypothesis A, the generalized equation for an arbitrary recovery and product water salinity from chemical potential equilibrium is easily obtained from Eq. (16):

$$W_{\min,\text{avg}} \cong R_u T_0 N_{w,p} \ln\left(x_{w,p} / x_{w,f\,\text{to}\,b}\Big|_{\text{log mean}} \right) \tag{31}$$

3.3. *Minimum separation work by vapor compression theory – principle of thermal desalination*

Theoretical minimum energy for desalination can be explained by the vapor compression theory, which is the principal of thermal desalination. First, two vessels can be assumed, one vessel is with pure product water and the other with feed saline water. There are no gases inside the vessels other than a steam vapor. Assuming thermal equilibrium between two vessels, which means the two vessels are connected through an infinitely large and thin heat transfer area, the pressure at the vessel of feed saline water is lower than the other vessel due to the BPE caused from the salinity. Therefore, if there is a vapor passage from the saline water vessel at a lower pressure to the pure water vessel at a higher pressure, with a suitable compressor to increase the vapor pressure, the desalination process could be maintained. Fig. 5 describes the schematic diagram of desalination by vapor compression.

Though Fig. 5 is the process of the single Effect(Stage) MVC (mechanical vapor compression) desalination, it is generally understood that the schematic diagram explains the key principle of thermal desalination. It is noted that the steam vapor inside the saline water vessel is at a superheated condition, because the temperature is the same to that of the product water vessel due to thermal equilibrium. Now, the minimum work for this process will be the required work for compressing vapor from $P_{v1} = P_{\text{sat}}(T_0 - BPE)$ to $P_{v2} = P_{\text{sat}}(T_0)$ through the isentropic (thus reversible) manner. In order to understand this cycle, a temperature–entropy diagram is provided in Fig. 6.

For a finite ΔT, the required work for this cycle is the blue pentagonal area of ⓐ-ⓑ-ⓒ-ⓓ-ⓔ-ⓐ. For an infinitesimal ΔT, the required work becomes much smaller, the red shaded triangular area of ⓖ-ⓑ-ⓕ-ⓖ, which will be the theoretical minimum work. In reality, the theoretical minimum work for thermal desalination would be obtained when $\Delta T = q/(U\,A) \to 0+$, therefore, an infinitely large heat transfer area A or an infinitely large overall heat transfer coefficient U is required for a finite heat transfer rate q (ultimate heat-transferability). Analogically, the condition for the theoretical minimum work for membrane desalination could be understood as $\Delta P - \Delta\pi = J/L_p \to 0+$, therefore, an infinitely small membrane resistance (or an infinitely large and thin membrane area) is required for a finite permeate flux of water J_w (ultimate membrane water-permeability L_p).

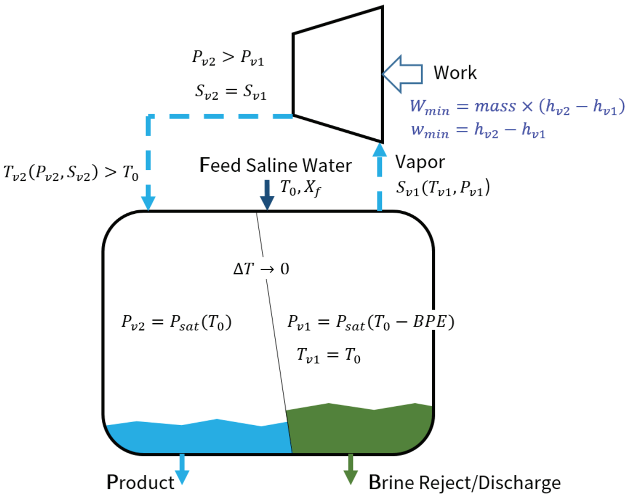

Fig. 5. Schematic diagram of desalination by vapor compression theory [9].

The theoretical minimum work from the vapor compression theory at $R = 0+$ and $X_p = 0$ ppm can be written as a function of X_f and T_0:

$$\begin{aligned} W_{\min} &= \text{mass} \times (h_{v2} - h_{v1}) \\ &= \text{mass} \times (h_{v2}(P_{\text{sat}}(T_0), s_{v2}) - h_{v1}(P_{\text{sat}}(T_0 - \text{BPE}(T_0, X_f)), s_{v1})) \end{aligned} \tag{32}$$

where h is specific enthalpy and s stands for specific entropy which values are:

$$s_{v2} = s_{v1} \tag{32a}$$

$$s_{v1} = s_{v1}(T_0, P_{\text{sat}}(T_0 - \text{BPE}(T_0, X_f))) \tag{32b}$$

In this paper, IAPWS-IF97 (International Association for the Properties of Water and Steam: Industrial Formulation 1997) is used to calculate all thermodynamic properties. As can be seen in Eq. (32), a BPE equation plays a crucial role for calculating the minimum work for desalination from the vapor compression theory. There are many equations for BPE of seawater, which are usually obtained either empirically or theoretically. Two BPE equations are tried in this paper to see the effect from different BPE on $W_{\min}$.

$$\text{BPE}(T, X) = \text{A}X + \text{B}X^2 + CX^3 \tag{33}$$

$$\text{A} = (8.325 \times 10^{-2} + 1.883 \times 10^{-4}\,T + 4.02 \times 10^{-6}\,T^2) \tag{33a}$$

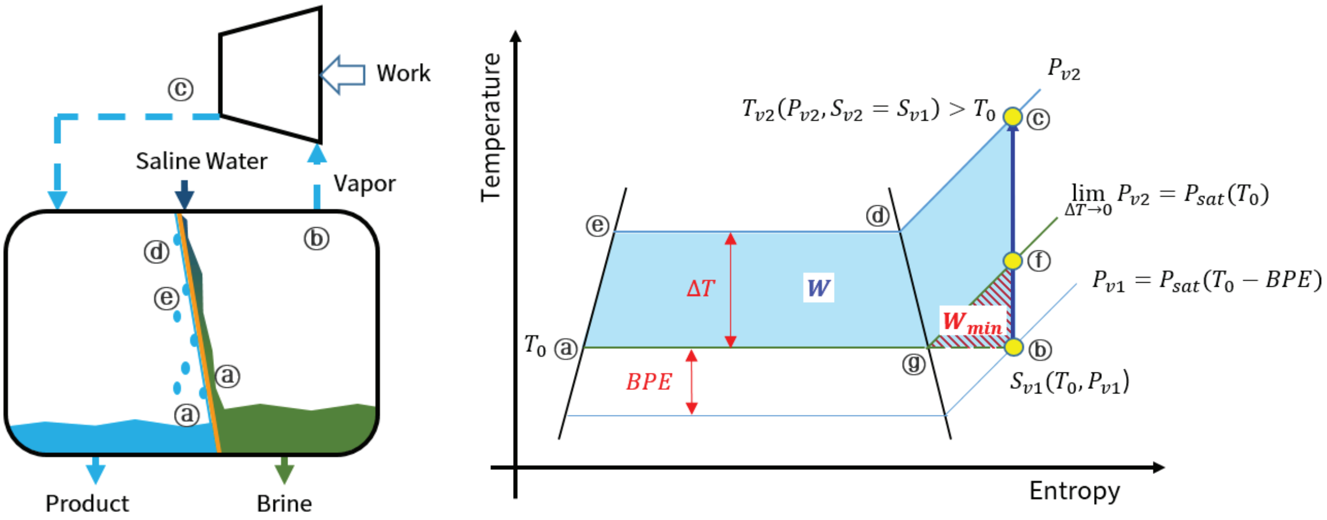

Fig. 6. Temperature–entropy diagram for vapor compression theory. (For a finite ΔT, the required work (W) for this cycle is the blue pentagonal area of ⓐ-ⓑ-ⓒ-ⓓ-ⓔ-ⓐ. For an infinitesimal ΔT, the required work is the red shaded triangular area of ⓖ-ⓑ-ⓕ-ⓖ, which is the theoretical minimum work (W_{min}).)

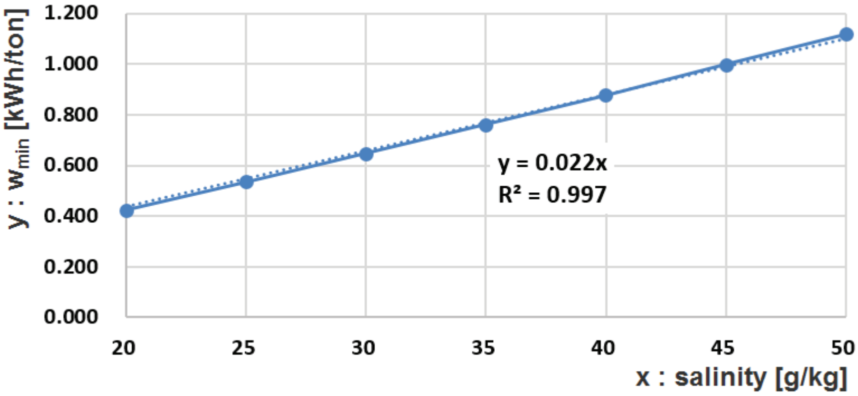

Fig. 7. w_{min} (kWh/ton) by vapor compression theory (BPE①, Eq. (34)) on salinity (g/kg) at 25°C.

$$B = (-7.625 \times 10^{-4} + 9.02 \times 10^{-5} T - 5.2 \times 10^{-7} T^2) \quad (33b)$$

$$C = (1.522 \times 10^{-4} - 3 \times 10^{-6} T - 3 \times 10^{-8} T^2) \quad (33c)$$

In Eq. (33) [15], BPE is in °C or K, and it is known to be valid for $1 \le X \le 16\%$ and $10 \le T \le 180$°C. Another BPE equation [16], simpler than Eq. (33), is as follows:

$$\mathrm{BPE}(T, X) = AX^2 + BX \quad (34)$$

$$A = (-4.584 \times 10^{-4}\ T^2 + 2.823 \times 10^{-1} T + 17.95) \quad (34a)$$

$$B = (1.536 \times 10^{-4} T^2 + 5.267 \times 10^{-2} T + 6.56) \quad (34b)$$

In Eq. (34), BPE is in °C or K again, and the accuracy is known to be within ±0.018 K for the applicable region of $0 \le X \le 0.12$ kg/kg and $0 \le T \le 120$°C. Care should be taken for the fact that the dimension of salinity in Eqs. (33) and (34) are different. It is also noted that the error range of ±0.018 K of Eq. (34) is not small, considering the typical BPE in desalination is in the range of 0°C–1°C.

When a unit mass of product water is considered at $R = 0+$ and $X_p = 0$, the linearity of Eq. (32) on the feed water salinity is numerically analyzed to apply Hypothesis A. Figs. 7 and 8 show the satisfactory results when Eqs. (34) and (35) are applied as a BPE equation, respectively.

It should be noticed that Figs. 4, 7 and 8 show a possible strategy to acquire a new BPE equation by comparing the minimum work calculated by the vapor compression theory with a candidate BPE equation with the minimum work calculated by any other theoretical method.

As per the Hypothesis A, now the generalized equation for an arbitrary recovery and product water salinity from the vapor compression theory is easily obtained:

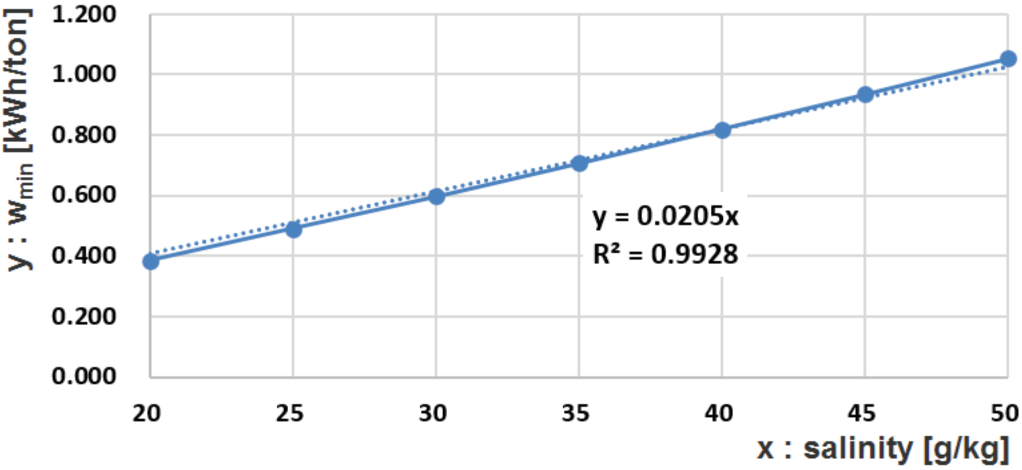

Fig. 8. $w_{\min}$ (kWh/ton) by vapor compression theory (BPE②, Eq. (35)) on salinity (g/kg) at 25°C.

$$\begin{aligned} W_{\min} &= \text{mass} \times \{h_{v2}(P_{\text{sat}}(T_0 - \text{BPE}(T_0, X_p)), s_{v2}) \\ &\quad - h_{v1}(P_{\text{sat}}(T_0 - \text{BPE}(T_0, X_f)), s_{v1})\} \\ &\quad /(X_f - X_p) \times \frac{X_b - X_f}{\ln\{(X_b - X_p)/(X_f - X_p)\}} \\ &= \text{mass} \times (h_{v2} - h_{v1})/(X_f - X_p) \times (X_{f\,\text{to}\,b} - X_p)_{\text{log mean}} \end{aligned} \tag{35}$$

where $s_{v2} = s_{v1} = s_{v1}(T_0, P_{\text{sat}}(T_0 - \text{BPE}(T_0, X_f)))$.

4. Results and discussion

In order to investigate each theoretical method in a quantitative manner, various cases are considered for comparison. Calculation cases for feed water salinities of 10,000, 35,000, 42,000 and 45,000 ppm, temperatures of 25°C, 30°C and 35°C, recoveries of 0+, 40% and 50%, and product water salinities of 0, 300, 1,000 and 3,000 ppm are carefully selected to observe the limits of and the quantitative differences between the equations for theoretical minimum work from different approaches and assumptions. All the calculations are made for producing a unit amount of product water. Some exemplary calculations for each theoretical method are described in Appendix B.

4.1. Minimum work calculation by the second law of thermodynamics

To understand the differences from each limiting assumptions, all the equations from (7) to (11) are considered for the calculation. Seawater is assumed as a NaCl solution with the dissociation constant of 1.8 in this chapter, while more precise calculation would be possible if major dissolved solids of seawater with proper dissociation constants for each component are considered. Table 1 is the summary of the calculation results.

For X_f = 35,000 ppm and X_p = 0 ppm, the theoretical minimum energy to produce a unit product water is calculated as 0.762 kWh/ton for R = 0+ and 1.068 kWh/ton for R = 50%. As Eq. (8) is for the R = 0+ limiting condition, the gap between Eqs. (7) and (8) becomes larger for the higher recovery. Eq. (9) which is valid for X_p = 0 ppm overestimates the minimum work for the higher X_p, because the results are always for X_p = 0 ppm cases while less energy will be required when the product has a certain salinity. Eq. (11) is true only when X_f is sufficiently low, and the quantitative error compared with Eq. (7) for R = 0+ and X_p = 0 ppm is found to be 0.99% for X_f = 35,000 ppm while the error becomes much smaller as 0.28% for X_f = 10,000 ppm, almost proportional to X_f at this range of feed water salinity.

4.2. Minimum work calculation by the osmotic pressure theory

For the same cases, the theoretical minimum energy requirements are calculated using Eqs. (16) and (31) from the osmotic pressure from chemical equilibrium, and using Eq. (18) and Eqs. (28) and (29) from the osmotic pressure from the van't Hoff equation. Again, a NaCl solution is assumed with the dissociation constant of 1.8. Results are summarized in Table 2.

Note that Eqs. (16) and (18) are valid only for R = 0+, X_p = 0 ppm, while Eq. (31) and Eqs. (28) and (29) are valid for other cases but not applicable for R = 0+, X_p = 0 ppm. At R = 0+, X_p = 0 ppm, Eq. (16) from the chemical equilibrium shows exactly the same calculation results to those from the second law of thermodynamics, 0.762 kWh/ton for 35,000 ppm and 0.214 kWh/ton for 10,000 ppm. This is logical because Eq. (16) becomes identical to Eq. (10) at this limiting condition. Instead, Eq. (18) from the van't Hoff equation results in 0.742 kWh/ton for 35,000 ppm and 0.212 kWh/ton for 10,000 ppm at R = 0+, X_p = 0 ppm. For other cases, the results from osmotic theory usually show higher values than the results from the second law of thermodynamics, and the results from chemical equilibrium are a bit larger than the results using van't Hoff. The difference between the results from Eq. (28) and the results from Eq. (29) shows that the difference between Eqs. (30a) and (30b) in the Hypothesis A is only 0%–0.25% for the studied cases.

4.3. Minimum work calculation by the vapor compression theory

Finally, the theoretical minimum works are calculated using Eq. (35) with BPE① (Eq. (33)) or BPE② (Eq. (34)), and

Table 1
Theoretical minimum energy requirement (kWh/ton) for desalination by the second law of thermodynamics

Feed	25°C, 35,000 ppm					25°C, 10,000 ppm		42,000 ppm			45,000 ppm
								25°C	30°C	35°C	35°C
Recovery	0+	50%	0+	50%	50%	0+	50%	40%	40%	40%	40%
Product	0 ppm	0 ppm	300 ppm	300 ppm	3,000 ppm	0 ppm	300 ppm	1,000 ppm			0 ppm
Eq. (7)	**0.762**	**1.068**	**0.725**	**1.026**	**0.799**	**0.214**	**0.264**	**0.986**	**1.003**	**1.020**	**1.217**
Eq. (8)	**0.762**	0.762	**0.725**	0.725	0.539	**0.214**	0.185	0.817	0.831	0.844	1.020
Eq. (9)	**0.762**	**1.068**	0.755	1.057	1.020	**0.214**	0.286	1.066	1.106	1.124	**1.217**
Eq. (10)	**0.762**	0.762	0.761	0.761	0.759	**0.214**	0.214	0.918	0.933	0.949	1.020
Eq. (11) (% to Eq. (7))	0.754 (99.01%)	0.754	0.754	0.754	0.752	0.213 (99.72%)	0.213	0.907	0.922	0.937	1.007

Note: Eq. (7) for all general cases, Eq. (8) for R = 0+, Eq. (9) for X_p = 0 ppm, Eq. (10) for R = 0+ and X_p = 0 ppm and Eq. (11) for R = 0+, X_p = 0 ppm and small enough X_f limiting conditions. The bold values stand for the results from valid cases of each corresponding equation.

Table 2
Theoretical minimum energy requirement (kWh/ton) for desalination by osmotic pressure theory

Feed	25°C, 35,000 ppm					25°C, 10,000 ppm		42,000 ppm			45,000 ppm
								25°C	30°C	35°C	35°C
Recovery	0+	50%	0+	50%	50%	0+	50%	40%	40%	40%	40%
Product	0 ppm	0 ppm	300 ppm	300 ppm	3,000 ppm	0 ppm	300 ppm	1,000 ppm			0 ppm
Eq. (7)	**0.762**	**1.068**	**0.725**	**1.026**	**0.799**	**0.214**	**0.264**	**0.986**	**1.003**	**1.020**	**1.217**
Eq. (16)	**0.762**	0.762	0.755	0.755	0.696	**0.214**	0.207	0.897	0.912	0.927	1.020
Eq. (31)	N/A	**1.162**	N/A	**1.152**	**1.060**	N/A	**0.312**	**1.211**	**1.231**	**1.251**	**1.379**
Eq. (18)	**0.742**	0.742	**0.736**	0.736	0.679	**0.212**	0.206	0.870	0.884	0.899	0.986
Eq. (28)	N/A	**1.0710**	N/A	**1.0618**	**0.9792**	N/A	**0.2968**	**1.1349**	**1.1539**	**1.1729**	**1.2874**
Eq. (29)	N/A	**1.0710**	N/A	**1.0620**	**0.9816**	N/A	**0.2971**	**1.1353**	**1.1544**	**1.1734**	**1.2874**
(% to Eq. (28))		(100.00%)		(100.02%)	(100.25%)		(100.09%)	(100.04%)	(100.04%)	(100.04%)	(100.00%)

Note: From chemical equilibrium, Eq. (16) for R = 0+, X_p = 0 ppm and Eq. (31) for other general cases. From van't Hoff, Eq. (18) for R = 0+, X_p = 0 ppm, Eqs. (28) and (29) for other general cases. Eq. (7) from the second law of thermodynamics is included for comparison purpose. The bold values stand for the results from valid cases of each corresponding equation.

the results are compared in Table 3 with other results from the second law of thermodynamics and the osmotic theory.

It is obvious that the results from the vapor compression theory are highly dependent on the applied BPE equation. For 25°C and 35,000 ppm feed water, Eq. (35) with BPE① results in 0.761 kWh/ton at R = 0+, X_p = 0 ppm, which is surprisingly similar to the results from Eqs. (7) and (16), while Eq. (35) with BPE② results in 0.706 kWh/ton. However, for the same feed water temperature and salinity, Eq. (35) with BPE① results in 1.090 kWh/ton at R = 50%, X_p = 300 ppm, while Eq. (35) with BPE② results in 1.010 kWh/ton. In this case, the result from Eq. (35) with BPE① is closer to the result from Eq. (31), while the result from Eq. (35) with BPE② is closer to the result from Eq. (7). In general, the calculation results from the vapor compression theory are mostly in the similar range to the calculation results from the second law of thermodynamics and the osmotic theory. Therefore, it is believed that the theoretical minimum energy requirement is not a function of the method of desalination, that is, the same minimum energy would be required for membrane, thermal and any other desalination methods.

All values are compared with the each corresponding result from the second law of thermodynamics for quantitative comparison. From all the data in Table 3, the standard deviation is 9.68%. If the interested regime is limited to the 25°C and 35,000 ppm feed water, excluding the case of X_p = 3,000 ppm, the standard deviation is calculated as 4.51%. If the results from Eq. (7), Eqs. (18) and (28) and Eq. (35) with BPE① are selected for the 25°C and 35,000 ppm feed water, excluding the case of X_p = 3,000 ppm, the standard deviation becomes 2.40%.

5. Conclusion

The methods for calculating the theoretical minimum energy required for desalting seawater have been compared.

Table 3
Comparison of theoretical minimum energy requirement (kWh/ton) for desalination

Feed	25°C, 35,000 ppm					25°C, 10,000 ppm		42,000 ppm			45,000 ppm
								25°C	30°C	35°C	35°C
Recovery	0+	50%	0+	50%	50%	0+	50%	40%	40%	40%	40%
Product	0 ppm	0 ppm	300 ppm	300 ppm	3,000 ppm	0 ppm	300 ppm	1,000 ppm			0 ppm
Eq. (7)	**0.762**	**1.068**	**0.725**	**1.026**	**0.799**	**0.214**	**0.264**	**0.986**	**1.003**	**1.020**	**1.217**
Eqs. (16) and (31)	**0.762**	**1.162**	**0.755**	**1.152**	**1.060**	**0.214**	**0.312**	**1.211**	**1.231**	**1.251**	**1.379**
(% to Eq. (7))	(100.00%)	(108.79%)	(104.19%)	(112.21%)	(132.65%)	(100.00%)	(118.32%)	(122.72%)	(122.72%)	(122.72%)	(113.27%)
Eqs. (18) and (28)	**0.742**	**1.071**	**0.736**	**1.062**	**0.979**	**0.212**	**0.297**	**1.135**	**1.154**	**1.173**	**1.287**
(% to Eq. (7))	(94.74%)	(100.26%)	(101.56%)	(103.44%)	(122.53%)	(99.28%)	(112.47%)	(115.04%)	(115.04%)	(115.04%)	(105.78%)
Eq. (35) w/BPE①	**0.761**	**1.098**	**0.755**	**1.090**	**1.009**	**0.209**	**0.292**	**1.181**	**1.191**	**1.201**	**1.324**
(% to Eq. (7))	(99.97%)	(102.84%)	(104.22%)	(106.14%)	(126.22%)	(97.74%)	(110.77%)	(119.67%)	(118.72%)	(117.80%)	(108.75%)
Eq. (35) w/BPE②	**0.706**	**1.019**	**0.701**	**1.011**	**0.939**	**0.187**	**0.262**	**1.105**	**1.124**	**1.144**	**1.263**
(% to Eq. (7))	(92.72%)	(95.37%)	(96.69%)	(98.48%)	(117.53%)	(87.61%)	(99.34%)	(111.97%)	(112.09%)	(112.18%)	(103.76%)

Note: Eq. (7) from the second law of thermodynamics, Eqs. (16) and (31) from the osmotic pressure theory with chemical equilibrium, Eqs. (18) and (28) from the osmotic pressure theory with the van't Hoff equation, Eq. (35) from the vapor compression theory with BPE① (Eq. (33)) or BPE② (Eq. (34)). The bold values stand for the results from valid cases of each corresponding equation.

For the same feed water, recovery and product water conditions, the required work would be believed the same in nature, while the calculation results could be different depending on which theoretical approach is taken with certain assumptions. The second law of thermodynamics, the osmotic theory and the vapor compression theory are studied and the equations for general and some limiting conditions are introduced. The calculation results for 25°C–35°C, 10,000–45,000 ppm feed water salinity with 0%–50% recovery and 0–3,000 ppm product water salinity have shown the followings:

- The equation based on a certain limiting condition, such as $R = 0+$ and/or $X_p = 0$ ppm, could keep its accuracy at its limiting condition(s) only.
- A generalized equation for an arbitrary recovery and product water salinity could be obtained from the equation at $R = 0+$ and $X_p = 0$ ppm, if the linearity of the equation is valid for the interested regime.
- Theoretical minimum energy for desalting 25°C and 35,000 ppm feed saline water is calculated as 0.762, 0.742 and 0.761 kWh/ton for $R = 0+$ and $X_p = 0$ ppm, and is calculated as 1.026, 1.062 and 1.090 kWh/ton for $R = 50\%$ and $X_p = 300$ ppm, by the second law of thermodynamics, the osmotic theory with the van't Hoff equation and the vapor compression theory with BPE①, respectively.
- The calculation of the theoretical minimum work could have 5%–10% difference depending on which theoretical approach is applied.

Overall, the theoretical minimum energy requirements from the three different approaches has been successfully evaluated and compared in a quantitative manner. From the fact that the osmotic theory, which is the principle of membrane desalination, and the vapor compression theory, which is the principle of thermal desalination, show the similar minimum energy, it is believed that the theoretical minimum energy for desalination is not a function of the method of desalination, that is, the same minimum energy would be required for any desalination methods when the same conditions are given. Additionally, the possibility of deriving a new BPE equation is found by comparing the minimum work calculation results, one by the vapor compression theory with an assumed BPE equation, the other by any other theoretical method or equation.

Acknowledgment

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Symbols

A	—	Heat transfer area, m^2
G	—	Gibbs free energy, kJ, $G = H - T\,S$
H	—	Enthalpy, kJ
J_w	—	Permeate flux of water, m/s
L_p	—	Membrane water-permeability, m/s/Pa
h	—	Specific enthalpy, kJ/kg
m	—	Molality, mol/kg
N	—	Number of moles, mol

P — Pressure, Pa
q — Heat transfer rate, W
R — Recovery, %, R = product flow/feed flow
R_u — Universal gas constant = 8.31446, J/mol/K
S — Entropy, kJ/K
s — Specific entropy, kJ/kgK
T — Temperature, K or °C
U — Overall heat transfer coefficient, W/m^2/K
V — Volume, m^3
X — Salinity, kg/kg, %, ppm
x_i — Mole fraction of the i-th component, $x_i = \dfrac{N_i}{\sum_j N_j}$
W — Work, kJ, kWh, or W [J] = P [N/m^2] × V [m^3]
w — Specific work, kJ/kg or kWh/ton
α — Degree of dissociation
$(1 + \alpha)$ — Dissociation constant
μ_i — Chemical potential of the i-th component, kJ/mol, $\mu_i = \left(\dfrac{\partial G}{\partial N_i}\right)_{P,T,N_j} = \bar{g}_i = \bar{h}_i - T\,\bar{s}_i$
π — Osmotic pressure, Pa

Subscripts

0 — Reference state
b — Brine reject (blowdown, discharge)
f — Feed saline water
p — Product (less saline water)
s — Salt
sat — At saturated
v — (water) vapor
w — (liquid) water

Appendix A. Minimum separation energy from the second law of thermodynamics

A.1 and A.2 are the rearrangement of the work of Cerci et al. [7] to derive the entropy of mixing of an ideal solution.

A.1. Gibbs energy of a mixture

Gibbs (free) energy is used to determine the spontaneity of a process that occurs at constant temperature and pressure. It is defined as follows:

$$\mathrm{G} = \mathrm{H} - \mathrm{T\,S}, \tag{A1}$$

where H is enthalpy, $H = U + PV$, U is internal energy, P is pressure and V is volume. For a process of $\Delta G < 0$, the process is spontaneous (the process occurs without external help).

For a pure substance:

$$\mathrm{dH} = V\,dP + T\,dS \tag{A2}$$

$$\mathrm{dG} = \mathrm{dH} - \mathrm{T\,dS} - \mathrm{S\,dT} = V\,dP - S\,dT \tag{A3}$$

For a mixture, however, G should be a function of substances as well, so:

$$G = G(P,T,N_1,\ldots,N_i,\ldots) \tag{A4}$$

and from the chain rule:

$$\mathrm{dG} = \left(\frac{\partial G}{\partial P}\right)_{T,N} dP + \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \sum_i \left(\frac{\partial G}{\partial N_i}\right)_{P,T,N_j} dN_i \tag{A5}$$

Comparing Eqs. (A3) and (A5) leads to:

$$\mathrm{dG} = V\,dP - S\,dT + \sum_i \mu_i dN_i \tag{A6}$$

where

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{P,T,N_j} = \bar{g}_i = \bar{h}_i - T\,\bar{s}_i \tag{A7}$$

In Appendix A, small letters are for the properties per mol, and overbar stands for a partial molar property in a mixture. In Eq. (A7), μ_i is chemical potential, which stands for the change of a Gibbs energy when 1 mol of the i-th substance is added. (For a pure substance, it is identical to the specific Gibbs energy: $\mu = g = h - T\,s$. Because the volume of individual substance is not conserved during mixing, the property of individual substance in a mixture is denoted with overbar.)

A.2. Ideal solution (ideal mixture)

If inter-molecular forces between difference substances can be neglected, a mixture is called an "ideal solution" or "ideal mixture". Many liquid mixtures can be assumed as an ideal solution, which assumption simplifies the equations for thermodynamic properties.

For any function $z = z(x,y)$, the following exactness test should be valid if the differential equation $\mathrm{d}z = M\mathrm{d}x + N\mathrm{d}y$ is perfect.

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \tag{A8}$$

where $M = \partial z/\partial x$ and $N = \partial z/\partial y$.

Material property is a state function, thus its differential equation should be perfect. Therefore, the differential equation of the Gibbs function, Eq. (A5) should be valid for the exactness test.

For constant P and N_j, Eq. (A5) is:

$$\mathrm{dG} = -S\,dT + \mu_i dN_i \tag{A9}$$

and for constant T and N_j, Eq. (A5) becomes:

$$\mathrm{dG} = V\,dP + \mu_i dN_i \tag{A10}$$

Exactness test for Eqs. (A9) and (A10) leads to:

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{N_i,P,N_j} = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} = -\left(\frac{\partial S}{\partial N_i}\right)_{T,P,N_j} \equiv -\bar{s}_i \tag{A11}$$

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{N_i,T,N_j} = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \left(\frac{\partial V}{\partial N_i}\right)_{P,T,N_j} \equiv \bar{v}_i \tag{A12}$$

From $\mu_i = \mu_i(P, T, x_1, \ldots, x_k)$:

$$d\mu_i = d\bar{g}_i = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,x_i} dP + \left(\frac{\partial \mu_i}{\partial T}\right)_{P,x_i} dT + \sum_i \left(\frac{\partial \mu_i}{\partial x_i}\right)_{P,T,x_i} dx_i \tag{A13}$$

Applying Eq. (A13) to Eqs. (A11) and (A12), the following equation is obtained:

$$d\mu_i = \bar{v}_i\, dP - \bar{s}_i\, dT + \sum_i \left(\frac{\partial \mu_i}{\partial x_i}\right)_{P,T,x_i} dx_i \tag{A14}$$

For an ideal mixture, the heat of mixing and the volume change due to mixing are zero [17]. Thus:

$$\Delta V_{\text{mixing, ideal}} = \sum_i N_i\left(\bar{v}_i - v_i\right) = 0 \tag{A15}$$

$$\Delta H_{\text{mixing, ideal}} = \sum_i N_i(\bar{h}_i - h_i) = 0 \tag{A16}$$

Eqs. (A15) and (A16) are identical equations, so $\bar{v}_i = v_i$ and $\bar{h}_i = h_i$.

Eq. (A14) is further simplified for constant T and N_j (assumption of Eq. (A10)) as:

$$d\mu_i = \bar{v}_i\, dP \tag{A17}$$

As the ideal gas equation of state (EOS) is valid for the individual substances in an ideal solution:

$$\bar{v}_i = R_u T/P \tag{A18}$$

Applying the Dalton's law of partial pressure and assuming no change in x_i leads to:

$$d\ln P_i = d\ln(x_i P) = d(\ln x_i + \ln P) = d\ln P \tag{A19}$$

Therefore, Eq. (A17) becomes:

$$d\mu_i = \bar{v}_i\, dP = \frac{R_u T}{P}\mathrm{dP} = R_u T\, d\ln P = R_u T\, d\ln P_i \tag{A20}$$

Integrating left hand-side (LHS) and right hand-side (RHS) of Eq. (A20) from P to P_i gives:

$$\text{LHS} = \int_P^{P_i} d\mu_i = \mu_i\left(T, P_i\right) - \mu_i\left(T, P\right) \tag{A21a}$$

$$\text{RHS} = \int_P^{P_i} R_u T\, d\ln P_i = R_u T(\ln P_i - \ln P) = R_u T \ln x_i \tag{A21b}$$

So, the chemical potential change during mixing can be obtained as:

$$\mu_i(T, P_i) = \mu_i(T, P) - R_u T \ln x_i \tag{A22}$$

Eq. (A22) shows the fact that the chemical potential of the i-th substance in a mixture, $\mu_i(T,P_i)$, is smaller than the chemical potential of a pure material, $\mu_i(T,P)$, by the amount of $R_u T \ln x_i$ (<0 for $0 < x_i < 1$).

In order to use the relation of Eq. (A11), the partial derivative of Eq. (A22) to temperature provides:

$$\text{LHS} = \left(\frac{\partial \mu_i(T, P_i)}{\partial T}\right)_{P,x} = -\bar{s}_i(T, P_i) \text{ and} \tag{A23a}$$

$$\text{RHS} = \left(\frac{\partial \mu_i(T, P)}{\partial T}\right)_{P,x} + R_u \ln x_i = -s_i(T, P) + R_u \ln x_i. \tag{A23b}$$

So, in terms of entropy:

$$\bar{s}_i(T, P_i) = s_i(T, P) - R_u \ln x_i, \tag{A24}$$

which shows the entropy of the i-th substance in a mixture ($0 < x_i < 1$) is greater than the entropy of its pure material.

Then, the entropy of mixing of an ideal solution is:

$$\Delta S_{\text{mixing, ideal}} = \sum_i N_i(\bar{s}_i - s_i) = -R_u \sum_i N_i \ln x_i \tag{A25}$$

A.3. Note on ideal solution (ideal mixture) assumption

The derivation in A.2 seems to be valid if liquid water could be assumed to follow the ideal gas law as well. However, this is usually not true considering a typical EOS for liquid water. For example, the cubic EOS for liquid water is given as:

$$(P + A)(v - b) = R_u T \tag{A26}$$

where A is an attraction parameter and b is an effective molecular volume.

Eq. (A26) becomes the van der Waals' EOS if $A = a/v^2$ and the Peng–Robinson EOS if $A = a\alpha(T)/(v^2 + 2bv - b^2)$ [18]. Usually A is in the order of 1.3×10^9 Pa [19], thus it cannot be ignored for the typical pressure regime of interest. Therefore, it seems it is difficult to apply the ideal gas law (including Dalton's law of partial pressure) on liquid water, while calculation results from the equations driven under ideal solution assumption for many aqueous solutions show this assumption is valid.

Appendix B. Exemplary calculations of minimum work for desalination

Though the equations for theoretical minimum work are derived for a certain amount of product water, calculations have been made for a unit water production. Therefore, molality m (mol/kg) is used instead of the number of moles N (mol) to have the results in kWh/ton instead of kWh or kJ. The calculation details are shown for the case of 25°C and 35,000 ppm feed water with 50% recovery and 300 ppm product water.

B.1. The second law of thermodynamics

Eq. (7) can be rewritten as follows:

$$\begin{aligned} w_{\min} = R_u T_0 (& m_{s,b} \ln(x_{s,b} / x_{s,f}) + m_{s,p} \ln(x_{s,p} / x_{s,f}) \\ & + m_{w,b} \ln(x_{w,b} / x_{w,f}) + m_{w,p} \ln(x_{w,p} / x_{w,f})) \end{aligned} \quad \text{(B1)}$$

For a 35,000 ppm NaCl solution with the dissociation constant of 1.8:

$$m_{s,f} = 1.8 \times 35[\text{g / kg}] / 58.44[\text{g / mol}] = 1.078[\text{mol / kg}],$$
$$m_{w,f} = (1000 - 35)[\text{g / kg}] / 18.02[\text{g / mol}] = 53.552[\text{mol / kg}],$$
$$x_{s,f} = m_{s,f} / (m_{s,f} + m_{w,f}) = 0.0197 \text{ and}$$
$$x_{w,f} = m_{w,f} / (m_{s,f} + m_{w,f}) = 1 - x_{s,f} = 0.9803$$

In the same way, at the product water side of 300 ppm, $m_{s,p}$ = 0.00924 mol/kg, $m_{w,p}$ = 55.477 mol/kg, $x_{s,p}$ = 0.0001665 and $x_{w,p}$ = 0.9998335, and at the brine reject side of 69,700 ppm, $m_{s,b}$ = 2.147 mol/kg, $m_{w,b}$ = 51.626 mol/kg, $x_{s,b}$ = 0.0399 and $x_{w,b}$ = 0.9601. Thus, Eq. (B1) is calculated as follows:

$$\begin{aligned} w_{\min} &= 8.3144621\left[\frac{J}{\text{mol} \cdot K}\right] \times 298.15[K] \\ &\quad \times \left\{2.147 \times \ln\left(\frac{0.0399}{0.0197}\right) + 0.00924 \times \ln\left(\frac{0.0001665}{0.0197}\right)\right. \\ &\quad \left. + 51.626 \times \ln\left(\frac{0.9601}{0.9803}\right) + 55.477 \times \ln\left(\frac{0.9998335}{0.9803}\right)\right\}\left[\frac{\text{mol}}{\text{kg}}\right] \\ &= 3695.3\left[\frac{\text{J}}{\text{kg}}\right] = 3.695\left[\frac{\text{kWs}}{\text{kg}}\right] = 1.026\left[\frac{\text{kWh}}{\text{ton}}\right] \end{aligned}$$

B.2. The osmotic pressure theory (van't Hoff)

Eq. (28) can be rewritten as follows:

$$w_{\min,\text{avg}} = R_u T_0 (m_{s,f\,\text{to}\,b} - m_{s,p})_{\text{log mean}} \quad \text{(B2)}$$

Referring the calculations in B.1:

$$\begin{aligned} w_{\min,\text{avg}} &= 8.3144621\left[\frac{J}{\text{mol} \cdot K}\right] \times 298.15[K] \times (1.078 - 2.147) \\ &\quad / \ln\left\{\frac{1.078 - 0.00924}{2.147 - 0.00924}\right\}[\text{mol / kg}] \\ &= 3822.4\left[\frac{\text{J}}{\text{kg}}\right] = 3.8224\left[\frac{\text{kWs}}{\text{kg}}\right] = 1.062\left[\frac{\text{kWh}}{\text{ton}}\right] \end{aligned}$$

B.3. The vapor compression theory (BPE①)

Eq. (35) can be rewritten as follows:

$$\begin{aligned} w_{\min} = \{ & h_{v2}(P_{\text{sat}}(T_0 - \text{BPE}(T_0, X_p)), s_{v2}) \\ & - h_{v1}\,(P_{\text{sat}}(T_0 - \text{BPE}(T_0, X_f)), s_{v1})\} \\ & / (X_f - X_p) \times \frac{X_b - X_f}{\ln\{(X_b - X_p) / (X_f - X_p)\}} \end{aligned} \quad \text{(B3)}$$

where $s_{v2} = s_{v1} = s_{v1}(T_0, P_{\text{sat}}(T_0 - \text{BPE}(T_0, X_f)))$.

For the given temperature and salinities, the boiling point elevation from BPE① (Eq. (33)) are:

$$\text{BPE①}\ (25°\text{C}, 0.035\,\text{kg / kg}) = 0.3093°\text{C and}$$
$$\text{BPE①}\ (25°\text{C}, 0.0003\text{kg / kg}) = 0.0024°\text{C}$$
$$P_{\text{sat}}(T_0 - \text{BPE}(T_0, X_f)) = (25 - 0.3093°\text{C}) = 0.0311\,\text{bara}$$
$$P_{\text{sat}}(T_0 - \text{BPE}(T_0, X_p)) = (25 - 0.0024°\text{C}) = 0.0317\,\text{bara}$$
$$\begin{aligned} s_{v2} &= s_{v1} = s_{v1}(T_0, P_{\text{sat}}(T_0 - \text{BPE}(T_0, X_f))) \\ &= s_{v1}(25°\text{C}, 0.0311\text{ bara}) = 8.566\left[\frac{\text{kJ}}{\text{kg} \cdot \text{K}}\right] \end{aligned}$$
$$\begin{aligned} & h_{v2}(P_{\text{sat}}(T_0 - \text{BPE}(T_0, X_p)),\, s_{v2}) = \\ & \quad h_{v2}(0.0317\text{ bara, } 8.566\,\text{kJ / kgK}) = 2549.296\,kJ / kg \end{aligned}$$
$$\begin{aligned} & h_{v1}(P_{\text{sat}}(T_0 - \text{BPE}(T_0, X_f)), s_{v1}) = \\ & \quad h_{v1}(0.0311\text{ bara}, 8.566\,\text{kJ / kgK}) = 2546.577\,\text{kJ / kg} \end{aligned}$$
$$\beta \equiv \frac{1}{(X_f - X_p)} \times \frac{X_b - X_f}{\ln\left\{\dfrac{(X_b - X_p)}{X_f - X_p}\right\}} = 1.4427$$

Now, from Eq. (B3):

$$\begin{aligned} w_{\min} &= (h_{v2} - h_{v1}) \times \beta \\ &= (2549.296 - 2546.577)\left[\frac{\text{kJ}}{\text{kg}}\right] \times 1.4427 \\ &= 2.719\left[\frac{\text{kWs}}{\text{kg}}\right] \times 1.4427 = 1.090\left[\frac{\text{kWh}}{\text{ton}}\right] \end{aligned}$$

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