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Derivation of the Theoretical Minimum Energy of Separation of Desalination Processes

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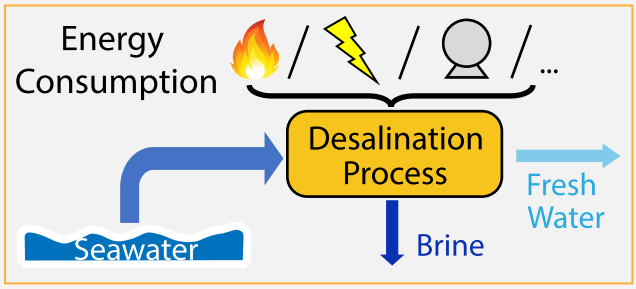
ABSTRACT: Minimizing the energy consumption of desalination processes is an important goal for augmenting freshwater production and mitigating water scarcity. Chemical, civil, mechanical, and environmental engineering students can derive and analyze the energy consumption of desalination processes by applying engineering fundamentals such as thermodynamics, transport phenomena, and process design. We explore the fundamental thermodynamic limits of the most prominent desalination technologies in a format designed for engineering students and instructors. Two thermodynamically reversible processes for reverse osmosis (RO) and electrodialysis (ED) are developed to demonstrate that reversible processes consume the theoretical minimum energy, which is the Gibbs free energy of separation. We then quantify the practical minimum energy consumption for RO and ED, showing that the energy consumption of these processes approaches the minimum thermodynamic limit with increased process staging.



KEYWORDS: *Upper-Division Undergraduate, Chemical Engineering, Separation Science, Water/Water Chemistry*

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■ INTRODUCTION

The security of pure and abundant freshwater is at risk because of climate change, population growth, and anthropogenic contamination. Water scarcity, defined as when local water demand exceeds local water supply for at least one month each year, currently impacts over half of the global population and is projected to increase dramatically in the coming decades.[1] Along with water conservation and infrastructure improvements, addressing this crisis will require augmenting freshwater production through water reuse and desalination.[2]

From a pedagogical perspective, water desalination presents an exceptional educational opportunity for engineering students to apply fundamentals such as transport phenomena, thermodynamics, and process design.[3] The array of available desalination technologies enables students to compare practical energy consumption, which depends on transport mechanism and design, to the thermodynamic minimum energy of separation. Thereby, the study of desalination offers chemical, civil, mechanical, and environmental engineering students an illustrative synthesis and application of engineering fundamentals toward a stimulating humanitarian challenge.

Mainstream desalination technologies may be categorized by three driving forces used to induce salt and water separation: thermal energy, pressure−volume work, and electrical work. Thermal desalination technologies, such as multieffect distillation, multistage flash distillation, and mechanical vapor compression, extract fresh water through vaporization and subsequent condensation.[4] These aged and highly energy-intensive processes are not considered in this analysis. Pressure-driven desalination is dominated by reverse osmosis (RO), in which applied pressure (i.e., pressure−volume work) drives water molecules from the saltwater feed stream across a salt-rejecting, semipermeable membrane to the purified product stream (Figure 1A).[5−7] To counteract spontaneous water migration from low to high solute concentration (i.e., osmosis), *reverse osmosis* requires the applied pressure to be greater than the osmotic pressure difference between the concentrated feed stream and dilute product stream. In an RO module, the unrecovered water that remains on the upstream side of the membrane exits the system as a more concentrated brine stream (Figure 1B).[8,9] Voltage-driven desalination technologies such as electrodialysis (ED) capitalize on the charged nature of salt ions to achieve separation. In ED, voltage is applied across a stack of ion-selective membranes to separate salt and water (Figure 1C).[10] As salt ions migrate toward their respective oppositely charged electrodes, they are systematically blocked by an arrangement of alternating cation- and anion-exchange membranes to create alternating channels

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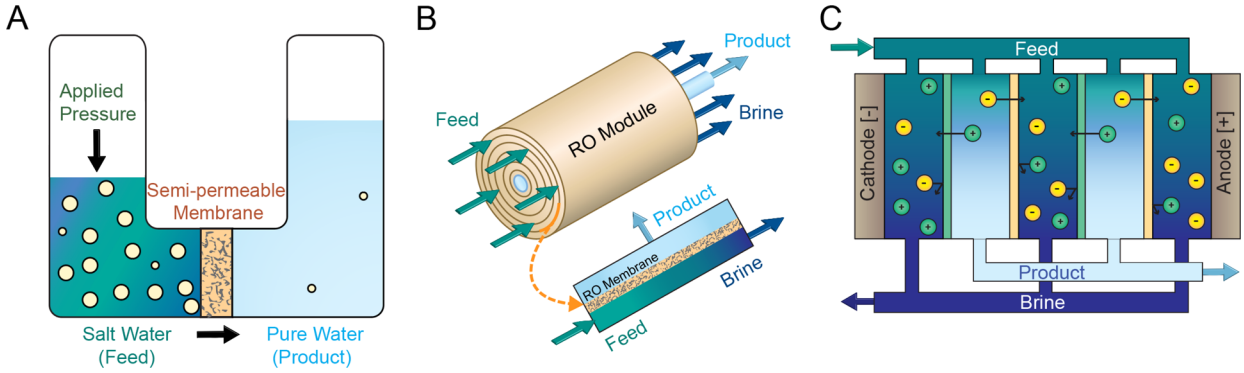

Figure 1. Process schematics of reverse osmosis (RO) and electrodialysis (ED) desalination. (A) RO utilizes applied hydraulic pressure to drive water through a salt-rejecting semipermeable membrane. The applied pressure increases the chemical potential of water on the saltwater side and drives water molecules across the membrane to the freshwater side. The applied pressure must be great enough to overcome the chemical potential difference (i.e., the osmotic pressure difference) between the feed and product streams. Salt cannot pass the semipermeable membrane, and thus, the concentrated feed becomes the brine. (B) RO modules comprise spiral wound RO membranes and operate in cross-flow configuration. Applied pressure drives water molecules axially from the salty feed stream toward the center of the module, where the freshwater product is collected. (C) ED utilizes ion exchange membranes (IEMs) and applied voltage to separate salt ions from water. Cations from the feed stream pass through adjacent cation-exchange membranes as they migrate toward the cathode, while anions pass through anion-exchange membranes as they migrate toward the anode. The arrangement of subsequent oppositely charged membranes results in alternating channels of high and low concentration which comprise the brine and product water streams, respectively.

of high and low salt concentrations, which comprise the brine and freshwater streams, respectively.

Chemical, civil, mechanical, and environmental engineering students may be exposed to the topic of desalination in undergraduate courses, such as Thermodynamics, Unit Operations, or Separation Processes, but the subject is not typically discussed at length until specialized graduate courses such as Desalination and Water Purification, Membrane Processes, Physicochemical Processes, and Wastewater Treatment. Although desalination processes and separation mechanisms are described in some of these courses, a comparative energy analysis of desalination technologies is often inaccessible to students and/or instructors. Considering that energy consumption of desalination plants makes up about half of produced water cost and results in significant greenhouse gas emissions,[11,12] it would be judicious for instructors to incorporate energy analysis into relevant coursework.

In this article, we present three derivations for the specific energy consumption (*SEC*) of desalination which are accessible to undergraduate or graduate students and instructors. We begin by deriving the general expression of thermodynamic minimum energy of desalination as the Gibbs free energy of separation. We then present the *SEC* of a thermodynamically reversible RO process using pressure–volume work, followed by the practical minimum energy consumption for single-stage RO and multistage RO. Lastly, the *SEC* for thermodynamically reversible and practical ED is developed from electrical work. The derived *SEC* equations of thermodynamically reversible RO and ED are shown to be equivalent to the Gibbs free energy of separation. Furthermore, we show that practical RO and ED processes approach the thermodynamic minimum energy of separation as the number of process stages increases. The derivations of desalination energy consumption presented here provide instructors and students with a toolkit to analyze the energy efficiency and consumption of some of the most prominent technologies used for alleviating global water scarcity.

THERMODYNAMIC MINIMUM ENERGY OF SEPARATION

The Gibbs free energy of separation is the minimum energy required to separate a mixture into its pure components, regardless of process path. It is equivalent in magnitude to the Gibbs free energy of mixing and is defined as the difference between the Gibbs free energy of the total mixed solution and the sum of the Gibbs free energies for each component species. In the case of desalination, it is thermodynamically impossible to separate salt from water using less energy than the Gibbs free energy of separation. This section quantifies the Gibbs free energy of separation for saltwater and uses this value to define the minimum specific energy consumption (SEC_{min}) of desalination, which is simply the Gibbs free energy of separation normalized by unit volume of product water. Throughout the analysis, we assume the activity coefficients for the species of interest are equal to unity. This assumption is valid for desalination processes as discussed in the Supporting Information.

The Gibbs free energy of mixing for an ideal two component solution with generic species 1 and 2 is given by[13]

$$\Delta_{mix}G = nRT[x_1\ln(x_1) + x_2\ln(x_2)] \quad (1)$$

where n is total moles of solution (including both species), R is the gas constant, T is absolute temperature, and x is the mole fraction of each component in the mixture. In the case of desalination where the components are salt (s) and water (w), $x_1 = x_w$, $x_2 = x_s$, and $x_w = 1 - x_s$, the Gibbs free energy of mixing may be expressed as

$$\Delta_{mix}G = nRT[x_s\ln(x_s) + (1 - x_s)\ln(1 - x_s)] \quad (2)$$

This can be further simplified with a Taylor series expansion and dilute solution approximation (i.e., $x_s \ll 1$) using $\ln(1 - x_s) \approx -x_s$ to yield

$$\Delta_{mix}G \approx nRTx_s[\ln(x_s) - 1] \quad (3)$$

The Gibbs free energy of separation for a desalination process, $\Delta_{sep}G$, is the difference between the free energy of mixing of

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the resulting streams—product water and brine—and the free energy of the initial feedwater:

$$\Delta_{sep}G = \Delta_{mix}G_p + \Delta_{mix}G_b - \Delta_{mix}G_f \quad (4)$$

where $\Delta_{mix}\ G_p$, $\Delta_{mix}\ G_b$, and $\Delta_{mix}\ G_f$ denote the product, brine, and feed streams, respectively. The molar Gibbs free energy of mixing ($\Delta_{mix}\ \hat{G} = \Delta_{mix}\ G/n$) for each stream, $\Delta_{mix}\ \hat{G}_i$, can be expressed in terms of its salt composition as follows:

$$\Delta_{mix}\hat{G}_f = RTx_f[\ln(x_f) - 1] \quad (5a)$$

$$\Delta_{mix}\hat{G}_p = RTx_p[\ln(x_p) - 1] \quad (5b)$$

$$\Delta_{mix}\hat{G}_b = RTx_b[\ln(x_b) - 1] \quad (5c)$$

where x_f, x_p, and x_b are the mole fractions of salt in the feed, product, and brine streams, respectively. For desalination processes operating at a given water recovery, R_w (defined as the ratio of pure product water over the total feed stream), eq 4 becomes

$$\Delta_{sep}\hat{G} = R_w\Delta_{mix}\hat{G}_p + (1 - R_w)\Delta_{mix}\hat{G}_b - \Delta_{mix}\hat{G}_f \quad (6)$$

Specific energy consumption is defined as the energy consumption per unit volume of product water. Hence, we divide by $R_w\hat{V}_w$, which is the water recovery multiplied by the molar volume of water, to convert eq 6 from *energy per mole* to *energy per volume* of product water:

$$SEC_{min} = \frac{R_w\Delta_{mix}\hat{G}_p + (1 - R_w)\Delta_{mix}\hat{G}_b - \Delta_{mix}\hat{G}_f}{R_w\hat{V}_w} \quad (7)$$

Substituting eqs 5a−5c into eq 7 and incorporating a mass balance on salt, i.e. $x_f = R_wx_p + (1 - R_w)\ x_b$, yields

$$SEC_{min} = \frac{RT}{\hat{V}_w}\left[\frac{x_f}{R_w}\ln\left(\frac{x_b}{x_f}\right) - x_p\ln\left(\frac{x_b}{x_p}\right)\right] \quad (8)$$

Using the relationship between mole fraction of dilute solute ions (x_s) and molar solute concentration (c_s), $x_s \approx \nu c_s\hat{V}_w$, where ν is the number of dissociated ions per salt molecule (e.g., 2 for NaCl), eq 8 may be expressed as

$$SEC_{min} = 2RT\left[\frac{c_f}{R_w}\ln\left(\frac{c_b}{c_f}\right) - c_p\ln\left(\frac{c_b}{c_p}\right)\right] \quad (9)$$

For complete salt rejection when the membrane perfectly selects water molecules over salt, $c_p = 0$, and thereby

$$SEC_{min} = \frac{2RTc_f}{R_w}\ln\left(\frac{c_b}{c_f}\right) \quad (10)$$

Using the mass balance relationship

$$\frac{c_b}{c_f} = \frac{1}{1 - R_w} \quad (11)$$

and the van't Hoff relation for the feedwater osmotic pressure ($\pi_f = 2RTc_f$),[13] eq 10 is simplified to

$$SEC_{min} = -\frac{\pi_f}{R_w}\ln(1 - R_w) \quad (12)$$

This important result tells us that the minimum thermodynamic energy consumption of a desalination process with complete salt rejection is determined only by the feed stream osmotic pressure and water recovery ratio. For example, desalinating seawater with a typical seawater salt concentration of 35 g L^{-1} (corresponding osmotic pressure of 29.7 bar) and 50% water recovery (i.e., 50% of the feed stream becomes purified water and 50% becomes brine) requires at least 1.1 kWh per cubic meter of purified water. Regardless of the desalination technology, it is impossible to desalinate water using less energy than that determined by eq 12.

■ ENERGY CONSUMPTION OF REVERSE OSMOSIS

RO as a Reversible Thermodynamic Process

In RO desalination, hydraulic pressure is applied to a saltwater feed stream to transfer water across a semipermeable membrane to a purified product stream.[5,14,15] The energy consumption of a thermodynamically reversible RO process can be derived using pressure−volume work and should be equivalent to the Gibbs free energy of separation.[16] In this section, we present the derivations for a thermodynamically reversible RO process as well as the practical minimum energy consumption for single-stage and multistage RO. These analyses rely on two primary assumptions: (i) the RO membrane is perfectly selective toward water (100% salt rejection) and (ii) osmotic pressure is proportional to salt concentration. These assumptions hold given that state-of-the-art RO membranes have >99% salt rejection[17] and seawater is dilute enough to apply the van't Hoff equation for osmotic pressure.[5]

The general equation for the electrochemical potential of species i of an ideal solution ($\overline{\mu}_i$) can be expressed as[18]

$$\overline{\mu}_i = \mu_i^0 + RT\ln(x_i) + \hat{V}_w(P - P^0) + z_iF(E_i - E_i^0) \quad (13)$$

where μ_i^0 is the standard electrochemical potential; x_i is the mole fraction of species i; P and P^0 are the pressure and reference pressure, respectively; z_i is the charge valence of species i; F is the Faraday constant; and E_i and E_i^0 are the electrostatic potential and reference electrostatic potential of component i in solution, respectively. For RO desalination, an applied pressure drives water across the membrane. Hence, eq 13 can be simplified by disregarding the electric potential contribution and rewriting for the chemical potential of water:

$$\mu_w = \mu_w^0 + RT\ln(x_w) + \hat{V}_w(P - P^0) \quad (14)$$

where μ_w and μ_w^0 are the chemical potential and standard chemical potential of water, respectively. The chemical potential of water must be identical on each side of the semipermeable membrane to satisfy equilibrium (i.e., $\Delta\mu_w = 0$). To maintain this equilibrium, the osmotic pressure balances the difference in water activity across the membrane. Using eq 14 and setting the chemical potential of the feed and permeate solutions equal, the osmotic pressure (π) may be defined as

$$\pi = -\frac{RT\ln(x_w)}{\hat{V}_w} \quad (15)$$

assuming the permeate solution is pure water and the activity coefficient of water is equal to unity.

In the context of pressure-driven RO, the minimum applied pressure required to prevent water transport from the dilute side of the membrane to the concentrated side is equal to the osmotic pressure of the brine stream. In a reversible RO process, which operates at thermodynamic equilibrium ($\Delta\mu_w =$

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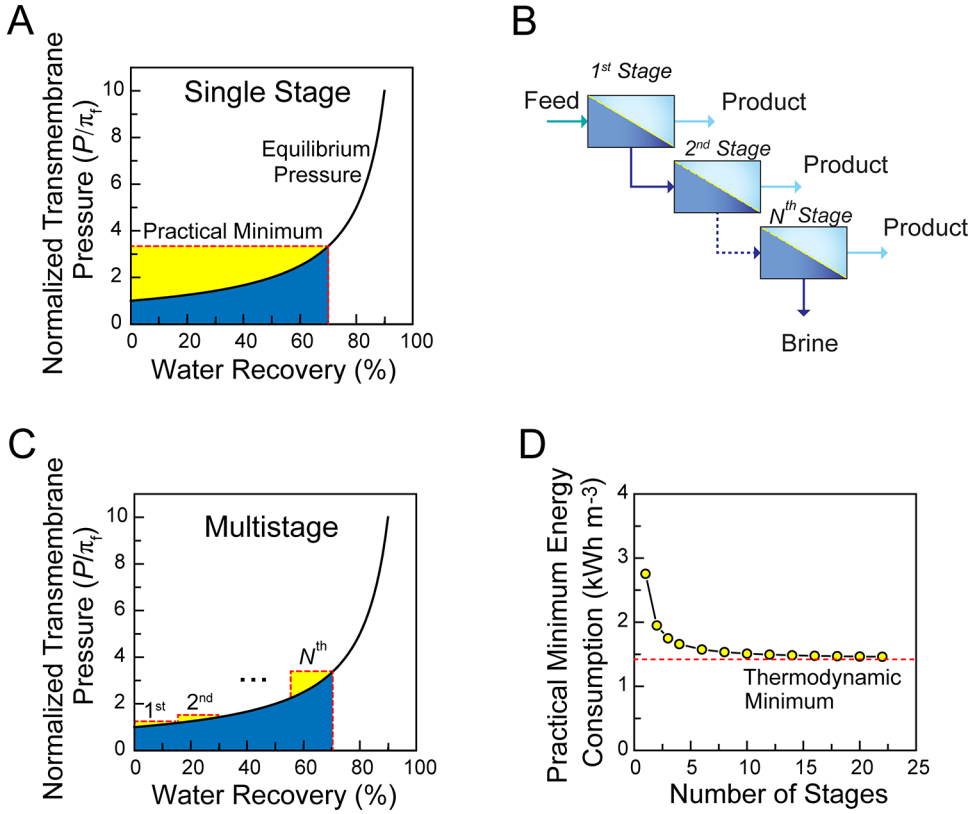

Figure 2. Energy consumption analysis of RO. (A) Transmembrane pressure of batch-mode RO, normalized to the initial osmotic pressure of the feed (π_f), as a function of water recovery. The applied pressure in a thermodynamically reversible process is equal to the osmotic pressure of the brine solution. The feed concentration was set to 600 mM and salt rejection to 100%. The blue area represents the minimum energy consumption for a thermodynamically reversible process where the applied pressure is constantly equal to the equilibrium brine pressure. The area bordered by the dashed red lines represents the practical minimum energy consumption, which occurs at constant operating pressure, for single-stage RO (in this example 70% water recovery). The yellow area represents the excess pressure, defined as the difference between the applied pressure and equilibrium pressure for single-stage operation. (B) Multiple RO stages may be used to reduce practical energy consumption. The brine stream from one stage feeds into the subsequent stage and product water is collected as permeate after each stage. (C) Normalized transmembrane pressure for multistage RO. The yellow area represents the excess pressure, or the difference between the applied pressure and equilibrium pressure, for each stage. (D) Practical minimum energy consumption of RO as a function of the number of stages. As the number of RO stages increase, the practical minimum energy consumption approaches the thermodynamic minimum. The feed concentration was set to 600 mM and the water recovery to 70%.

0), a variable hydraulic pressure is applied which is infinitesimally larger than the osmotic pressure of the brine (Figure 2A) so that water transports from the feed side through the membrane to the permeate side. Taking into account the applied pressure and using eqs 14 and 15, the change in chemical potential across the membrane can be expressed as

$$\Delta\mu_w = \hat{V}_w \Delta P - \hat{V}_w \Delta\pi \tag{16}$$

where ΔP and $\Delta\pi$ are the applied pressure and osmotic pressure differences across the membrane, respectively. Simplifying eq 16, the hydraulic pressure applied in an RO system operating at a thermodynamic minimum energy is characterized by

$$\Delta P = \Delta\pi = \pi_b \tag{17}$$

where π_b is the osmotic pressure of the brine.

To calculate the theoretical minimum energy of RO, consider an RO batch system where the water is recovered continuously (Figure 2A). As such, the brine concentration increases as the process proceeds. To satisfy a reversible thermodynamic process, we assume the applied pressure closely approaches the brine pressure throughout the process. A salt mass balance shows that the brine concentration (c_b) is related to the feed concentration (c_f) through the variable water recovery (r) by $c_b = c_f\left(\frac{1}{1-r}\right)$, where r is defined as the cumulative fraction of feedwater that becomes product water in the desalination process ($r \leq R_w$). With the assumption that osmotic pressure is linearly dependent on salt concentration, the previous relationship may be rewritten as $\pi_b = \pi_f\left(\frac{1}{1-r}\right)$.

The pressure−volume reversible work (W_{rev}) can then be represented in terms of the permeate volume (V_p), π_f, and r to derive the theoretical minimum energy consumption of RO:

$$W_{rev} = \int_0^{V_p} P dV = \int_0^{V_p} \pi_b dV = \int_0^{V_p} \frac{\pi_f}{1-r} dV \tag{18}$$

The permeate volume and feed volume (V_f) is related to the final water recovery of the module via $R_w = \frac{V_p}{V_f}$, such that the integral can be solved with respect to r, noting that at any time along the desalination process $dV = V_f dr$:

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$$W_{\text{rev}} = \int_0^{R_w} \frac{\pi_f V_f}{1 - r} dr = -\pi_f V_f \ln(1 - R_w) \tag{19}$$

The *SEC* of thermodynamically reversible RO desalination can then be calculated by normalizing eq 19 by V_p:

$$SEC_{\text{min}}^{\text{RO}} = \frac{W_{\text{rev}}}{V_p} = -\frac{\pi_f}{R_w} \ln(1 - R_w) \tag{20}$$

eq 20 is identical to the Gibbs free energy of separation developed in the previous section (eq 12), indicating that RO desalination can theoretically approach the universal minimum energy of desalination.

When no water is recovered by the RO membrane (i.e., $R_w \to 0$), then $\ln(1 - R_w) = -R_w$. Hence, the *SEC* based on eq 20 is reduced to π_f. In this case, the *SEC* of RO is only dependent upon the feed concentration and equal to π_f.

Practical Minimum Energy of RO

Single Stage. When an RO module operates at the thermodynamic limit, the applied pressure is equal to the osmotic pressure of the brine solution. However, the variable pressure described in the previous section for a reversible thermodynamic process is impractical when a finite water flux is desired. In practical operation, the applied pressure remains constant above the osmotic pressure of the brine (Figure 2A). Therefore, the pressure−volume work (W_1^{RO}) and *SEC* for a practical single-stage RO may be described by

$$W_1^{\text{RO}} = \pi_b V_p \tag{21}$$

$$SEC_1^{\text{RO}} = \frac{W_1^{\text{RO}}}{V_p} = \frac{\pi_f}{1 - R_w} \tag{22}$$

which assumes ideal (i.e., 100% efficiency) pumps and energy recovery devices.[19−21] The practical minimum *SEC* is proportional to the rectangular area under the dashed horizontal line in Figure 2A, and the thermodynamically reversible energy is proportional to the blue area. As an example, desalinating 35 g L^{-1} seawater at 50% water recovery has a theoretical minimum energy requirement of 1.1 kWh m^{-3} and a practical minimum of 1.6 kWh m^{-3}. At higher water recoveries, the yellow area in Figure 2A becomes larger, suggesting that the excess energy required by constant pressure operation increases with greater water recovery.

Multistage. In multistage operation, RO modules are placed in series, where the brine solution from the prior module is received as the feed solution for the subsequent RO unit (Figure 2B).[22] As water is recovered, the feed becomes more concentrated with each RO stage. The applied pressure also increases in each stage to match the brine osmotic pressure (Figure 2C).

We begin by first deriving equations for the brine pressure ($\pi_{b,i}$), permeate volume ($V_{p,i}$), and cumulative water recovery (r_i) at stage *i*. Assuming the difference between applied pressures in two consecutive RO stages is constant, the brine osmotic pressure at stage *i* can be expressed as

$$\pi_{b,i} = \frac{i}{N}(\pi_b - \pi_f) + \pi_f = \frac{i}{N}\left(\frac{\pi_f}{1 - R_w} - \pi_f\right) + \pi_f \tag{23a}$$

$$\pi_{b,i} = \frac{R_w}{1 - R_w}\frac{i}{N}\pi_f + \pi_f \tag{23b}$$

where *N* is the total number of RO stages in series. The permeate volume at stage *i* ($V_{p,i}$) can be determined by

$$V_{p,i} = V_f(r_i - r_{i-1}) \tag{24}$$

where V_f is the total feed volume and r_i is the cumulative water recovery in stage *i*. Finally, to determine the cumulative water recovery at stage *i*, recall the initial pressure (π_f) and brine pressure in stage *i* ($\pi_{b,i}$) are related by the following equation, assuming an ideal solution that can be described using the van't Hoff equation:[13]

$$\pi_{b,i} = \frac{\pi_f}{1 - r_i} \tag{25}$$

By setting eqs 23 and 25 equal and simplifying, we arrive at a formulation for the cumulative water recovery for stage *i*, or the ratio of cumulative permeate volume at stage *i* to the total feed volume:

$$\frac{1}{1 - r_i} = \frac{R_w}{1 - R_w}\frac{i}{N} + 1 \tag{26a}$$

$$r_i = \frac{R_w i}{(1 - R_w)N + R_w i} \tag{26b}$$

Similar to eq 22, the total practical minimum *SEC* for an *N*-stage RO operation can be calculated as the cumulative pressure−volume work normalized to the permeate volume for *N* stages:

$$SEC_N^{\text{RO}} = \frac{\sum_{i=1}^N \pi_{b,i} V_{p,i}}{\sum_{i=1}^N V_{p,i}} = \frac{\sum_{i=1}^N \left(\frac{R_w}{1 - R_w}\frac{i}{N}\pi_f + \pi_f\right) V_f(r_i - r_{i-1})}{\sum_{i=1}^N V_{p,i}} \tag{27}$$

With the definition of water recovery, $R_w = \sum_{i=1}^N V_{p,i}/V_f$, eq 27 becomes

$$SEC_N^{\text{RO}} = \frac{\sum_{i=1}^N \left(\frac{R_w}{1 - R_w}\frac{i}{N}\pi_f + \pi_f\right)(r_i - r_{i-1})}{R_w} \tag{28a}$$

$$SEC_N^{\text{RO}} = \frac{\pi_f}{R_w}\sum_{i=1}^N \left(\frac{R_w}{1 - R_w}\frac{i}{N} + 1\right)(r_i - r_{i-1}) \tag{28b}$$

By substituting eq 26a into eq 28b, we arrive at the following equation:

$$SEC_N^{\text{RO}} = \frac{\pi_f}{R_w}\sum_{i=1}^N \left(\frac{1}{1 - r_i}\right)(r_i - r_{i-1}) \tag{29}$$

As the number of stages approaches infinity, the summation term can be represented as an integral from $r_i = 0$ to $r_i = R_w$:

$$\lim_{N \to \infty} SEC_N^{\text{RO}} = \frac{\pi_f}{R_w}\int_0^{R_w} \frac{1}{1 - r_i} dr_i \tag{30}$$

The integration of eq 30 becomes

$$\lim_{N \to \infty} SEC_N^{\text{RO}} = -\frac{\pi_f}{R_w}\ln(1 - R_w) \tag{31}$$

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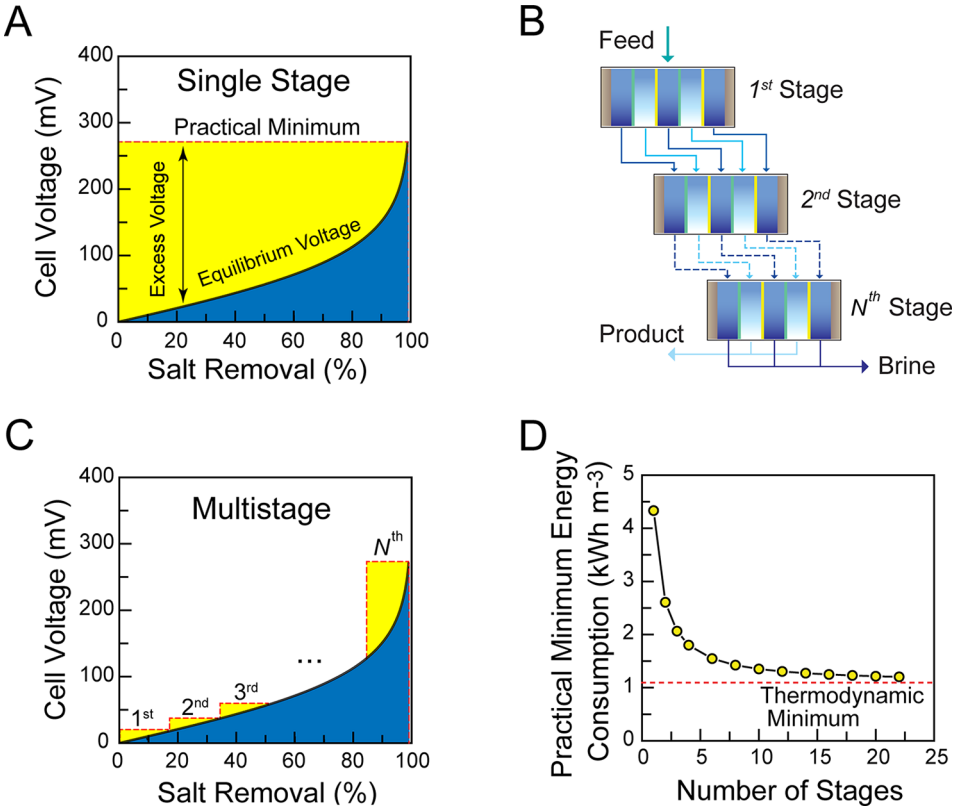

Figure 3. Energy consumption analysis of ED. (A) Equilibrium voltage of ED as a function of salt removal. The feed concentration was set to 600 mM and the water recovery to 50%. The blue area represents a thermodynamically reversible process where the voltage is constantly changing along the equilibrium voltage curve. The practical minimum energy consumption for single-stage ED is the area under the dashed red line. (B) Multistage ED processes are configured so that the dilute and brine streams from one stage are fed into the subsequent stage. The product stream is obtained after the last process stage. (C) Cell voltage of each stage of ED in a multistage operation. The water recovery increases with the number of stages. The yellow area represents the excess voltage in each stage. (D) Practical minimum energy consumption as a function of the number of stages. The feed concentration was set to 600 mM, the water recovery to 50%, and salt rejection to 99%.

which is equivalent to the *SEC* of a thermodynamically reversible process and the Gibbs free energy of separation (eqs 12 and 20, respectively).

The energy consumption for multistage operation becomes clearly smaller than that for single-stage operation, represented by the dashed rectangular areas in Figure 2C and Figure 2A, respectively. In summary, increasing the number of stages decreases the *SEC* of RO desalination, albeit with diminishing returns (Figure 2D).

More RO modules in series also presents a substantial increase in capital costs. An alternative configuration that can theoretically approach the thermodynamic limit is a batch RO process,[23,24] where the brine is recycled to the feed tank until the target recovery is reached. However, process inefficiencies such as salt concentration polarization at the membrane surface and frictional losses prevent ideal batch performance, leading single-stage RO configuration to be most common in current systems.[14,23]

■ ENERGY CONSUMPTION OF ELECTRODIALYSIS

Electrodialysis as a Reversible Thermodynamic Process

ED utilizes electrical energy to desalinate water by selectively transporting cations and anions through ion exchange membranes (IEMs).[9,25,26] Note that while water molecules are transported across the membrane in RO, ions are the transported species in ED. Negatively charged cation exchange membranes (CEMs) allow passage of cations, while positively charged anion exchange membranes (AEMs) enable passage of anions.[27] These membranes are arranged in an alternating stack of CEMs and AEMs to produce alternating channels of concentrated brine and product streams when voltage is applied (Figure 1C). For simplicity, this analysis will only consider one cell pair comprising one AEM and one CEM, but a complete ED stack is an arrangement of repeating unit cells. This analysis also assumes ideal IEMs with perfect co-ion rejection (i.e., CEM rejects all anions and AEM rejects all cations).

In order to develop an expression for the specific energy consumption of ED, we first determine the electrochemical potential difference between salt ions in the brine and product streams, as this determines the voltage which must be applied to transport ions across the IEM. Recall eq 13 for the electrochemical potential, expressed for cations as

$$\overline{\mu}_c = \mu_c^0 + RT\ln(x_c) + F(E_c - E_c^0) \tag{32}$$

The difference in electrochemical potential across the CEM must be overcome by the applied electrical voltage to transport cations from the feed stream to the brine stream. We assume activity coefficients are equal to one and $x_c = c_c V/n$, where c_c is the molar concentration of cations, and V and n are total solution volume (including water and salt) and total solution moles (the sum of the moles of water and salt), respectively. The ratio of V/n is nearly the same for both brine and product streams (dominated by water molecules). Hence, using eq 32,

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the difference in electrochemical potential for cations across the CEM may be expressed by

$$\Delta E_{\mathrm{CEM}} = \frac{RT}{F}\ln\frac{c_b'}{c_p'} \tag{33}$$

where c_b' and c_p' are the brine and product stream cations concentrations at any point during the desalination, respectively, and F is the Faraday constant. Note that c_b' and c_p' continuously change during the desalination process.

An identical expression as eq 33 can be generated for anions (i.e., ΔE_{AEM}) due to cell symmetry. Hence, the voltage across the pair of IEMs is the sum of ΔE_{AEM} and ΔE_{CEM}, leading to

$$\Delta E_{eq} = 2\frac{RT}{F}\ln\frac{c_b'}{c_p'} \tag{34}$$

Here, ΔE_{eq} is the *equilibrium voltage* required to maintain a specific salt concentration ratio of brine and product streams. As salt is removed from the product stream, the brine and product concentrations continuously change as charge is transferred across the membrane, resulting in increasing concentration ratio and equilibrium voltage.[28] A typical equilibrium voltage as a function of salt removal is shown Figure 3A. We note that the equilibrium voltage is independent of the kinetics of ion transport and is only a function of the concentration ratio of the brine and product streams.

A thermodynamically reversible ED process may be envisioned as a batch process with an applied voltage that is always infinitesimally larger than the equilibrium voltage. The electrical work for such a process can be calculated by integrating the equilibrium voltage (ΔE_{eq}) over the cumulative transferred charge (q):

$$W_{\mathrm{rev}} = \int_0^Q \Delta E_{\mathrm{eq}}\,dq \tag{35}$$

where Q is the ultimate transferred charge. W_{rev} is proportional to the blue area shown in Figure 3A,C. The electric charge transferred across the IEM (q) is related to the moles of salt transported (n_s) by the Faraday constant, i.e., $dq = Fdn_s$, assuming one electric charge in the external circuit corresponds to one ionic charge transferred across the membrane (i.e., perfect co-ion repulsion). After substituting ΔE_{eq} from eq 34, eq 35 becomes

$$W_{\mathrm{rev}} = 2RT\int_0^{n_T}\ln\frac{c_b'}{c_p'}dn_s \tag{36}$$

where n_T is the ultimate moles of salt removed from the feed stream.

For monovalent salts such as NaCl, the moles of salt removed is equivalent to the moles of cations (or anions) removed. Therefore, the moles of salt removed may be determined from the brine and product stream concentrations according to simple mass balances:

$$c_b' = c_f + n_s/V_b \tag{37a}$$

$$c_p' = c_f - n_s/V_p \tag{37b}$$

where c_f is the feed salt concentration, and V_b and V_p are the brine and product volumes, respectively. We note that at the end of the desalination process (i.e., when $n_s = n_T$), $c_b' = c_b$ and $c_p' = c_p$.

Substituting eq 37 in eq 36 yields

$$\begin{aligned} W_{\mathrm{rev}} &= 2RT\int_0^{n_T}(\ln c_b - \ln c_p)dn_s \\ &= 2RT\int_0^{n_T}\left[\ln\left(c_f + \frac{n_s}{V_b}\right) - \ln\left(c_f - \frac{n_s}{V_p}\right)\right]dn_s \end{aligned} \tag{38}$$

The integration of eq 38 becomes

$$\begin{aligned} W_{\mathrm{rev}} = 2RT[&V_bc_b(\ln c_b - 1) - V_bc_f(\ln c_f - 1) \\ &+ V_pc_p(\ln c_p - 1) - V_pc_f(\ln c_f - 1)] \end{aligned} \tag{39}$$

Incorporating a mass balance wherein the number of moles of salt *removed* from the permeate is equal the number of moles of salt *enriched* in the brine, $(c_b - c_f)\,V_b = (c_f - c_p)\,V_p$, into eq 39 yields

$$W_{\mathrm{rev}} = 2RT(V_bc_b\ln c_b - V_bc_f\ln c_f + V_pc_p\ln c_p - V_pc_f\ln c_f) \tag{40}$$

The minimum specific energy of a reversible ED process ($SEC_{\mathrm{min}}^{\mathrm{ED}}$) is obtained by normalizing eq 40 by the volume of product water (V_p):

$$SEC_{\mathrm{min}}^{\mathrm{ED}} = 2RT\left(\frac{V_b}{V_p}c_b\ln c_b - \frac{V_b}{V_p}c_f\ln c_f + c_p\ln c_p - c_f\ln c_f\right) \tag{41}$$

eq 41 may be expressed in terms of water recovery, given that $\frac{V_b}{V_p} = \frac{1-R_w}{R_w}$:

$$SEC_{\mathrm{min}}^{\mathrm{ED}} = 2RT\left(\frac{1-R_w}{R_w}c_b\ln c_b - \frac{c_f}{R_w}\ln c_f + c_p\ln c_p\right) \tag{42}$$

Applying the salt mass balance $c_f = c_pR_w + c_b\,(1 - R_w)$ and rearranging eq 42 yields

$$SEC_{\mathrm{min}}^{\mathrm{ED}} = 2RT\left[\frac{c_f}{R_w}\ln\left(\frac{c_b}{c_f}\right) - c_p\ln\left(\frac{c_b}{c_p}\right)\right] \tag{43}$$

Comparing eqs 43 and 9 illustrates that a thermodynamically reversible ED process consumes the same specific energy as the Gibbs free energy of separation.

Practical Minimum Energy Consumption of ED

Even though a reversible process consumes the lowest energy, this process is impractical as it takes an infinitely long time to achieve separation.[29] In the following subsections, we discuss two practical operational modes for ED and analyze their corresponding energy consumptions.

Single Stage. In single stage operation, the applied voltage is equally distributed between cell pairs.[27] To achieve a specific salt removal, the applied voltage has to be larger than the equilibrium voltage at the end of the separation. Therefore, a practical minimum voltage, ΔE_1, can be determined for a target salt separation. The practical minimum voltage for one cell pair is determined by the final concentration ratio across the IEMs at the end of the separation process:

$$\Delta E_1 = 2\frac{RT}{F}\ln\frac{c_b}{c_p} \tag{44}$$

The practical minimum voltage, ΔE_1, is shown as the dashed horizontal line in Figure 3A. The practical minimum voltage

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for the entire membrane stack is determined by multiplying ΔE_1 by the number of cell pairs.

Based on the assumption of IEMs that perfectly exclude co-ions and only transport counterions, the transferred electrical charge at the end of separation is equal to the transferred ionic charge:

$$Q = V_p(c_f - c_p)F \tag{45}$$

As the voltage is constantly applied across the cell, it does not vary with charge transfer. The practical minimum *SEC* is therefore calculated by multiplying $\Delta E_{\mathrm{min},1}$ and Q, and normalizing by V_p:

$$SEC_1^{\mathrm{ED}} = 2RT(c_f - c_p)\ln\frac{c_b}{c_p} \tag{46}$$

This expression is proportional to the rectangular area under the dashed horizontal line in Figure 3A. The difference between the practical minimum energy and the thermodynamically reversible energy is defined as the excess energy, which is proportional to the yellow area in Figure 3A. This excess energy is necessary to render a finite desalination rate (i.e., salt removal rate) for practical application. The difference between the applied voltage and the equilibrium voltage, or *excess voltage*, diminishes as salt is removed, which results in a slower rate of ion transport through the IEMs toward the end of separation.

Multistage. The energy consumption of ED may be reduced by incorporating multiple stages of membrane stacks so that the product stream of one membrane stack enters as a feed stream in the subsequent stack (Figure 3B).[30,31] The energy consumption for multistage operation, represented by the sum of the yellow and blue areas in Figure 3C, becomes smaller than that for single-stage operation, represented by the rectangular area in Figure 3A. To demonstrate the effects of staging, we numerically calculated the practical minimum energy as a function of the number of stages (Figure 3D). In our calculations, the salt removal was assumed identical across all stages; for instance, to achieve 99% salt removal in a three-stage operation, each stage removes 33%. As the concentrations of the product and the brine streams continuously change from the first to last stage, the applied voltage increases accordingly with each stage. Operating with multiple stages reduces the excess voltage and thereby saves energy. As such, the amount of energy required beyond the theoretical minimum is smaller in multistage operation (Figure 3C) than single-stage operation (Figure 3A).

In the example in Figure 3D, we show that to achieve 90% salt removal from a 600 mM feed stream with a water recovery of 50%, the *SEC* reduces nearly 40% from 4.33 to 2.61 kWh m^{-3} by moving from single-stage to two-stage operation (Figure 3D). Further increasing the number of stages from two to three, the *SEC* only reduces 20% to 2.06 kWh m^{-3}. As the number of stages increases, the *SEC* approaches the thermodynamic limit. For example, *SEC* becomes 1.20 kWh m^{-3} when the process is configured with 22 stages, which is only 10% larger than the thermodynamic minimum of 1.09 kWh m^{-3}.

■ SUMMARY

In this paper, we demonstrate how to calculate the theoretical minimum and practical minimum energy consumption for two typical desalination processes, RO and ED, in a format tailored for instructors and students. We first derive the general expression of the thermodynamic minimum energy of separation determined by the Gibbs free energy, which is independent of the method of desalination. We then introduce the equilibrium driving force for RO and ED and construct thermodynamically reversible RO and ED processes by equating the applied driving force to the equilibrium driving force. Specifically, a reversible thermodynamic process of RO is achieved when the applied hydraulic pressure equals the brine osmotic pressure, whereas in ED it is obtained if the applied voltage is equal to the equilibrium voltage required to maintain a specific salt concentration ratio of brine and product streams across the IEM. We demonstrate that regardless of driving force, a thermodynamically reversible desalination process consumes the Gibbs free energy of separation.

Although thermodynamically reversible processes consume the least energy, they are impractical because they require infinite time to complete. As such, we illustrate the practical minimum energy consumption of RO and ED for single and multistage configurations. Single-stage RO and ED consume much more energy than the thermodynamic minimum Gibbs free energy of separation, whereas multistage operation decreases energy consumption to approach the thermodynamic minimum with increasing number of stages. Multistage configuration, however, will significantly increase capital cost, thereby demonstrating a trade-off between energy consumption and capital cost. The energy consumption analysis and discussion provided here supplies students with an understanding of the energy consumption of various desalination processes while reinforcing concepts from thermodynamics, transport phenomena, and process design. To teach this content in the classroom, instructors may use the lecture slides available in the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available at https://pubs.acs.org/doi/10.1021/acs.jchemed.0c01194.

Effect of solution activity on the equilibrium driving force for desalination; nomenclature (PDF)

Lecture slides (PDF)

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Notes

The authors declare no competing financial interest.

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