IMPROVING THE THERMODYNAMIC AND ECONOMIC EFFICIENCIES OF DESALINATION PLANTS: MINIMUM WORK REQUIRED FOR DESALINATION AND CASE STUDIES OF FOUR WORKING PLANTS

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Yunus Cerci, Yunus Cengel, Byard Wood, Nafiz Kahraman, and E. Sinan Karakas

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Reverse osmosis, distillation, and freeze desalination processes were analyzed using the first and second-laws of thermodynamics with particular attention to the minimum separation work requirement and the flow exergy. The minimum work for complete separation was investigated by first considering reversible processes for which entropy generation and exergy destruction are zero. Minimum work relations for complete separation of mixtures were obtained and presented in various convenient forms. These relations were later employed to develop the minimum separation work for incomplete separation of saline water solution encountered in desalination plants. The minimum work input was determined for various salinities of incoming saline water and outgoing brine and product water, and the results were tabulated and plotted. The minimum work values show that a lower and an upper limit for the minimum work exist at corresponding recovery ratios of 0 percent and 100 percent. The plots of the minimum work versus recovery ratio at various salinities of the incoming saline water also show that there is an optimum value of the recovery ratio which decreases with increasing salinity. Using reverse osmosis, distillation, and freeze desalination processes, it is shown that the minimum separation work is independent of any hardware or process and thus the same for all processes.

Next, the exergy analysis of typical ideal and actual desalination processes was conducted together with the discussion of the minimum separation work requirement. The exergy changes of major components were calculated and illustrated using exergy flow diagrams for four desalination systems using actual plant operation data. Three systems were part of a brackish water desalination plant in California that incorporates RO (reverse osmosis), NF (nano-filtration), and EDR (electrodialysis reversal) units. Each unit produces about one million gallons of fresh water per day. The fourth plant is located near the city of Al-Jubail at the Arabian Gulf coast. This MSF (multi-stage flash) plant consists of 40 distillation units, and each unit consists of 22 flashing stages. The plant is capable of producing distilled water at a rate of 230 million gallons per day. Exergy flow rates were evaluated throughout the plant, and the exergy flow diagrams were prepared. The rates of exergy destruction and their percentage were indicated on the diagram so that the locations of highest exergy destruction could easily be identified. The analysis showed that most exergy destruction occurs in the pump/motor and the separation units. The fraction of exergy destruction in the pump/motor units is 39.7 percent for the RO unit, 23.6 percent for the NF unit, 54.1 percent for the EDR unit and 78 percent for the MSF unit. Therefore, using high-efficiency pumps and motors equipped with VFD drives can reduce the cost of desalination significantly. The second-law efficiencies for these systems were: 8.0 percent for the RO unit, 9.7 percent for the NF unit, 6.3 percent for the EDR unit, and 4 percent for the MSF unit. These very low efficiencies indicate that there are major opportunities in the plant to improve thermodynamic performance by reducing exergy destruction and thus the amount of energy supplied, making the operation of the plant more cost effective.

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Mission Statements

U.S. Department of the Interior

The mission of the Department of the Interior is to protect and provide access to our Nation's natural and cultural heritage and honor our trust responsibilities to tribes.

Bureau of Reclamation

The mission of the Bureau of Reclamation is to manage, develop, and protect water and related resources in an environmentally and economically sound manner in the interest of the American public.

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PREFACE

The views and conclusions contained in this document are those of the authors and should not be interpreted as representing the opinions or policies of the U.S. Government. Mention of trade names or commercial products does not constitute their endorsement by the U.S. Government.

The research reported in this document includes the research completed by Dr. Yunus Cerci for his Ph.D. dissertation. As typically is the case, he spent far more labor hours completing the research than he was compensated via this project.

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NOMENCLATURE

a	Specific Helmhotz function, kJ/kmol
C_{ps}	The specific heat of salt, kJ/kmol K
dP	Pressure rise, kPa
EDR	Electrodialysis reversal
f	Fraction of exergy
G	Total Gibbs function, kJ
g	Specific Gibbs function, kJ/kmol
h	Specific enthalpy, kJ/kmol
H	Total enthalpy, kJ
M	Molar mass, kg/kmol
mf	Mass fraction
$\dot{m}$	Mass flow rate, kg/s
MSF	Multi-stage flash distillation
N	Number of moles
$\dot{N}$	Molar flow rate, kmol/s
$\dot{N}_s$	Molar flow rate of salt in incoming saline water, kmol/s
$\dot{N}_w$	Molar flow rate of pure water in incoming saline water, kmol/s
NF	Nano filtration
P	Pressure, kPa
P_o	Incoming saline water pressure, kPa
$\dot{Q}$	Heat transfer rate, Kw
R	Gas constant, kJ/kmol K
R_u	Universal gas constant, kJ/kmol K
RO	Reverse osmosis
S	Total entropy, kJ/kmol K
T	Temperature, K
T_o	Incoming saline water and environment temperature, K
TDS	Total dissolved solids
u	Internal energy, kJ/kmol
v	Specific volume, m^3/kmol
V	Total volume m^3

w	Work per unit mole, kJ/kmol
$\dot{W}$	Power, kW
X	Exergy
x	Mole fraction
x_s	Mole fraction of salt in incoming saline water
x_w	Mole fraction of water in incoming saline water

Greek

μ	Chemical potential, kJ/kmol
η_{II}	Second law efficiency
ψ	Flow exergy, kJ/kmol

Subscripts

m	Incoming saline water
s	Salt
w	Pure water
i	*i*th component
gen	Generation
min	Minimum
product	Product water
rev	Reversible

Superscripts

· (dot)	Quantity per unit time
– (bar)	Quantity per unit mole

1 MINIMUM WORK REQUIRED FOR DESALINATION

1.1 INTRODUCTION

This study is part of an overall effort by the US Bureau of Reclamation to develop more efficient and economical ways of desalination.

The continual research and development of desalination processes have resulted in a variety of commercial desalination methods over the years. These processes can be classified into major and minor desalting processes depending upon their commercial success. The major desalination processes include multi-stage flash distillation, multiple effect distillation, vapor compression, and reverse osmosis, while the minor processes include freezing, solar humidification, and electrodialysis. At present, the multi-stage flash distillation and the reverse osmosis process are the systems of choice for obtaining fresh water from seawater and brackish water (Wangnick, 2000).

An analysis of operating data from several desalination plants in the world revealed that the second-law efficiency of such plants is less than 10 percent, which points out that there may be significant opportunities in such plants for improvements. In contrast, the second-law efficiency of modern power plants is over 50 percent. The second-law analysis of thermodynamics has been used extensively in recent years to identify the sites of greatest losses, and to improve the performance of power plants. This can certainly be done for existing desalination plants. The current second-law efficiency of about 10 percent is relatively low for any engineering system. Experiences from other industries suggest that it should be possible to at least double these values economically. Doubling of the second law efficiencies will result in reducing the current energy usage for desalination by half. Raising the efficiencies to 20 to 40 percent is a very realistic goal since many engineering systems in operation have second-law efficiencies well over 50 percent.

The thermodynamic analysis of ideal desalination processes along with actual plant operational data can be useful to put various desalination techniques in perspective, and the best analytical tool to do this is the second law analysis. Thus the analysis in this report starts from a basic separation process which is the main objective of all desalination process, and conducts a comprehensive analysis using actual operation data from major desalination processes.

1.2 DESALINATION METHODS

There are numerous pilot plant reports and technical publications related to all aspects of desalination processes. Most of these studies were carried out during the 1950s and 1960s, and financed by the Office of Saline Water of the U.S. Department of the Interior as well as several industrial firms. These investigations mostly focused on the design of desalination plants and components, the analysis of advantages and limitations of desalination processes, and the evaluation of experimental and pilot plant data. The review of these studies showed that an intensive study of the basic matter and the minimum separation work of desalination processes were rather meager. The authors found only two papers in the open literature related to the thermodynamic analysis of desalination processes. Dodge and Eshaya (1960) conducted the minimum work analysis of some desalination processes, and Curran (1960) analyzed the minimum work requirements for idealized freezing processes. It appears that no comprehensive study of the minimum work analysis of desalination processes has been published other than these two papers. The second law analysis of desalting plants, on the other hand, seems not to be available, although there are some total energy comparison papers in the literature. The present work emphasizes the minimum work of separation and desalination process as well as the second law analysis of desalination plants.

Desalination methods are numerous, but some of them can be disregarded because they are not well established. The present section gives historical perspective and concept of the main conversion processes such as distillation and reverse osmosis. Freezing is also included, although it is still at the development stage, because it is one of the more interesting methods of desalination.

1.2.1 Distillation

Distillation is a very old technique and dates back more than two thousand years. The historical records show that some civilizations such as Egyptians, Persians, and Greeks studied obtaining fresh water from seawater. Hippocrates, a well-known philosopher, stated that "vapor produced from seawater when condensed is no longer salty" and taught his students the concept of desalting. The Arabs, on the other hand, developed a distiller called "alembic" which was very similar to a single-effect distillation process known today. The alembic was used to refine perfumes and other high value products. Also, sailors in the Mediterranean used distillation to supply the make-up water for ships while at sea. During the 19th century, land-based seawater distillation units installed and differed very little from the marine units. At the beginning of the 20th century, multiple-effect distillation (MED) was the first saline water distillation process to be developed for large scale applications. It was not too long afterwards that during World War II military establishments in arid zones of the world required the further development of desalination of seawater. In the 1950s and 1960s, the work on desalination continued, and the United States spent about $300 million for the development of desalting technologies. These studies resulted in new desalination methods such as vapor compression, reverse osmosis, electrodialysis, and freezing. A world wide survey done in 1997 showed that the world's total desalination capacity was about 6,007 million gallons per day (Wangnick, 1998).

Distillation is a separation process in which a volatile component of a solution is first evaporated and subsequently condensed. It is commonly used in chemical processes as well as desalination, and it is the oldest of all desalting technologies. The separation process for desalination of saline water, in essence, is based on the fact that only pure water is volatile, whereas the salts are not. Therefore, the dissolved salts remain behind as the pure water vapor evaporates. The pure water is first evaporated by the transfer of heat to a body of saline water. Then, the pure water vapor is removed from contact with the saline water it originated from, and condensed by the removal of heat. Thus, the pure liquid water is formed.

In a multiple-effect distillation process, the incoming saline water is heated in the first chamber by an external heat source, and then passed through a series of chambers or "effects". The water vapor given off by the hot saline water is transferred to the second chamber, and condensed on the inside of the tubes, thereby providing heat for the evaporation of the saline water in the second chamber. The hot saline water, on the other hand, is pumped to the second chamber where it is heated by the condensation of the vapor in the tubes. Therefore, the second chamber acts as a condenser for the water vapor produced in the first chamber, and an evaporator for the hot saline water coming from the first. Thus, the water vapor produced in the first chamber is used as heat source for the second chamber and so on. This evaporation-and-condensation process is repeated through several chambers until most of the heat supplied to the first chamber is recovered. The transfer of heat from condensing vapor to the saline water, however, requires that the temperature of the saline water be lower than that of the vapor in the tubes. The temperature of the saline water can be reduced successively by lowering the vapor pressure of the chambers to permit boiling and further evaporation in each chamber. As the saline water progresses through the series of chambers, its temperature decreases progressively. The temperature and pressure of a chamber or effect, therefore, are lower than in the previous one. The pressures in the last stages are usually lower than atmospheric pressure, and thus pumps are required to draw the brine and fresh water from the chambers.

In a multi-stage flash distillation process, the vaporization of saline water is primarily achieved by successively lowered pressures in each stage. The saline water is, of course, heated, but it is not allowed to boil, reducing the precipitation of scale forming materials. The incoming saline water first enters a condenser where it is preheated by condensing water vapor. It then passes into a heater in which its temperature is raised to the boiling point, but since the pressure is maintained at a higher value, no boiling occurs. The pressurized hot saline water is introduced into a chamber where the pressure is sufficiently low to cause an immediate phase change of part of the saline water. Vaporization of part of the water results in a considerable decrease in the remaining water temperature, because the entire amount of phase change heat comes from the remaining water itself. The water vapor is condensed by the incoming saline cold saline water to the heater. Then, the relatively cold saline water enters the next chamber where the pressure is lower than in the previous chamber. Again, some of the water instantly flashes into vapor and the water temperature is reduced. This process is repeated up to 50 stages in a typical multi-stage distillation plant. The water vapor produced in each stage is condensed on the outside of tubes conveying the incoming cold saline water to the heater, resulting in an increase of the temperature of the saline water in each stage before entering the heater. Since in this process the saline water is not boiled, it offers the advantage that scale risks are reduced. Consequently, the multi-stage flash distillation process (MSF) received a wide spread acceptance such that about half of the world's desalting capacity is produced by this process.

The multi-stage flash distillation process requires an external heat source and vacuum pumps to produce pure water. In the vapor compression method, however, only a mechanical compressor is employed to recycle the latent heat from the evaporating side of a tube wall to the condensing side of the same tube. In this process, the water vapor in the evaporator is drawn off by the compressor and compressed to a high pressure. This compression causes the condensation of the vapor that supplies heat for the production of additional vapor from the saline water. The distillate and the brine are cooled further in a heat exchanger in which the incoming saline water is preheated nearly close to its boiling point at the evaporator vapor pressure. This process requires the work input to the compressor rather that heat sources. Most of the energy is consumed by the compressor which not only compresses the vapor but also reduces the vapor pressure in the evaporator. The vapor compression distillation units are usually built in compact sizes and typically powered by diesel engines. These units are generally used on ships, at remote construction sites, and at resort hotels in arid regions of the world. The vapor compression distillation units only account for about 2 percent of the world's desalinated water capacity (Wangnick, 1998).

1.2.2 Reverse Osmosis

Reverse osmosis is a very appealing process of saline water desalination, and is becoming a leading method in the commercial desalination industry. A number of factors have affected the advance of the reverse osmosis process. The foremost is the lower energy consumption of the reverse osmosis plants compared to distillation plants. The reverse osmosis is a semi-permeable membrane process in which pure water from pressurized saline water is separated from the dissolved salts by forcing it to flow through the membrane. Generally speaking, it is the transport of the preferential material through the membrane against the osmotic pressure. Therefore, the reverse osmosis does not deal with heating or phase change which is the chief feature of distillation and freezing desalination processes. The major energy required for desalting in the reverse osmosis process is for pressurizing the incoming saline water.

Before proceeding into the reverse osmosis in detail, it would be better to understand the term "osmosis". Osmosis is a term indicating the spontaneous passage of a liquid from a dilute to a more concentrated solution across a semi-permeable membrane which allows the passage of the solvent but not the solutes. The movement of the liquid takes place in a direction that tended to equalize the concentrations of the liquids on the two sides of the membrane. For instance, the water is transferred through the membrane from the less concentrated solution to the more concentrated one. The transfer of solvent continues until the pressure on the more concentrated solution is large enough to prevent any net transfer of the solvent across the membrane. At equilibrium, the quantity of solvent passing in either direction is equal, which means that there is no net transfer of the solvent. In essence, the phenomenon of osmosis has a great importance in nature, because it is essential to plant and animal life as we know it. The outgrowth of this concept led to the discovery that osmosis could be applied to desalination.

As indicated previously, the osmotic pressure occurs as a result of a semi-permeable membrane between two solutions of different concentrations. If a pressure greater than the osmotic pressure is applied on the more concentrated solution side of the membrane, then solvent starts passing through from the more concentrated solution to the less concentrated one. This reverse phenomenon is the basis of the reverse-osmosis method of desalination. The reverse osmosis is sometimes called "hyperfiltration" and has in the past been referred to as "ultrafiltration". But now that there is an entirely different filtration process called ultrafiltration, it would be confusing to use that term for reverse osmosis. That process does not separate dissolved salts, but only very large molecules small particles. Although there is some resemblance to filtration, there are significant differences between the reverse osmosis and any kind of filtration.

The knowledge of osmotic phenomena dates back to 1748, when Abbe Nollet first discovered diffusion of water through animal membranes (Merten, 1966). It was over a hundred years later that in 1877 Preffer made the first quantitative measurements of osmotic pressure using a membrane made of copper ferrocyanide precipitated in the pores of clay cups. In the late 19th and early 20th centuries, most scientists started looking for theoretical explanations, and a detailed investigation of osmosis was done by H.N. Morse and his co-workers at John Hopkins University, and E.G.J. Hartley in England. A chief part of theoretical development was carried on by van't Hoff with the help of Preffer's experimental results. These studies were really advanced by the work of J.W. Gibbs in thermodynamics, and largely completed by 1920. But in the late 1940s, potable water shortages in some arid locations of the world led researchers to look for ways in which fresh water can be extracted from saline water. Until the 1960s, only a few research projects were funded by the US government. One of these investigations in 1959 by Samuel Yuster and two of his students, Sidney Loeb and Srinivasa Sourirajan at University of California-Los Angeles (UCLA) advanced the seawater conversion technology using artificial cellulose acetate membrane. They produced synthetic membranes which were capable of rejecting salt and passing product water at reasonable flow rates and low pressures. The operating pressures of the membranes ranged from 800 to 1000 lb/in^2 for sea water and 200 to 400 lb/in^2 for brackish water. In 1960, the US Saline Water Conversion laboratory decided to build a small pilot plant in the California town of Colinga using the new UCLA desalination technique. This plant began operation in 1965 and became the world's first commercial reverse osmosis plant. This facility was producing up to 6,000 gallons per day of fresh water from brackish ground water. The second reverse osmosis pilot plant was built in La Jolla, California, and was dealing with the much tougher problem of producing fresh water from seawater. Today, reverse osmosis desalination plants produce about 30 percent of total world's desalination capacity (Wagnick, 1998).

There have been four reverse osmosis module designs: plate-and-frame, tubular, spiral wound, and hollow-fine fiber (Spiegler, 1977). Now however there are only spiral wound reverse osmosis modules made in the U.S. and a hollow fine fiber module made by Torray in Japan. In these design configurations, the most important considerations are the support of membranes, and maintenance of a flow channel on either side of the membrane. The spiral wound configurations use membrane in sheet form folded into envelopes. There is a permeate water carrier inside and a feed channel spacer between envelopes to maintain a flow channel. The open end of each envelop is attached to a perforated central pipe for collecting the fresh water, several envelopes are used to form a spiral of up to 16 in (40 cm) in diameter and 40 or 60 in. in length (101 cm or 152 cm). Up to seven of these modules are inserted into a large pressure vessel in series. The vessels can be staged in a 2-1 array such that 4 vessels feed a second set of two. The second set can treat either the concentrate or the product from the first set either increasing recovery or product water purity. The problem with this design is that the passages for saline water and fresh water are narrow. As much as one third of the energy is used in moving water through the vessels.

The hollow-fine fiber reverse osmosis modules consist of large numbers of hollow-fine fibers of the size of a human hair. The ends of the fibers are bundled together with an epoxy resin forming a tube-end block. The bundle enclosed in a pressure vessel into which saline water is pumped under pressure. The advantages of the hollow-fine fiber are its extremely high membrane surface area to volume ratio, and its competitive manufacturing costs. The comparative surface areas of reverse osmosis membrane modules can be given to be 300 m^2/m^3 for spiral wound assemblies, and 5000 m^2/m^3 for hollow-fine fiber assemblies (Bakish, 1973). The principle disadvantage of hollow-fine fiber assemblies is that the saline water passages between fibers are quite small, and can be easily clogged up by suspended particles present in the saline water. Special care must therefore be taken for the pretreatment of the saline water.

Several theories for the mechanism of the mass transport through membranes have been proposed. The simplest and the most obvious theory is that the membrane functions as a molecular sieve. Sodium and chloride ions are slightly larger than the water molecules. However, the ions would be able to pass through the membrane rather well due to the small difference in size. As a result, the sieve concept appears to be questionable. A second theory suggested by Callendar was that solvent is transmitted through the membrane by means of distillation. That is, the solvent is transported through the membrane as vapor. Currently it is understood that there are two methods of separation acting in concert. Convective transport is similar to the sieving theory in that solvent travels convectively through slightly larger openings in the membrane polymer structure and may take some solute with it. At the same time, both solvent and solute dissolve into the membrane polymer and diffuse to the other side. Separation is due to the slow diffusion rate of ions compared to the solvent.

1.2.3 Freezing

Crystallization is a fairly sophisticated method of separation and purification in a broad variety of industries, and has been utilized for a long time. The crystallization technique is commonly used in the production of electronic materials and in the chemical industry for the purification of many chemicals. The product spectrum may range from basic materials such as sucrose, sugar, and sodium chloride to semi-conductors, ferroelectrics and piezoelectrics. In general, when valuable and temperature susceptible substances are involved, the crystallization becomes an attractive and relevant method of separation and purification. Since the chief purpose of crystallization process is the production of a pure component from solution, crystallization technique can be applied to saline water by crystallizing out the water in the form of ice. This is inevitably the case when a salt solution is cooled to its freezing temperature, the solution deposits ice crystals of pure water. Therefore, freezing is considered to be a means of desalination of saline water. This principle forms the basis for desalting water by the freezing process.

The idea of extracting fresh water from saline water by freezing is not new and has been known for centuries. Some civilizations in the cold and arid zones of the world such as Central Asia, Western Siberia, and Antarctica have practiced the desalination of saline water by freezing. To make their potable water in these regions, they are known to collect sea ice during the winter and use it during the summer. Although this habit has continued for a long time, interest in freezing as a separation process on a large scale began after World War II. One of the earliest investigators of desalination by freezing was Vacino who published a report in 1945 on an experimental plant in Italy. In 1947, Thompson, University of Washington, Seattle, Washington, started working on freeze desalination and his work was followed by Henderickson and Moulton at the same university. These early studies showed that the separation of brine-ice slurry was an important obstacle that needs to be overcome. Then studies were directed towards separation methods in which centrifuging, gravity drainage, filtration, and squeezing are involved. Steinbach carried out experiments concerning the centrifugal separation of ice and brine and published his results in 1951. Nelson and Thompson wrote a paper on obtaining fresh water from cylinders of sea water ice by slow melting in 1954. In the same year, Howe, Sharfer and Mulford published a report on the analysis of vapor compression freezing. In 1955 Curran reported his experimental results on the formation of ice-brine semi solids in a drum freezer on the centrifugal separation of ice and brine. These studies resulted in a considerable amount of theoretical and experimental data on ice formation and separation, and encouraged several industrial firms as well as the Office of Saline Water of the U.S. Department of the Interior to build pilot plants. Carrier Corporation first built a 15,000 gallon per day (435 m^3/day) plant using lithium bromide absorption of the water vapor in 1959, and the plant operated successfully. Then, Struthers Scientific and International Corporation built two pilot plants using the principle of direct contact secondary refrigerant in Wrightsville Beach, N.C. At about the same time other companies such as Blaw-Knox and Fairbanks-Morse, and the several universities were working on respective components of freeze desalination. The Office of Saline Water supported most of the research and development. In the late 1950s, the freeze desalination accounted for about 7 percent of the U.S. total desalinated capacity due to these pilot plants. In the early 1960s, numerous reports on freezing appeared in the literature and various types of freezing processes also proposed. However, none of these processes has proven to economically competitive with other processes. Therefore, today no commercial freeze desalination plant exists.

It is a well-known fact of physical chemistry that when the temperature of a salt solution is reduced to its freezing point, the ice crystals which form in the solution are ideally salt-free. The mechanism of this separation is that when an ice crystal grows from a salt solution, the dissolved salts and other impurities pile up ahead of the advancing solid-liquid interface, and thus provides an excellent means for purifying water. Practically, the separation process is not perfect, and an ice crystal may contain some salt. This is due to either the nature of freezing process or the effects of morphology of the freezing interface. These two aspects may be affected by the salt concentration or the temperature gradient. As an ice crystal grows, the salt solution around the crystal becomes more concentrated than the bulk of brine and causes different morphological effects. A smooth solid-liquid interface, for example, may turn into a rough one. If the temperature difference between the crystal and its surroundings is very large, a smooth solid-liquid interface is lost, and dendritic growth of the ice crystal occurs. The dendritic crystals are broken into numerous small fragments which act as nuclei for ice crystals. Although the dendritic formation of ice crystal increases the ice crystal growth, the dendritic morphology provides excellent conditions for the entrapment of brine between ice crystals. Experimental studies showed that the temperature difference should be lower than 0.2 ºC to prevent the dendritic formation of ice crystals.

The low temperatures provide obvious advantages of the freezing method over other desalination techniques. The risk of scaling and corrosion is greatly reduced due to the relatively low temperatures involved in the freezing method. The low temperature also allows the use of lower-cost construction materials and equipment, and thus reduces capital investment for the freezing processes. Although the freezing method eliminates problems commonly encountered in other methods, it has the inherent problem of separating the ice crystals from the brine. Several methods such as centrifugation, compression, and counter-current washing have been developed to separate ice from brine in the freeze desalination processes, but none of the separation methods were entirely satisfactory. Experimental studies showed that the cost of fresh water could be substantial due to the cost of and difficulty of the separation.

The common freeze desalination methods are vacuum-freezing vapor compression, secondary refrigerant freezing, and vapor absorption freezing. They have essentially the same components, but differing only in the method by which freezing is accomplished. The incoming saline water first enters a heat exchanger in which it is cooled to about its freezing temperature by heat exchange with the outgoing waste brine and fresh water streams. The relatively cold saline water is then introduced into a freezer where the different types of freezing are accomplished as explained previously. The slurry of ice crystals and brine is pumped to a wash column. In the wash column, the ice crystals are separated from the brine and compacted into an ice bed and washed with about 5 percent of the fresh water produced. While the waste brine is routed to the heat exchanger, the ice crystals are transferred to a melter where they absorb their latent heat of fusion from the heat pumped from the freezer, and become liquid fresh water. The fresh water leaves the system through the heat exchanger.

In a vacuum-freezing vapor compression process, the saline water is passed through a de-aerator that removes air and dissolved gasses. The de-aerated water flows through a heat exchanger where the saline water is pre-cooled by heat exchange with the product water and waste-brine streams. The saline water is almost cooled to its freezing point and then sprayed into a freezing chamber which is maintained at a low pressure. Due to the low pressure, a portion of the saline water immediately flashes into vapor and removes the latent heat of fusion from the remaining water. Since the freezing chamber is well-insulated, the heat of vaporization comes from only the body of the water itself, and the saline water cools down and eventually freezes. Approximately, 7.5 kg of ice are frozen for each kilogram of vapor produced. The slurry, or mixture, of ice crystals and brine leaves the freezing chamber, and then is introduced into the bottom of a counter washer (a separation column). The slurry flows upward within the counter washer and the ice crystals consolidate forming a porous bed of ice. At about the middle of the counter washer, the brine flows horizontally through the bed and outward through the screens. The rising ice bed continues vertically past the screens and meets a countercurrent stream of wash water which removes adhering brine. The amount of wash water is usually less than 5 percent of the total fresh water product. The wash water leaves the counter washer with the brine. The ice bed is removed by a scraper at the top of the column, and the scrapings are transferred to a melter. The water vapor, on the other hand, is compressed by a mechanical compressor, and introduced into the melter where it comes into contact with the ice from the counter washer. In the melter, as heat is transferred from the vapor to the ice crystals, the ice is melted and the vapor is condensed to form the fresh water. The concentrated brine from the counter washer is discharged from the process to waste disposal.

The vacuum-freezing vapor compression process requires leak free large installations at low pressure. Technical difficulties arising from the high vacuum conditions can be eliminated by using an immiscible refrigerant other than water. A suitable secondary refrigerant such as isobutane or octafluorocyclobutane evaporates in direct contact with the saline water, thus removing the latent heat of crystallization and causing some of the water to freeze. This method was first proposed by H.F. Wiegant at Cornell University in 1963 and so-called the secondary-refrigerant freezing process. In this process, the incoming saline water is pre-cooled by a heat exchanger where sensible heat is removed by heat exchange with cold waste brine and cold fresh water product. The saline water leaves the heat exchanger at about its freezing temperature and enters a freezer where liquid refrigerant is dispersed in the saline water. The refrigerant flashes into vapor and lowers the saline water temperature. As the temperature drops, salt-free ice crystals are formed in concentrated saline water. The ice-brine slurry is then transferred to a washer-melter where the ice is separated and washed. The slurry moves upward in the column and the brine leaves the washer through screens on the wall. The ice crystals form a porous bed of ice and are pushed upward by the brine flowing through the bed. The porous bed of ice is washed with about 5 percent of the desalted water produced in the system. The ice is then removed into a melting section where the compressed refrigerant vapor comes into contact with it. The compressed vapor which contains the heat removed to form ice condenses on the ice, giving up its latent heat and melting the ice. The condensed refrigerant and the fresh water are pumped to a decanter where the two liquids are separated. The fresh water leaves the process through the heat exchanger, and the liquid refrigerant is returned to the freezer. The chief energy consumer of this system is a compressor which is used to compress the refrigerant.

The vapor absorption freezing process is similar to the vacuum freezing vapor compression process except that the water vapor is absorbed rather than compressed. The idea of the vapor absorption for freezing was first developed and tested by the Carrier Corporation at Syracuse, New York in the late 1950s. A 15,000 gallon per day (435 m^3/day) pilot plant using lithium bromide absorption system was built in 1959 and operated without any major problem. As in the previous freezing methods, the incoming saline water is first pre-cooled by heat exchange with the outgoing waste brine and product water streams. The cold saline water is dispersed by spray nozzles into a freezing chamber. Part of the saline water evaporates due to absorbent in the chamber and thereby reduces the temperature of the remainder, forming salt-free ice crystals in the brine. The ice crystals and residual brine leave the freezer and enter the wash column. The ice crystals are separated from the brine as described in the other freeze desalination methods and the crystals are washed with about 5 percent of the previously made freshwater. Then, the ice crystals are routed to a melter where they are melted by warm desalted water coming from an absorber and a generator. In the absorber, the water vapor originated from the freezer is absorbed by an absorbent such as lithium bromide. The dilute absorbent is passed trough a heat exchanger to the generator where it is heated. In this way, the water vapor is driven out of the absorbent and condensed by the cold incoming saline water. The condensed vapor is used to melt the ice crystals in the melter and becomes part of the desalted water. The concentrated absorbent is transferred through the heat exchanger to the absorber. As noticed in the system, the major amount of energy in the form of heat is supplied to the generator, and removed in the condenser by the incoming saline water.

1.3 THERMODYNAMIC ANALYSIS

This section starts with a second-law analysis of separation processes of mixtures, and continues with the discussion of the minimum work input needed for separation. Then, the minimum separation work is extended to reverse osmosis, distillation, and freezing processes that involve an incomplete separation.

1.3.1 Technical Background

A desalination plant essentially separates incoming saline water into product water and brine. The product water contains a low concentration of dissolved salts and the brine contains the remaining high concentration of dissolved salts. The plant, of course, requires the expenditure of a certain amount of energy in the form of either heat or work, and can use several different processes for the separation. Dodge and Eshaya (1960) studied the thermodynamic analysis of some desalting processes and carried out the minimum separation work relations using two different methods. Curran (1960), on the other hand, developed the minimum work relations for four idealized freezing processes. A review of both papers will be given in this section.

Dodge and Eshaya (1960) employed two methods to determine the minimum separation work of saline water. They first considered the removal of pure water from a certain amount of saline water. Utilizing the well-known Gibbs function and ideal gas relation, they derived the minimum separation work. The work relation obtained was dependent on the initial and final number of moles of saline solution, the universal gas constant, the separation temperature, and the activity of water in the saline solution. The term “activity” used in the paper refers to the mole fraction which is a common term in chemical science. The minimum separation work required to extract pure water from a 3.5 percent NaCl solution at 25 C was calculated for different recovery ratios. The authors pointed out that the minimum separation work at negligible recovery ratio is unrealistic since it is based on a very small amount of pure water extraction from a large amount of saline water. They also noted that the pumping energy is a significant fraction of the power required. The minimum separation work values at 50 percent recovery were also listed at different head losses and pump efficiencies. Later, they carried out the minimum separation work relation a step further and developed a general work relation. Employing the chemical potential and Gibbs functions, they obtained the general minimum work relation which is similar to the equation found by Cerci et al. (1999), i.e.

$$W = -RT \ln a \tag{1.1}$$

where R is the universal gas constant, T is the temperature at which the separation takes place, a is the activity of water in the brine stream.

The general work relation was simplified for a special case that corresponds to the production of pure water as product. Since the equation involved the activity of water and salt, they had to modify activity coefficients for the special case. Using the simplified equation, the minimum separation work values at recovery ratios of 50 percent and 90 percent were calculated. For a recovery ratio of 0 percent, they stated that the equation was indeterminate. However, for recovery ratios higher than 0 percent the minimum separation value showed good agreement with those obtained using Eq. (1.1).

Dodge and Eshaya (1960) concluded that there is essentially no difference between the minimum work requirements for a distillation and a freezing process, and thus these processes including all desalination techniques require the same amount of minimum work input. They also pointed out that the minimum separation work input is not a unique quantity but depends on certain variables such as temperatures, salinities, and recovery ratios. The authors, on the other hand, gave no details on the derivation of the minimum separation work relations and did not discuss the restrictions of them. For instance, Eq. 1.1 was put forward without derivation and directly applied to a range from 0 to 100 percent recovery, although it is not applicable to every recovery ratio. Yet, the minimum separation work values were given as a function of recovery ratios, but the description of the recovery ratio was not stated clearly. Therefore, the analysis of the minimum separation work was not very determinate, and thus they created a source of confusion.

Curran (1960), on the other hand, investigated the minimum work requirement for idealized freezing process utilizing Carnot refrigerators. Main assumptions, freezing point depression, and the description of the recovery ratio were given first, and then the analysis of the minimum work was presented. Four types of freezing processes were proposed and their minimum work requirement relations were derived. The freezing processes and the minimum work derivation were discussed in sufficient detail, but they were somewhat unclear. The relations for the proposed idealized freezing processes were entirely different from one another. Therefore, these results created another source of confusion, because Dodge and Eshaya (1960) stated that all desalination processes require the same amount of minimum work input regardless of process type.

In this work, the authors attempt to end the confusion by considering a general desalination process, and determining the minimum work using a fundamental approach based on the second-law of thermodynamics. The relation developed is applicable for all recovery ratios and all salinities of incoming and outgoing streams.

1.3.2 Second Law Analysis of Separation Processes of Mixtures

Mixing and separation processes are commonly encountered in a wide range of industries in practice. Separation processes require a work input (or, more generally, exergy). Minimizing this required work input is an important part of the design process of separation plants. The presence of dissimilar molecules in a mixture affect each other, and therefore the influence of composition on the properties must be taken into consideration in any thermodynamic analysis. We will first analyze the general mixtures and the mixing processes, with particular attention to ideal solutions, and determine the entropy generation and exergy destruction. We then consider the reverse process of separation, and determine the minimum (or reversible) work input needed for separation. We show sufficient detail to enable the reader to follow the procedure with relative ease. The results presented can readily be used in the calculation of minimum work input and the determination of the second law efficiency of separation processes.

The specific Gibbs function (or Gibbs free energy) *g* is defined as the combination property $g = h - Ts$. Using the relation $dh = vdP - Tds$, the differential change of the Gibbs function of a pure substance (a substance that has a fixed chemical composition) is obtained by differentiation to be

$$dg = vdP - sdT \qquad \text{or} \qquad dG = VdP - SdT \qquad \text{(pure substance)} \tag{1.2}$$

The second relation is in term of the total properties. For a mixture, the total Gibbs function is a function of two independent intensive properties as well as the composition, and can be expressed as $G = G(P, T, N_1, N_2, ...N_i)$. Its differential is (Bejan, 1997)

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,N} dP + \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \sum_i \left(\frac{\partial G}{\partial N_i}\right)_{P,T,N_j} dN_i \qquad \text{(mixture)} \tag{1.3}$$

where the subscript N_j indicates that the mole numbers of all components in the mixture other than component *i* are to be held constant during differentiation. For a pure substance, the last term drops out since the composition is fixed, and the equation above must reduce to the one for a pure substance. Then comparing Eqs. (1.2) and (1.3) gives

$$dG = VdP - SdT + \sum_i \mu_i dN_i \qquad \text{(mixture)} \tag{1.4}$$

The relation above can also be expressed on a per unit mole basis by dividing both sides by the total number of moles of the mixture N_m. It gives

$$dg = vdP - sdT + \sum_i \mu_i dx_i \qquad \text{(mixture - per unit mole of mixture)} \tag{1.5}$$

where $x_i = N_i / N_m$ is the mole fraction of component *i*. The intensive property

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{P,T,N_j} = \bar{g}_i = \bar{h}_i - T\bar{s}_i \qquad \text{(component } i \text{ of a mixture)} \tag{1.6}$$

is called the "chemical potential", which is of great value in the analysis of mixtures. It represents the change in the Gibbs function of the mixture in a specified phase when a unit amount of component i in the same phase is added as pressure, temperature, and the amounts of all other components are held constant. Note that the summation term in Eq. (1.4) is zero for a system of fixed composition, and thus the chemical potential has no value for such systems. For a pure (or a single component) system in a given phase, the chemical potential is equivalent to the molar Gibbs function since $G = Ng = N\mu$ where

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{P,T} = g = h - Ts \qquad \text{(pure substance)} \tag{1.7}$$

Therefore, the difference between the chemical potential and the Gibbs function is due to the effect of dissimilar molecules in a mixture on each other. It is because of this molecular effect that the volume of the mixture of two miscible liquids may be more or less than the sum of the initial volumes of the individual liquids. Likewise, the total enthalpy of the mixture of two components at the same pressure and temperature, in general, is not equal to the sum of the total enthalpies of the individual components before mixing, the difference being the enthalpy (or heat) of mixing, which is the heat released or absorbed as two or more components are mixed isothermally. For example, the volume of an ethyl alcohol - water mixture is a few percent less than the sum of the volumes of the individual liquids before mixing. Likewise, when water and flour are mixed to make dough, the temperature of the dough rises noticeably due to the heat of mixing released.

For reasons explained above, the partial molar properties of the components (denoted by an overbar, such as $\bar{v}, \bar{h}, \text{and } \bar{s}$) should be used in the evaluation of the extensive properties of a mixture (such as *V, H,* and *S*) instead of the specific properties of the pure components (denoted without an overbar, such as *v, h,* and *s*). For example, the total volume, enthalpy, and entropy of a mixture should be determined from, respectively,

$$V = \sum_i N_i \bar{v}_i \,, \qquad H = \sum_i N_i \bar{h}_i \,, \quad \text{and} \quad S = \sum_i N_i \bar{s}_i \qquad \text{(mixture)} \tag{1.8}$$

in stead of

$$V^* = \sum_i N_i v_i \,, \qquad H^* = \sum_i N_i h_i \,, \quad \text{and} \quad S^* = \sum_i N_i s_i \tag{1.9}$$

Then the changes in these extensive properties during mixing become

$$\Delta V_{\text{mixing}} = \sum_i N_i(\bar{v}_i - v_i)\,,\ \Delta H_{\text{mixing}} = \sum_i N_i(\bar{h}_i - h_i)\,, \text{ and } \Delta S_{\text{mixing}} = \sum_i N_i(\bar{s}_i - s_i) \tag{1.10}$$

where ΔH_{mixing} is the enthalpy of mixing and ΔS_{mixing} is the entropy of mixing. The enthalpy of mixing is positive for exothermic mixing processes, negative for endothermic mixing processes, and zero for isothermal mixing processes during which no heat is absorbed or released. Note that mixing is an irreversible process, and thus the entropy of mixing must be a positive quantity during an adiabatic process.

The specific volume, enthalpy, and entropy of a mixture are determined from

$$v = \sum_i x_i \bar{v}_i \,,\ h = \sum_i x_i \bar{h}_i \,, \text{ and } s = \sum_i x_i \bar{s}_i \tag{1.11}$$

The combination properties such as enthalpy and Gibbs function for a homogeneous mixture are also expressed in terms of the partial molar properties as

$$\bar{h}_i = \bar{u}_i + P\bar{v}_i \quad \text{and} \quad \bar{g}_i = \bar{h}_i - T\bar{s}_i = \mu_i \tag{1.12}$$

1.3.3 Ideal Solutions

When the effect of dissimilar molecules in a mixture on each other is negligible, the mixture is said to be an "ideal mixture" or "ideal solution," and the chemical potential of a component in such a mixture is simply taken to be the Gibbs function of the pure component. A more formal definition of ideal solutions will be given later in the analysis. Many liquid solutions encountered in practice, satisfy this condition very closely, and can be considered to be ideal solutions with negligible error. As expected, the ideal solution approximation greatly simplifies the thermodynamic analysis of mixtures, as shown below.

Reconsider Eq. (1.4) for dG. Note that properties are point functions, and they have exact differentials. Therefore, the test of exactness can be applied to the right-hand side of Eq. (1.4) to obtain some important relations. Recall that for the differential $dz = Mdx + Ndy$ of a function $z(x, y)$, the test of exactness is expressed as

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \tag{1.13}$$

For P = constant and N_j = constant, Eq. (1.3) simplifies to

$$dG = -SdT + \mu_i dN_i \tag{1.14}$$

Also, for T = constant and N_j = constant, it simplifies to

$$dG = VdP + \mu_i dN_i \tag{1.15}$$

Applying the test of exactness to both of these relations gives

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} = -\left(\frac{\partial S}{\partial N_i}\right)_{T,P,N_j} = -\bar{s}_i \tag{1.16}$$

and

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_j} = \bar{v}_i \tag{1.17}$$

where the subscript N indicates that the mole numbers of all components (and thus the composition of the mixture) is to remain constant. Taking the chemical potential of a component to be a function of temperature, pressure, and composition and thus $\mu_i = \mu_i(P, T, x_1, x_2, ...x_j)$, its total differential can be expressed as

$$d\mu_i = d\bar{g}_i = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,x_i} dP + \left(\frac{\partial \mu_i}{\partial T}\right)_{P,x_j} dT + \sum_i \left(\frac{\partial \mu_i}{\partial x_i}\right)_{P,T,x_j} dx_i \tag{1.18}$$

Substituting Eqs. (1.16) and (1.17) into the above relation gives

$$d\mu_i = \bar{v}_i dP - \bar{s}_i dT + \sum_i \left(\frac{\partial \mu_i}{\partial x_i} \right)_{P,T,x_j} dx_i \tag{1.19}$$

For a mixture of fixed composition undergoing an isothermal process, the differential change of the chemical potential given above simplified to

$$d\mu_i = \bar{v}_i dP \qquad (T = \text{constant},\ x_\text{i} = \text{constant}) \tag{1.20}$$

For an ideal gas mixture, the partial molar volume of a component *i* is $\bar{v}_i = R_u T / P$. Substituting this relation into Eq. (1.20) gives

$$d\mu_i = \frac{R_u T}{P} dP = R_u T d \ln P = R_u T d \ln P_i \qquad (T = \text{constant},\ x_\text{i} = \text{constant, ideal gas}) \tag{1.21}$$

since, from Dalton's law of additive pressures, $P_\text{i} = x_\text{i} P$ for an ideal gas mixture, and

$$d \ln P_i = d \ln(x_i P) = d(\ln x_i + \ln P) = d \ln P \qquad (x_\text{i} = \text{constant}) \tag{1.22}$$

Integrating this relation at constant temperature from the total mixture pressure *P* to the component pressure P_i of component *i* gives

$$\mu_i(T, P_i) = \mu_i(T, P) + R_u T \ln \frac{P_i}{P} = \mu_i(T, P) + R_u T \ln x_i \qquad \text{(ideal gas)} \tag{1.23}$$

For $x_\text{i} = 1$ (i.e., a pure substance of component *i* alone), the last term in the above equation drops out and we end up with $\mu_i(T, P_i) = \mu_i(T, P)$, which is the value for the pure substance *i*. Therefore, the term $\mu_i(T, P)$ is simply the chemical potential of the pure substance *i* when it exists alone at total mixture pressure and temperature. Note that this is equivalent to the Gibbs function since the chemical potential and the Gibbs function are identical for pure substances. Also note that the term $\mu_i(T, P)$ is independent of mixture composition and mole fractions, and its value can be determined from the property tables or charts of that pure substance. Then Eq. (1.23) can be rewritten more explicitly as

$$\mu_{i,\text{mixture, ideal}}(T, P_i) = \mu_{i,\text{pure}}(T, P) + R_u T \ln x_i \qquad \text{(ideal gas)} \tag{1.24}$$

Note that the chemical potential of a component of an ideal gas mixture depends on the mole fraction of the components as well as the mixture temperature and pressure, and is independent of the identity of the other constituent gases. This is not surprising since the molecules of an ideal gas behave like they exist alone, and are not influenced by the presence of other molecules.

Equation (1.24) is developed for an ideal gas mixture, but it is also applicable to mixtures or solutions that behave the same way - that is, mixtures or solutions in which the effects of molecules of different components on each other are negligible. The class of such mixtures is called "ideal solutions" (or ideal mixtures), as discussed above. The ideal gas mixture described above is just one category of ideal solutions. Another major category of ideal solutions is the dilute liquid solutions, such as the saline water.

It can be shown that the heat of mixing and the volume change due to mixing are zero for ideal solutions (Wark, 1995). That is,

$$\Delta V_{\text{mixing,ideal}} = \sum_i N_i(\bar{v}_i - v_i) = 0 \qquad \text{(ideal solution)} \qquad (1.25)$$

and

$$\Delta H_{\text{mixing, ideal}} = \sum_i N_i(\bar{h}_i - h_i) = 0 \qquad \text{(ideal solution)} \qquad (1.26)$$

Then it follows that $\bar{v}_i = v_i$ and $\bar{h}_i = h_i$. That is, the partial molar volume and the partial molar enthalpy of a component in a solution equal the specific volume and enthalpy of that component when it existed alone as a pure substance at the mixture temperature and pressure. Therefore, the specific volume and enthalpy of individual components do not change during mixing if they form an ideal solution. Then the specific volume and enthalpy of an ideal solution can be expressed as

$$v_{\text{mixture, ideal}} = \sum_i x_i \bar{v}_i = \sum_i x_i v_{i,\text{pure}} \qquad \text{(ideal solution)} \qquad (1.27)$$

and

$$h_{\text{mixture, ideal}} = \sum_i x_i \bar{h}_i = \sum_i x_i h_{i,\text{pure}} \qquad \text{(ideal solution)} \qquad (1.28)$$

Note that this is not the case for entropy and the properties that involve entropy such as the Gibbs function, even for ideal solutions. To obtain a relation for the entropy of a mixture, we differentiate Eq. (1.24) with respect to temperature at constant pressure and mole fraction,

$$\left(\frac{\partial \mu_{i,\text{mixture}}(T,P_i)}{\partial T}\right)_{P,x} = \left(\frac{\partial \mu_{i,\text{pure}}(T,P)}{\partial T}\right)_{P,x} + R_u \ln x_i \qquad (1.29)$$

We note from Eq. (1.16) that the two partial derivatives above are simply the negative of the partial molar entropies. Then substitution gives

$$\bar{s}_{i,\text{mixture, ideal}}(T,P_i) = s_{i,\text{pure}}(T,P) - R_u \ln x_i \qquad \text{(ideal solution)} \qquad (1.30)$$

Note that ln x_i is a negative quantity since $x_i < 1$, and thus $-R_u$ ln x_i is always a positive quantity. Therefore, the entropy of component in a mixture is always greater than the entropy of that component when it existed alone at the mixture temperature and pressure. Then the entropy of mixing of an ideal solution is determined by substituting Eq. (1.30) into Eq. (1.10) to be

$$\Delta S_{\text{mixing, ideal}} = \sum_i N_i(\bar{s}_i - s_i) = -R_u \sum_i N_i \ln x_i \qquad \text{(ideal solution)} \qquad (1.31a)$$

The entropy of mixing per unit mole of the mixture is obtained by dividing by the total number of moles of the mixture N_m to be

$$\Delta s_{\text{mixing, ideal}} = \sum_i x_i(\bar{s}_i - s_i) = -R_u \sum_i x_i \ln x_i \qquad \text{(per unit mole of mixture)} \qquad (1.31b)$$

Noting that the entropy balance for a steady flow system is expressed as (Cengel and Boles, 1998)

$$\underbrace{S_{\text{in}} - S_{\text{out}}}_{\text{by heat and mass}} + S_{\text{gen}} = \Delta S_{\text{system}} /^{0} = 0 \qquad \text{(steady)} \qquad (1.32)$$

and entropy can be transferred by heat and mass only, the entropy generation during an adiabatic mixing process that forms an ideal solution becomes

$$S_{\text{gen, ideal}} = S_{\text{out}} - S_{\text{in}} = \Delta S_{\text{mixing, ideal}} = -R_u \sum_i N_i \ln x_i \qquad \text{(ideal solution)} \tag{1.33a}$$

and $$s_{\text{gen, ideal}} = s_{\text{out}} - s_{\text{in}} = \Delta s_{\text{mixing, ideal}} = -R_u \sum_i x_i \ln x_i \text{ (per unit mole of mixture)} \tag{1.33b}$$

Then noting that $X_{\text{destroyed}} = T_0 S_{\text{gen}}$, the exergy destroyed during this process (and any other process) is obtained by multiplying the entropy generation by the temperature of the environment T_0. It gives

$$X_{\text{destroyed, ideal}} = T_0 S_{\text{gen, ideal}} = -R_u T_0 \sum_i N_i \ln x_i \qquad \text{(ideal solution)} \tag{1.34a}$$

and $$x_{\text{destroyed, ideal}} = T_0 s_{\text{gen, ideal}} = -R_u T_0 \sum_i x_i \ln x_i \quad \text{(per unit mole of mixture)} \tag{1.34b}$$

The exergy destruction represents the wasted work potential - the work that could have been produced but wasn't. For a "reversible" or "thermodynamically perfect" process, the entropy generation and thus the exergy destroyed is zero. Also, for reversible processes, the work output is a maximum (or, the work input is a minimum if the process does not occur naturally and requires input). The difference between the reversible work and the actual useful work is due to irreversibilities, and is equal to the exergy destruction. Therefore, $X_{\text{destroyed}} = W_{\text{rev}} - W_{\text{actual}}$. Then it follows that for a naturally occurring process during which no work is produced, the reversible work is equal to the exergy destruction. Therefore, for the adiabatic mixing process that forms an ideal solution, the reversible work is, from Eq. (1.34),

$$W_{\text{rev, ideal}} = -R_u T_0 \sum_i N_i \ln x_i \qquad \text{(ideal solution)} \tag{1.35a}$$

and $$w_{\text{rev, ideal}} = -R_u T_0 \sum_i x_i \ln x_i \qquad \text{(per unit mole of mixture)} \tag{1.35b}$$

A reversible process, by definition, is a process that can be reversed without leaving any trace in the surroundings. This requires that when a process is reversed, the direction of all interactions be reversed, but their numerical values remain unchanged. Therefore, when a mixing process is reversed, we have a separation process, and the reversible work output given in Eq. (1.35) becomes the reversible work input. This is the minimum work input required for the separation process, and is expressed as

$$W_{\text{rev, ideal}} = -R_u T_0 \sum_i N_i \ln x_i \qquad \text{(ideal solution)} \quad \text{(in kJ)} \tag{1.36a}$$

and

$$w_{\text{min, in}} = -R_u T_0 \sum_i x_i \ln x_i \qquad \text{(per unit mole of mixture, in kJ/kmol)} \tag{1.36b}$$

It can also be expressed in the rate form as

$$\dot{W}_{\text{min, in}} = -R_u T_0 \sum_i \dot{N}_i \ln x_i = -\dot{N}_m R_u T_0 \sum_i x_i \ln x_i \qquad \text{(in kW)} \qquad (1.36c)$$

where $\dot{W}_{\text{min, in}}$ is the minimum power input required to separate a solution that approaches at a rate of $\dot{N}$ kmol/s into its components. Noting that the mass and mole flow rates are related to each other by $\dot{m} = \dot{N}M$ where M is the apparent molar mass of the mixture, Eq. (1.36c) can be expressed in alternative forms using mass flow rates. Further, Eq. (1.36) can also be expressed in terms of the mass fractions mf_i by converting the mole fractions x_i to mass fractions using appropriate relations, as shown below.

1.3.4 Using Mass Fractions instead of Mole Fractions

The molar mass of a substance M is the mass of a unit mole of that substance, and mass m and the mole numbers N of a system are related to each other by $m = NM$. Then the relation between the mass and mole fractions of a component i is determined to be

$$mf_i = \frac{m_i}{m_m} = \frac{N_i M_i}{N_m M_m} = x_i \frac{M_i}{M_m} \qquad (1.37)$$

where the apparent molar mass of the mixture is

$$M_m = \frac{m_m}{N_m} = \frac{\sum N_i M_i}{N_m} = \sum_i \frac{N_i M_i}{N_m} = \sum_i x_i M_i \qquad (1.38)$$

Noting that the gas constant of a substance i is related to the universal gas constant R_u by $R_i = R_u/M_i$, the substitution of mf_i relation into Eq. (1.36) and dividing the result by the molar mass of the mixture M_m (to obtain the minimum work per unit mass instead of per unit mole) yields

$$\dot{W}_{\text{min, in}} = -\dot{m}_m T_0 \sum_i R_i mf_i \ln\left(mf_i \frac{M_m}{M_i} \right) \qquad \text{(ideal solution)} \quad \text{(in kW)} \qquad (1.39a)$$

and $$w_{\text{min, in}} = -T_0 \sum_i R_i mf_i \ln\left(mf_i \frac{M_m}{M_i} \right) \qquad \text{(per unit mass of mixture, in kJ/kg)} \qquad (1.39b)$$

Note that the relations obtained using mass fractions are more cumbersome. Therefore, it is more convenient to work with mole fractions, and, if desired, to express the results per unit mass basis by dividing by the apparent molar mass of the mixture.

1.3.5 Alternative Approach: Exergy Balance

The work potential of a flow stream is simply its flow exergy, ψ. When the kinetic and potential energies are negligible, the flow exergy is expressed on a unit mole basis as $\psi_i = (h_i - h_0) - T_0(s_i - s_0)$. Taking the final state to be the "pure state" (and thus using pure substance properties) and the initial state to be the state in the mixture (and thus using partial molar properties), the exergy change during the separation per unit mole of a component i becomes

$$\begin{aligned}\Delta\psi_i &= \psi_{i,\text{pure}} - \bar{\psi}_{i,\text{mixture}} \\ &= [(h_i - h_0) - T_0(s_i - s_0)] - [(\bar{h}_i - h_0) - T_0(\bar{s}_i - s_0)] \\ &= (h_i - \bar{h}_i) - T_0(s_i - \bar{s}_i) \\ &= T_0(\bar{s}_i - s_i)\end{aligned} \qquad \text{(ideal solution)} \tag{1.40}$$

where we have utilized the ideal solution approximation by taking the enthalpy of mixing to be zero.

The minimum work (or power) input relations can be obtained from an exergy balance performed on the separation chamber as an ideal solution undergoes a reversible adiabatic isothermal process steadily. The general exergy balance in this case simplifies to (Cengel and Boles, 1998)

$$\underbrace{X_{\text{in}} - X_{\text{out}}}_{\text{by heat, work, and mass}} - X_{\text{destroyed}}\,/^{0} = \Delta X_{\text{system}}\,/^{0} = 0 \tag{1.41}$$

Noting that the process is reversible (no exergy destruction), steady (no change in the exergy of the system), and adiabatic (no exergy transfer by heat), and noting that the exergy input by work is simply the work input, the relation above simplifies to

$$W_{\text{min, in}} + X_{\text{in, by mass}} - X_{\text{out, by mass}} = 0 \tag{1.42}$$

Rearranging and substituting the exergy change relation from Eq. (1.40) gives

$$\begin{aligned}W_{\text{min, in}} &= X_{\text{out, by mass}} - X_{\text{in, by mass}} \\ &= X_{\text{pure}} - X_{\text{mixture}} = \Delta X_{\text{separation}} \\ &= \sum_i N_i(\psi_{i,\text{pure}} - \bar{\psi}_{,\text{mixture}i}) \\ &= \sum_i N_i T_0(\bar{s}_i - s_i)\end{aligned} \tag{1.43}$$

Now substituting the entropy of mixing relation from Eq. (1.31), the minimum power input is determined in the rate and per unit mole form to be

$$\dot{W}_{\text{min, in}} = -R_u T_0 \sum_i \dot{N}_i \ln x_i = -\dot{N}_m R_u T_0 \sum_i x_i \ln x_i \quad \text{(ideal solution) (in kW)} \tag{1.44a}$$

and $$w_{\text{min, in}} = -R_u T_0 \sum_i x_i \ln x_i \qquad \text{(per unit mole of mixture, in kJ/kmol)} \tag{1.44b}$$

which are identical to the relations for minimum work input Eq. (1.36) obtained before, as expected. Therefore, minimum work input relations developed above can be used with confidence for separation processes provided that the mixtures can be approximated as ideal solutions with reasonable accuracy.

1.3.6 Separation of a Two-Component Mixture

Consider a mixture of two components *A* and *B* whose mole fractions are x_A and x_B. Noting that $x_B = 1 - x_A$, the minimum work input relations from Eqs. 34 simplify to

$$W_{\text{rev, ideal}} = -R_u T_0 (N_A \ln x_A + N_B \ln x_B) \qquad \text{(in kJ)} \tag{1.45a}$$
$$= -R_u T_0 [N_A \ln x_A + (N_m - N_A) \ln(1 - x_A)]$$

$$w_{\text{min, in}} = -R_u T_0 (x_A \ln x_A + x_B \ln x_B) \qquad \text{(in kJ/kmol mixture)} \tag{1.45b}$$
$$= -R_u T_0 [x_A \ln x_A + (1 - x_A) \ln(1 - x_A)]$$

$$\dot{W}_{\text{min, in}} = -\dot{N}_m R_u T_0 (x_A \ln x_A + x_B \ln x_B) \qquad \text{(in kW)} \tag{1.45c}$$
$$= -\dot{N}_m R_u T_0 [x_A \ln x_A + (1 - x_A) \ln(1 - x_A)$$

The relations above can be used directly for desalination processes, by taking the water (the solvent) to be component *A*, and the salts (the solute) to be component *B*. The relations above will then give the minimum input required to separate saline water, at the environmental temperature of T_0, completely into pure salt and fresh water.

The relations above are for complete separation of the components in the mixture. The required work input will be less if the exiting streams are not pure. The reversible work for incomplete separation can be determined by taking the minimum separation work for the incoming mixture and the minimum separation works for the outgoing mixtures, and then taking their difference.

1.3.6 The Minimum Separation Work for Desalination Processes

A general relation is obtained for the minimum work input requirement for desalination processes using the second-law of thermodynamics. The relation developed can be used to determine the minimum work input for any salinity of the incoming water, and the recovery ratio. It is also shown that there is a lower and an upper limit for the minimum work, corresponding to recovery ratios of 0 and 100 percent, respectively. The minimum work input per unit mass of fresh water produced is determined for various salinities of incoming water, and the salinities of fresh water produced, and the results are tabulated and plotted. It is shown that the minimum work is a strong function of salinity, and increases with salinity and the recovery ratio. It is also shown that the minimum work input requirement remains fairly constant for recovery ratios of up to about 80 percent. The minimum work increases drastically at high recovery ratios, and an optimum value of recovery ratio exists to minimize the power consumption of actual desalination plants. But the value of this optimum recovery ratio decreases with increasing salinity of the incoming saline water. The results presented in this study can be used as a basis to evaluate the performance of actual desalination plants.

It is well-established that the work output is a maximum and the work input is minimum for reversible processes, and that the work output becomes the work input when a reversible process is reversed. Therefore, the minimum work input requirement for a separation process is equivalent to the maximum work that could be produced during a mixing process. That is,

$$W_{\text{max, out, mixing}} = W_{\text{min, in, separation}} \qquad \text{(in kJ)} \tag{1.46}$$

The minimum work input required for a separation process, which is equivalent to the work potential wasted during the corresponding mixing process, is given in the rate form, on a unit mole basis, and per unit mass of mixture as (Cengel et al, 1999)

$$\dot{W}_{\min} = -R_u T_0 \sum_i \dot{N}_i \ln x_i = -\dot{N}_m R_u T_0 \sum_i x_i \ln x_i \qquad \text{(in kW)} \qquad (1.47a)$$

and

$$\overline{w}_{\min} = -R_u T_0 \sum_i x_i \ln x_i \qquad \text{(kJ/kmol mixture)} \qquad (1.47b)$$

and

$$w_{\min} = \frac{\overline{w}_{\min}}{M_m} = -\frac{R_u T_0}{M_m} \sum_i x_i \ln x_i = -R_m T_0 \sum_i x_i \ln x_i \qquad \text{(kJ/kg mixture)} \qquad (1.47c)$$

where T_0 is the temperature of the incoming saline water, which is taken to be the same as the environment temperature, R_u is the universal gas constant, x_i is the mole fraction of component *i*, and $\dot{N}_i$ and $\dot{N}_m$ are the molar flow rates of component *i* and the mixture, respectively, R_m is the gas constant, and M_m is the molar mass of the mixture.

The primary restriction on Eq. (1.47) is that the solution be an ideal solution. That is, the effect of dissimilar molecules in the mixture on each other is negligible, and the partial molar volume and the partial molar enthalpy of a component in a solution equal the specific volume and enthalpy of that component, when it existed alone as a pure substance at the mixture temperature and pressure. Therefore, the specific volume and enthalpy of individual components do not change during mixing if they form an ideal solution, and the volume change due to mixing and the heat of mixing, which is the heat released or absorbed as two or more components are mixed isothermally, are negligible.

Many liquid solutions encountered in practice satisfy this condition very closely, and can be considered to be ideal solutions with negligible error. The heat of mixing for saline solutions has been determined experimentally at different salinities (Singh, 1973), and appears to be small relative to the energy interactions involved during actual desalination processes. For example, the energy consumption in a multistage flash distillation plant is about 15,000 kJ per m^3 of fresh water produced (Wade, 1993). The experimentally determined values of the heat of mixing, on the other hand, ranged from 1 to 100 kJ per m^3 of mixture over a wide range of temperatures and salinities. Therefore, brackish or sea water at concentrations encountered in practice can be treated as an ideal solution with negligible error.

For a two-component mixture such as the saline water, Eq. (1.47) can be expressed as

$$\dot{W}_{\min} = -\dot{N}_m R_u T_0 (x_s \ln x_s + x_w \ln x_w) = -R_u T_0 (\dot{N}_s \ln x_s + \dot{N}_w \ln x_w) \qquad \text{(in kW)} \qquad (1.48a)$$

and

$$\overline{w}_{\min} = -R_u T_0 (x_s \ln x_s + x_w \ln x_w) \qquad \text{(kJ/kmol saline water)} \qquad (1.48b)$$

and

$$w_{\min} = -R_m T_0 (x_s \ln x_s + x_w \ln x_w) \qquad \text{(kJ/kg saline water)} \qquad (1.48c)$$

where x_s and x_w are the mole fractions of the salt and the pure water in the incoming saline water, $\dot{N}_s$ and $\dot{N}_w$ are the molar flow rates of the salt and the water, respectively, and $\dot{N}_m = \dot{N}_s + \dot{N}_w$ is the molar flow rate of the incoming saline water. The molar mass *M* is the mass of a unit mole of a substance, and mass *m* and the mole numbers *N* of a system are related to each other by $m = NM$. Then the relation between the mass fraction and mole fraction for saline solutions becomes

$$mf_s = \frac{m_s}{m_m} = \frac{N_s M_s}{N_m M_m} = x_s \frac{M_s}{M_m} \qquad \text{and} \qquad mf_w = x_w \frac{M_w}{M_m} \tag{1.49}$$

where the apparent molar mass of the saline water is

$$M_m = \frac{m_m}{N_m} = \frac{N_s M_s + N_w M_w}{N_m} = x_s M_s + x_w M_w \tag{1.50}$$

The molar masses of NaCl and water are 58.5 kg/kmol and 18.0 kg/kmol, respectively. Salinity is usually given in terms of mass fractions, but the minimum work calculations require mole fractions. Combining Eqs. (1.49) and (1.50) and noting that $x_s + x_w = 1$ gives the following convenient relations for converting mass fractions to mole fractions,

$$x_s = \frac{M_w}{M_s(1/mf_s - 1) + M_w} = \frac{18}{58.5(1/mf_s - 1) + 18} \tag{1.51a}$$

and

$$x_w = \frac{M_s}{M_w(1/mf_w - 1) + M_s} = \frac{58.5}{18(1/mf_w - 1) + 58.5} = 1 - x_s \tag{1.51b}$$

For example, the average salinity of sea water is 3.5 percent, and thus the mass fractions are $mf_s = 0.035$ are $mf_w = 0.965$. The mole fractions are $x_s = 0.011$ are $x_w = 0.989$. Therefore, the average molar salinity of sea water is about 1.1 percent. Salinity is also expressed in parts per million (MG/L), which is defined as

$$\text{PPM} = \frac{m_{\text{solute}}}{m_{\text{solution}}} \times 10^6 = \frac{m_s}{m_m} \times 10^6 = mf_s \times 10^6 \tag{1.52}$$

Thus, the average salinity of 3.5 percent for sea water corresponds to 35,000 mg/L.

1.3.8 Minimum Work Input for Partial Separation

The minimum work relations above give the minimum input required to separate saline water completely into pure salt and pure water. In reality, however, separation is not complete, and the outgoing brine contains pure water, while the product (or fresh) water contains some salt. The required work input will be less when separation is not complete and thus the exiting streams are not pure. The minimum work input for incomplete separation can be determined by first finding the minimum separation work for the incoming saline water and the minimum separation works for the outgoing streams, and then taking their difference, as shown below.

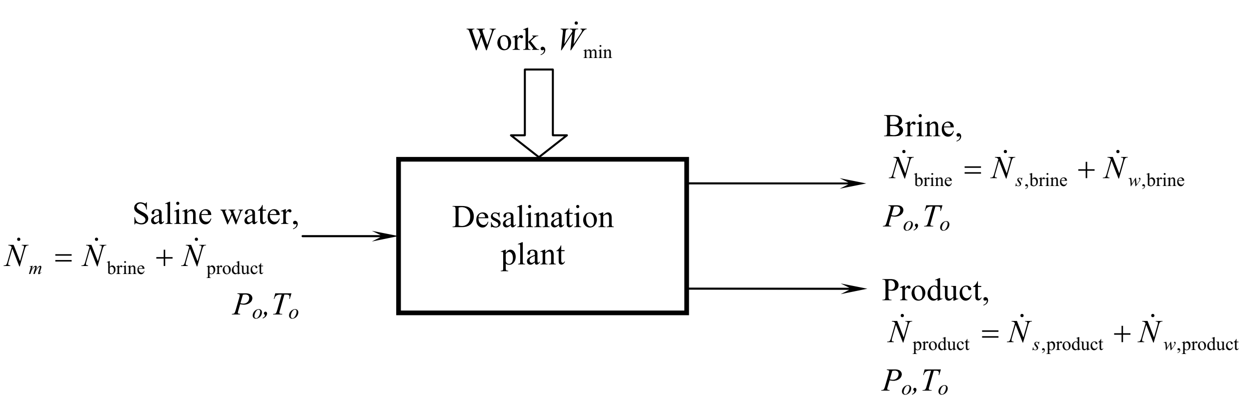

Figure 1.1.—Schematic of Single-Stage Desalination Plant.

Consider a general desalination plant shown schematically in Figure 1.1 operating steadily at a constant temperature of T_o and constant pressure of P_o. All streams also flow into and out of the plant at T_o and P_o. Saline water enters the plant at a molar flow rate of $\dot{N}_m$, and separates into two streams: the high-salinity brine leaving at a molar flow rate of $\dot{N}_{\text{brine}}$, and the low-salinity product water leaving at a molar flow rate of $\dot{N}_{\text{product}}$. Note that neither stream is pure. Also, from conservation of mass,

$$\dot{N}_{\text{brine}} = \dot{N}_{s,\text{brine}} + \dot{N}_{w,\text{brine}} \tag{1.52a}$$

$$\dot{N}_{\text{product}} = \dot{N}_{s,\text{product}} + \dot{N}_{w,\text{product}} \tag{1.52b}$$

and

$$\dot{N}_m = \dot{N}_{\text{brine}} + \dot{N}_{\text{product}} = (\dot{N}_{s,\text{brine}} + \dot{N}_{w,\text{brine}}) + (\dot{N}_{s,\text{product}} + \dot{N}_{w,\text{product}}) \tag{1.53}$$

where the subscripts s and w stand for salt and water content, respectively, in the brine and product water streams. Also, from the mass balances of salt and water we have

$$\dot{N}_m = \dot{N}_s + \dot{N}_w = (\dot{N}_{s,\text{brine}} + \dot{N}_{s,\text{product}}) + (\dot{N}_{w,\text{brine}} + \dot{N}_{w,\text{product}}) \tag{1.54}$$

Now we have three streams of water-salt solutions, and the minimum work of separation for each stream can be determined independently from Eq. (1.48a), provided that we know the salinity of each stream. Let the mole fractions of water and salt in the outgoing brine be $x_{w,\text{ brine}}$ and $x_{s,\text{ brine}}$, respectively, and the mole fractions of water and salt in the outgoing product water stream be $x_{w,\text{ product}}$ and $x_{s,\text{ product}}$. Then the minimum work for each stream becomes

$$\begin{aligned}\dot{W}_{\text{min, brine}} &= -\dot{N}_{\text{brine}} R_u T_0 (x_{s,\text{brine}} \ln x_{s,\text{brine}} + x_{w,\text{brine}} \ln x_{w,\text{brine}}) \\ &= -R_u T_0 (\dot{N}_{s,\text{brine}} \ln x_{s,\text{brine}} + \dot{N}_{w,\text{brine}} \ln x_{w,\text{brine}})\end{aligned} \tag{1.55a}$$

$$\begin{aligned}\dot{W}_{\text{min, product}} &= -\dot{N}_{\text{product}} R_u T_0 (x_{s,\text{product}} \ln x_{s,\text{product}} + x_{w,\text{product}} \ln x_{w,\text{product}}) \\ &= -R_u T_0 (\dot{N}_{s,\text{product}} \ln x_{s,\text{product}} + \dot{N}_{w,\text{product}} \ln x_{w,\text{product}})\end{aligned} \tag{1.55b}$$

The two minimum work relations above give the additional minimum work needed to separate the two outgoing impure streams completely. Then we conclude that the minimum work input for the partial separation of the incoming saline water must be that much less, and thus

$$\dot{W}_{\text{min}} = \dot{W}_{\text{min,complete}} - (\dot{W}_{\text{min,brine}} + \dot{W}_{\text{min,product}}) \tag{1.56}$$

where $\dot{W}_{\text{min,complete}}$ is simply the minimum work for complete separation of incoming saline water, and is given earlier by Eq. (1.48a). Substituting Eqs. (1.48a), (1.55a), and (1.55b) into Eq. (1.56) gives, after some manipulations,

$$\dot{W}_{\text{min}} = R_u T_0 (\dot{N}_{s,\text{brine}} \ln \frac{x_{s,\text{brine}}}{x_s} + \dot{N}_{s,\text{product}} \ln \frac{x_{s,\text{product}}}{x_s} + \dot{N}_{w,\text{brine}} \ln \frac{x_{w,\text{brine}}}{x_w} + \dot{N}_{w,\text{product}} \ln \frac{x_{w,\text{product}}}{x_w}) \tag{1.57}$$

or

$$\begin{aligned} \dot{W}_{\text{min}} = R_u T_0 [\dot{N}_{\text{brine}} (x_{s,\text{brine}} \ln \frac{x_{s,\text{brine}}}{x_s} + x_{w,\text{brine}} \ln \frac{x_{w,\text{brine}}}{x_w}) \\ + \dot{N}_{\text{product}} (x_{s,\text{product}} \ln \frac{x_{s,\text{product}}}{x_s} + x_{w,\text{product}} \ln \frac{x_{w,\text{product}}}{x_w})] \end{aligned} \tag{1.58}$$

The equation above is a general relation for the minimum work input required for the separation of incoming saline water of known salinity x_s into two streams of known salinities $x_{s,\text{ brine}}$ and $x_{s,\text{ product}}$. It gives the minimum separation work for a range of 0 to 100 percent recovery of fresh water for any combination of salinities of the incoming saline water and the outgoing product water and brine. The minimum work input per unit mole of the incoming saline water is determined by dividing Eq. (1.58) by the molar flow rate of incoming saline water $\dot{N}_m$.

Note that once the salinities of the two outgoing streams (brine and product water) are fixed, the molar flow rates of these two streams are also fixed, and thus they cannot be varied independently. Therefore, the separation process of a given saline water stream can be described completely by specifying the salinities of the brine and product water streams. Once the salinities of brine and product water ($x_{s,\text{ brine}}$ and $x_{s,\text{ product}}$) are specified together with the salinity x_s and molar flow rate $\dot{N}_m$ of incoming saline water, the molar flow rates of brine and product water are determined from mass balances of salt and water as follows:

$$\text{Salt}: \quad \dot{N}_s = \dot{N}_{s,\text{brine}} + \dot{N}_{s,\text{product}} \longrightarrow x_s \dot{N}_m = x_{s,\text{brine}} \dot{N}_{\text{brine}} + x_{s,\text{product}} \dot{N}_{\text{product}} \tag{1.59a}$$

$$\text{Water}: \quad \dot{N}_w = \dot{N}_{w,\text{brine}} + \dot{N}_{w,\text{product}} \longrightarrow x_w \dot{N}_m = x_{w,\text{brine}} \dot{N}_{\text{brine}} + x_{w,\text{product}} \dot{N}_{\text{product}} \tag{1.59b}$$

Eqs. (1.59a) and (1.59b) are two equations in the two unknowns of $\dot{N}_{\text{brine}}$ and $\dot{N}_{\text{product}}$, and their solution is

$$\dot{N}_{\text{brine}} = \frac{x_s x_{w,\text{product}} - x_w x_{s,\text{product}}}{x_{s,\text{brine}} x_{w,\text{product}} - x_{w,\text{brine}} x_{s,\text{product}}} \dot{N}_m \quad \text{and} \quad \dot{N}_{\text{product}} = \frac{x_w x_{s,\text{brine}} - x_s x_{w,\text{brine}}}{x_{s,\text{brine}} x_{w,\text{product}} - x_{w,\text{brine}} x_{s,\text{product}}} \dot{N}_m \tag{1.60}$$

The performance of desalination plants is usually expressed on the basis of cost per unit mass (or mole) of product water delivered rather than per unit amount of incoming saline water processed. The minimum work input per unit mole of fresh water produced is determined by dividing Eq. (1.58) by the molar flow rate of product water $\dot{N}_{\text{product}}$. It gives

$$\overline{w}_{\min} = R_u T_0 [\frac{\dot{N}_{\text{brine}}}{\dot{N}_{\text{product}}} (x_{s,\text{brine}} \ln \frac{x_{s,\text{brine}}}{x_s} + x_{w,\text{brine}} \ln \frac{x_{w,\text{brine}}}{x_w}) + x_{s,\text{product}} \ln \frac{x_{s,\text{product}}}{x_s} + x_{w,\text{product}} \ln \frac{x_{w,\text{product}}}{x_w}] \tag{1.61}$$

(kJ/kmol product)

The minimum work input per unit mass of product water is obtained by dividing Eq. (1.59) by the molar mass of the product water M_{product}. Also substituting the $\dot{N}_{\text{brine}}$ and $\dot{N}_{\text{product}}$ relations from Eq. 1.60 gives

$$w_{\min} = \frac{R_u T_0}{M_{\text{product}}} [\frac{x_s x_{w,\text{product}} - x_w x_{s,\text{product}}}{x_w x_{s,\text{brine}} - x_s x_{w,\text{brine}}} (x_{s,\text{brine}} \ln \frac{x_{s,\text{brine}}}{x_s} + x_{w,\text{brine}} \ln \frac{x_{w,\text{brine}}}{x_w}) + x_{s,\text{product}} \ln \frac{x_{s,\text{product}}}{x_s} + x_{w,\text{product}} \ln \frac{x_{w,\text{product}}}{x_w}] \tag{1.62}$$

(kJ/kg product)

The salinity of product water is usually very small (much less than 1 percent), and thus its molar mass can be replaced by the molar mass of water with negligible error. That is, $R_u / M_{\text{product}} = R_{\text{product}} \cong R_{\text{water}} = 0.4615$ kJ/kg.K. Also, the minimum power input needed to produce fresh water at a specified mass flow rate can be determined from Eq. (1.62) by multiplying it by the mass flow rate of the product water, $\dot{m}_{\text{product}}$.

It is important to note from the equation above that the minimum work of separation depends only on the properties of the incoming saline water and the outgoing product water and brine, and it is independent of the hardware used or the actual mechanism of desalination process utilized. Therefore, the results obtained from the above relations are applicable to any desalination plant to determine the minimum work or power input.

As for the validity of Eq. (1.56), we offer the following discussion. The single-stage separation process shown in Figure 1.1 can be accomplished in multi-stages, as illustrated in Figure 1.2. In the first stage, the incoming saline water is partially separated into two streams of brine and product water reversibly. Then each stream is separated completely into their components reversibly, and thus the minimum work for each of these two processes can be determined from Eq. (1.48a). The total minimum work input in this case can be expressed as

$$\dot{W}_{\text{min, multistage}} = \dot{W}_{\text{min, partial}} + \dot{W}_{\text{min,brine}} + \dot{W}_{\text{min,product}} \tag{1.63}$$

We now compare this stepwise process to the single overall process of the separation of the incoming saline water completely into pure salt and pure water, as shown in Figure 1.1. The minimum work input in this case is, from Eq. (1.48a),

$$\dot{W}_{\text{min, single stage}} = \dot{W}_{\text{min, complete}} \tag{1.64}$$

The processes in Figures 1.1 and 1.2 are identical, and they accomplish the same thing. Since the work interactions for reversible processes between specified states are independent of the details of the processes, the work input for both single- and multi-step cases must be the same. Then setting right hand side of Eqs. (1.63) and (1.64) equal to each other gives Eq. (1.56).

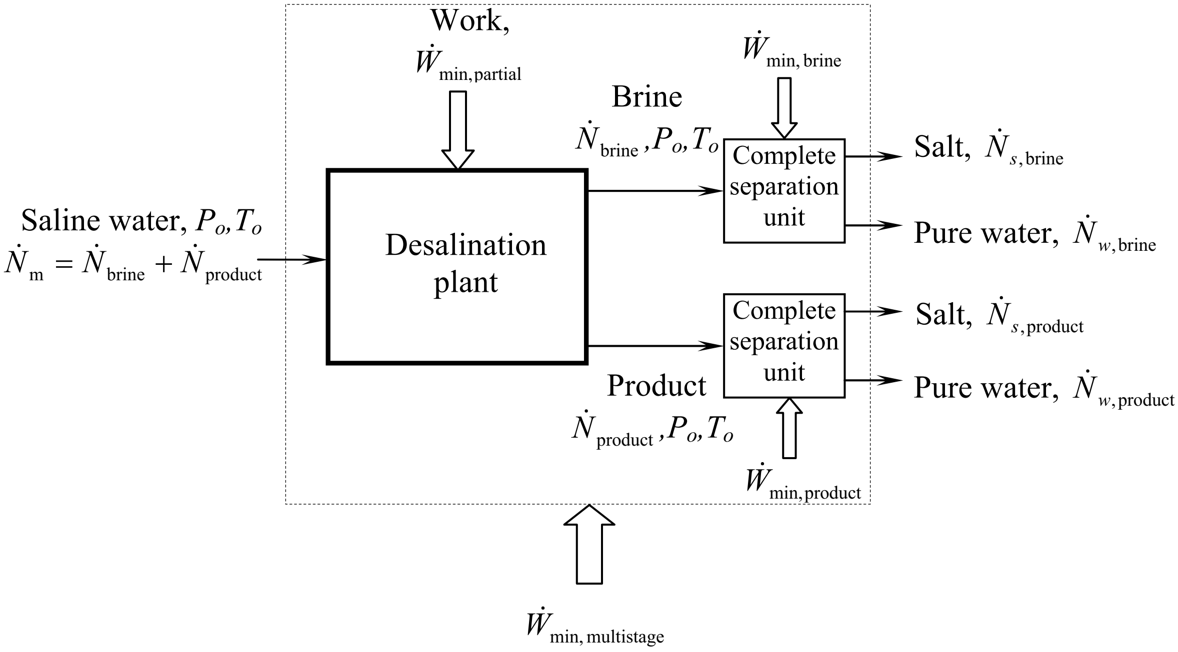

Figure 1.2.—Equivalent Multi-Stage Desalination Plant.

Another way of arguing the validity of Eq. (1.56) on the superposition of reversible works is to consider an equivalent process that involves reversible mixing as follows: $\dot{W}_{\text{min,complete}}$ is the minimum work input required for complete separation of incoming saline water into pure salt and pure water. Then if we were to mix the pure water and salt obtained reversibly in two separate streams, one with salinity $x_{s,\text{brine}}$ and the other with salinity $x_{s,\text{product}}$, the work produced would be, on the basis of Eq. (1.46), $\dot{W}_{\text{min,brine}} + \dot{W}_{\text{min,product}}$. Then the net work for this combined separation-mixing process is $\dot{W}_{\text{min,complete}} - (\dot{W}_{\text{min,brine}} + \dot{W}_{\text{min,product}})$, which is the minimum work relation for incomplete separation given in Eq. (1.56).

1.3.9 Recovery Ratio

A measure of performance of desalination plants is the "recovery ratio," which is the fraction of water reclaimed from the saline water. In a strict sense, it can be defined as the mass ratio of pure water produced to the water content of the incoming saline water. With this definition, the recovery ratio becomes exactly 100 percent when the incoming saline water is separated completely into pure water and salt. But in practice, the produced fresh water with acceptable salinity is considered to be the recovered water, and the recovery ratio is defined as the ratio of the mass of water produced (including the small amount of salt in it) to the mass of incoming saline water (including the salt in it) (Curran, 1960). That is,

$$\text{Recovery ratio} = \frac{\text{Mass flow rate of outgoing product water}}{\text{Mass flow rate of incoming saline water}} \quad \text{or} \quad r_r = \frac{\dot{m}_{\text{product}}}{\dot{m}_m} \tag{1.65}$$

We will use the practical definition of recovery ratio above in this report.

When the recovery ratio and the mass fraction of salt in the product water are known, the mass fraction of salt in the brine can be determined from a mass balance on the salt expressed as

$$\text{Salt}: \quad \dot{m}_s = \dot{m}_{s,\text{brine}} + \dot{m}_{s,\text{product}} \longrightarrow mf_s\dot{m}_m = mf_{s,\text{brine}}\dot{m}_{\text{brine}} + mf_{s,\text{product}}\dot{m}_{\text{product}} \tag{1.66}$$

Dividing both sides of this equation by $\dot{m}_m$, noting that $\dot{m}_{\text{brine}} = \dot{m}_m - \dot{m}_{\text{product}}$, and using the definition of recovery ratio from Eq. (1.65), and solving the resulting equation for the mass fraction of salt in the brine gives

$$mf_{s,\text{brine}} = \frac{mf_s - r_r mf_{s,\text{product}}}{1 - r_r} \tag{1.67}$$

For example, when the salinity of incoming saline water is 3.5 percent, the recovery ratio is 60 percent, and the salinity of the product water is 500 mg/L (or 0.05 percent), the salinity of the outgoing brine is determined from Eq. (1.67) to be 8.68 percent. Once the mass fractions are available, the mole fractions can be determined form Eq. (1.51) for use in the minimum work relations.

Although the recovery ratio does not appear in the minimum work input relations directly, it has a major influence on the minimum work input requirement of the desalination process because of its indirect effect on the salinity of the outgoing brine. The higher the recovery ratio, the higher the salinity of the discharged brine, and thus the larger the minimum work required per unit mass of the fresh water produced.

There are two special cases of interest that correspond to recovery ratios of 0 and 100 percent. Several terms in Eq. (1.59) drop out in both cases, and the equation simplifies greatly, as shown below.

1.3.9.1 Special Case 1: Negligible Recovery of Fresh Water (lower limit)

The lower limit for minimum work is obtained when the recovery ratio is nearly 0 percent or just zero. That is, the rate of pure water production is so low compared to the flow rate of incoming saline water that the salinity of the outgoing brine is practically equal to the salinity of the incoming saline water. Also, the mass (or molar) flow rate of brine is nearly equal to the mass flow rate of the incoming brine. The minimum work input in this case per kmol of fresh water produced is obtained from Eq. (1.59) by setting $x_{s,\text{brine}} \cong x_s$, $x_{w,\text{brine}} \cong x_w$, $x_{s,\text{product}} = 0$, $x_{w,\text{product}} = 1$, and $\dot{N}_{\text{product}} = 1$. It gives, after taking the appropriate limits,

$$\overline{w}_{\min} = -R_u T_o \ln x_w \qquad \text{(negligible recovery, kJ/kmol fresh water)} \tag{1.68}$$

The simplified relation above is the only relation available in the literature for minimum work (Dodge, 1960), and the severe restrictions on it are usually not stated. Therefore, it can be very misleading. The values obtained from the relation above are not a realistic measure of comparison for actual desalination processes since the salinity of the waste brine is considerably above the salinity of the incoming saline water. But Eq. (1.68) will give a reasonable approximation when a large amount of saline water is used to produce a small amount of fresh water.

The minimum work obtained from Eq. (1.68) is less than that obtained from Eq. (1.59) since the extraction of a small fraction of pure water from the saline solution requires less work input than that of a large fraction of pure water. Therefore, the minimum work is highest when the recovery is 100 percent, and it is the lowest when the recovery approaches 0 percent.

Equation (1.68) can be simplified even further. For $x_w \cong 1$, which is the case for most brackish and saline water encountered in practice, the logarithmic term can be approximated as $\ln x_w \cong 1 - x_w = x_s$. Therefore, the minimum work relation above further reduces to

$$\overline{w}_{\min} \cong -R_u T_0 x_s \qquad \text{(negligible recovery, } x_w \cong 1\text{)} \qquad (1.69)$$

Although approximate, this relation is of great value since it clearly shows that the minimum work input for desalination processes is nearly proportional to the salinity (on a mole basis) of the incoming saline water. The greater the salinity (or the difference between the salinity of the saline water and the salinity of fresh water produced), the greater the work input required. That is, it takes more work to move fresh water across a larger concentration difference. This is analogous to a heat pump or refrigerator requiring more work per kJ of heat removal across a larger temperature difference, or a pump requiring more work per kg of water pumped across a higher elevation. Eq. (1.68) can also be expressed per unit mass by dividing it by the molar mass of water.

1.3.9.2 Special Case 2: Full recovery of Fresh Water (upper limit)

The upper limit for minimum work is obtained when the recovery ratio is 100 percent. That is, the incoming saline water is separated completely into salt and pure water, and thus the entire content of the saline water leaves the desalination plant as product water, resulting in a recovery ratio of 100 percent. Also, the brine stream in this case consists of salt only, and thus the mole fraction of water in the brine is zero. The minimum work input in this case per kmol of fresh water produced is obtained from Eq. (1.59) by setting $x_{s,\text{brine}} = 1$, $x_{w,\text{brine}} = 0$, $x_{s,\text{product}} = 0$, $x_{w,\text{product}} = 1$, $\dot{N}_{\text{brine}} = x_s \dot{N}_m$, and $\dot{N}_{\text{product}} = x_w \dot{N}_m$. It gives

$$\overline{w}_{\min} = -R_u T_0 \left(\frac{x_s}{x_w} \ln x_s + \ln x_w \right) \qquad \text{(full recovery, kJ/kmol fresh water)} \qquad (1.70)$$

We could also obtain Eq. (1.70) directly from Eq. (1.48b) by expressing it per unit mole of product water. The value of minimum work obtained from Eq. (1.70) represents the upper limit for minimum work input needed to obtain fresh water from saline water of specified salinity since the salinity of water increases during the separation process (it becomes 100 percent when the last drop of water separates from salt), and the work of separation required is proportional to the salinity of the incoming water. This is not surprising since the salinity of the water in this case increases from x_s at the beginning, to 1 at the end of the process. Thus we conclude that the minimum work is maximum when the recovery is 100 percent, and it is minimum when the recovery nearly 0 percent.

A relation for the ratio of the upper and lower limits of minimum work can be obtained by dividing Eq. (1.68) by (1.70). After simplification, it gives

$$\frac{\overline{w}_{\text{min, highest}}}{\overline{w}_{\text{min, lowest}}} = 1 + \frac{x_s \ln x_s}{x_w \ln x_w} \approx 1 + \frac{\ln x_s}{1 - x_s} \tag{1.71}$$

1.3.10 Second-Law Efficiency

The second-law efficiency is a measure of how closely a process approximates a corresponding reversible process, and it indicates the range available for potential improvements. Noting that the second-law efficiency ranges from 0 for a totally irreversible process to 100 percent for a totally reversible process, the second-law efficiency for a desalination process can be defined as

$$\eta_{II,\text{desalination}} = \frac{w_{\text{min}}}{w_{\text{act}}} \tag{1.72}$$

where w_{act} is the actual work input (or exergy consumption) of the desalination plant, and the minimum work input w_{min} is calculated from Eq. (1.62) for the same recovery ratio. The minimum work input and the second-law efficiency provide a basis for comparison of actual desalination processes to the "idealized" ones, and they can be very valuable tools for assessing the thermodynamic performance of desalination plants.

1.3.11 Results and Discussion

Minimum separation work input values are calculated from Eq. (1.62) for saline water solutions of different concentrations with varying recovery ratios at 15ºC, and the results are tabulated in Table 1.1. As can be seen from the table, typical seawater has a minimum work of separation of 1.477 kJ/kg of pure water produced at 0 percent recovery. For the same recovery, it decreases to 1.219 kJ/kg of product water with 1500 mg/L. This decrease in the work input requirement is expected since a certain amount of salt is contained in the product water and thus separation is not complete. As the recovery ratio increases to 100 percent, we see that the minimum work input requirement reaches 8.169 kJ/kg of pure water produced. This is again no surprise since separation at high salinity at the later stages requires considerably more work input. Therefore, in actual desalination plants, the benefits of higher recovery ratios should be weighed against the additional work input.

The minimum works of separation to extract pure water from saline water with salinities (by mass) of 4.6, 3.5, 2.0, 1.0, and 0.2 percent at 15ºC are plotted in Figure 1.3 as a function of recovery ratio using values from Table 1.1. The second curve from the top corresponds to the extraction of pure water from 3.5 percent salt solution (mass basis), which is typical sea water. It is important to note that the 0 percent recovery on this chart does not indicate no production of fresh water, which would require no work input. Rather, it corresponds to extracting negligible amount of fresh water from a very high flow rate stream of incoming saline water so that the salinity of the outgoing brine is essentially the same as that of incoming saline water.

For recovery ratios larger than 80 percent, the minimum work increases dramatically and reaches its maximum value of 8.169 kJ at 100 percent recovery. The lowest curve in the figure corresponds to the extraction of pure water from 0.2 percent salt solution. The minimum work of separation almost remains constant up to about 95 percent recovery, and then reaches its maximum value of 0.689 kJ/kg of pure water produced. In a range from 95 percent to 100 percent recovery, the minimum work value is almost quadrupled. Therefore, an optimum value of the recovery ratio exits at certain salinities of the incoming saline water, and it decreases with increasing salinity of the incoming saline water. Therefore, careful attention should be given to the recovery ratios when designing and operating desalination plants.

The variation of minimum work with the salinity (mole basis) of the incoming saline water is plotted in Figure 1.4. The two curves indicate the lower and upper limits of minimum work that correspond to 0 percent and 100 percent recovery ratios. Note that the minimum work increases with increasing salinity, and the increase is nearly linear at low salinities. Also note that the highest value of minimum work can be several times the lowest value at certain salinities.

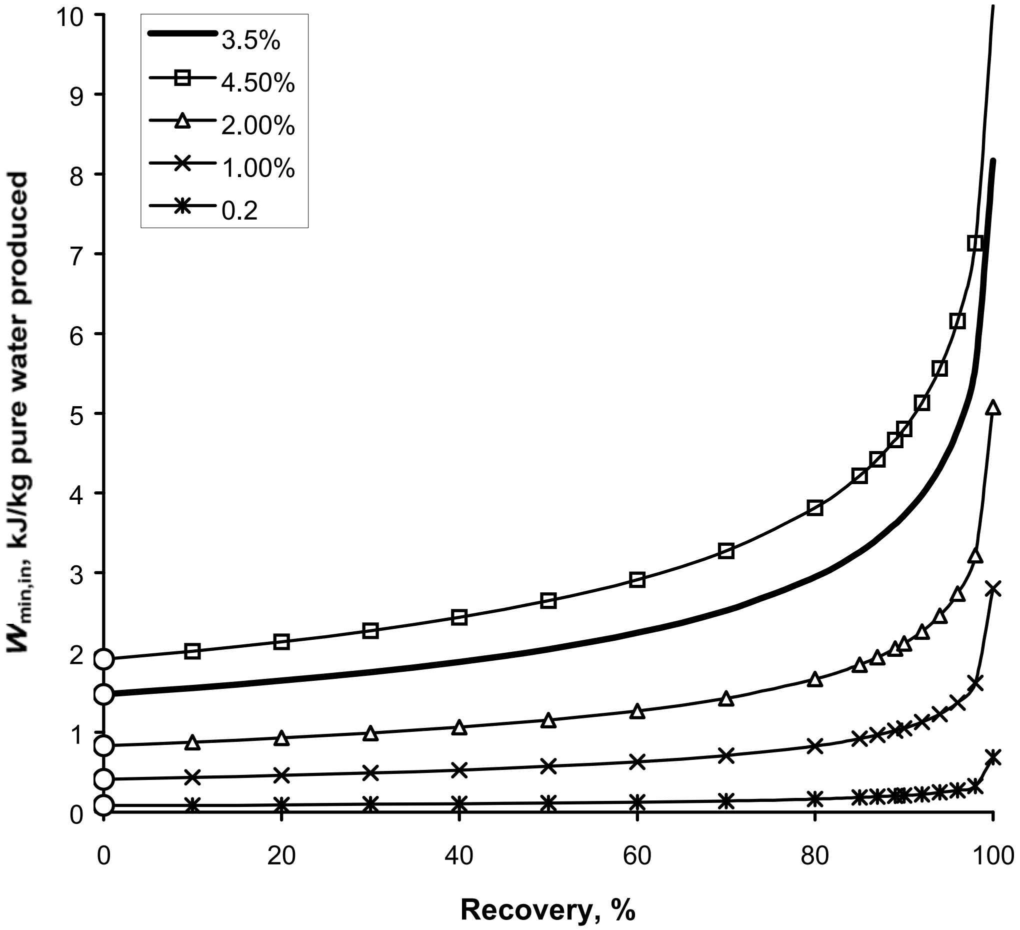

Figure 1.3.—Minimum work of separation to extract pure water from 4.5, 3.5, 2.0, 1.0, and 0.2 percent salt solutions at 15°C as a function of recovery ratio.

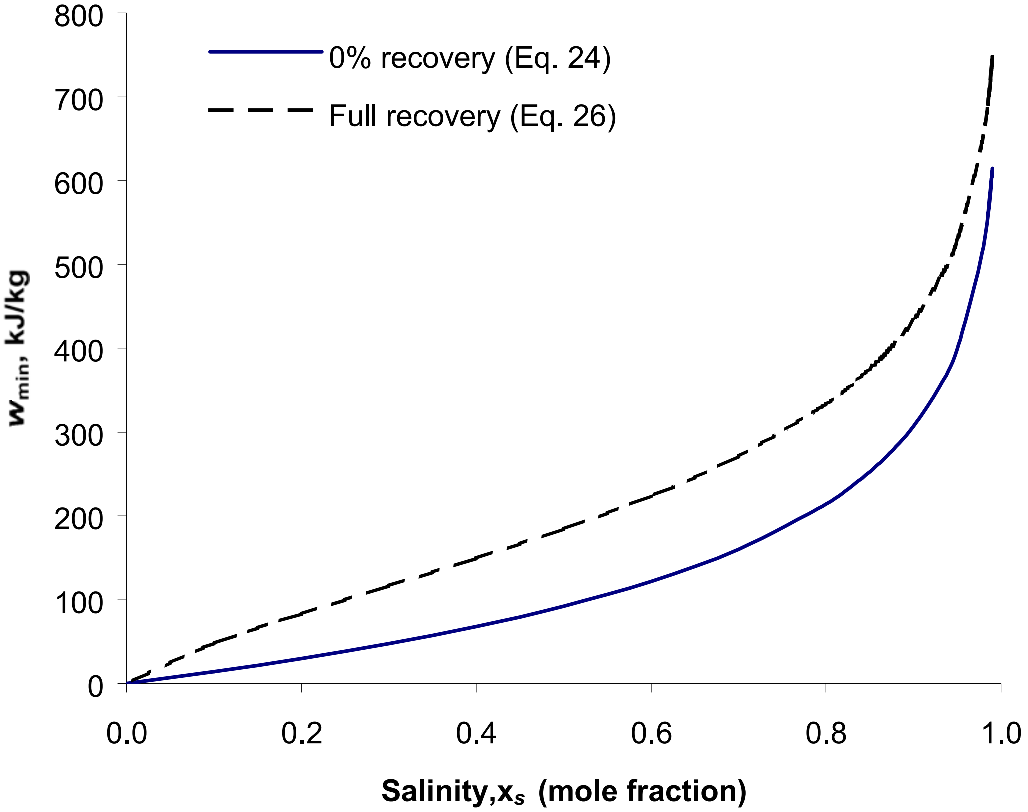

Figure 1.4.—The variation of the upper and lower limits of minimum work with the salinity of incoming saline water.

Table 1.1. Minimum work of separation for saline water at 15ºC (expressed as mass fractions).

Type of saline water	Salinity percent	Recovery percent	Minimum work of separation, kJ/kg product water produced					
			Product water, mg/L					
			0	100	300	500	1000	1500
Brackish water	0.2	0	0.082	0.066	0.046	0.033	0.013	0.003
		20	0.092	0.074	0.053	0.039	0.015	0.003
		40	0.105	0.086	0.063	0.046	0.019	0.004
		60	0.125	0.105	0.079	0.059	0.025	0.006
		80	0.165	0.143	0.111	0.086	0.039	0.011
		100	0.689	0.642	0.562	0.488	0.316	0.154
	1.0	0	0.413	0.390	0.357	0.331	0.277	0.234
		20	0.461	0.437	0.403	0.375	0.316	0.269
		40	0.529	0.504	0.467	0.436	0.372	0.320
		60	0.634	0.607	0.567	0.533	0.461	0.400
		80	0.842	0.812	0.766	0.726	0.639	0.564
		100	2.802	2.755	2.675	2.601	2.427	2.265
Seawater	2.0	0	0.833	0.807	0.769	0.736	0.668	0.611
		20	0.931	0.905	0.864	0.830	0.757	0.695
		40	1.070	1.041	0.999	0.962	0.883	0.815
		60	1.287	1.257	1.210	1.170	1.082	1.006
		80	1.721	1.688	1.635	1.588	1.485	1.393
		100	5.076	5.028	4.947	4.872	4.698	4.534
	3.5 (Typical seawater)	0	1.477	1.449	1.406	1.368	1.288	1.219
		20	1.654	1.625	1.580	1.541	1.455	1.381
		40	1.904	1.874	1.826	1.784	1.693	1.612
		60	2.301	2.268	2.217	2.172	2.071	1.981
		80	3.117	3.081	3.023	2.970	2.852	2.744
		100	8.169	8.122	8.040	7.965	7.789	7.624
	4.5	0	1.916	1.886	1.841	1.802	1.716	1.641
		20	2.148	2.117	2.070	2.029	1.938	1.858
		40	2.477	2.445	2.395	2.351	2.254	2.167
		60	3.002	2.969	2.915	2.867	2.760	2.664
		80	4.105	4.068	4.006	3.951	3.825	3.710
		100	10.111	10.063	9.982	9.906	9.729	9.563
Industrial waste water	6.0	0	2.589	2.558	2.510	2.468	2.376	2.294
		20	2.907	2.875	2.825	2.760	2.781	2.597
		40	3.361	3.328	3.275	3.165	3.228	3.031
		60	4.095	4.060	4.003	3.790	3.952	3.734
		80	5.684	5.645	5.580	4.982	5.520	5.260
		100	12.910	12.862	12.780	12.703	12.525	12.357
	8.0	0	3.514	3.482	3.432	3.387	3.288	3.200
		20	3.956	3.922	3.870	3.823	3.719	3.625
		40	4.591	4.556	4.500	4.451	4.339	4.239
		60	5.634	5.597	5.537	5.483	5.360	5.249
		80	8.002	7.960	7.890	7.825	7.678	7.541
		100	16.499	16.451	16.367	16.290	16.110	15.941
	10.0	0	4.474	4.441	4.388	4.341	4.237	4.144
		20	5.048	5.014	4.959	4.910	4.800	4.701
		40	5.882	5.846	5.788	5.736	5.619	5.512
		60	7.275	7.237	7.174	7.117	6.987	6.869
		80	10.617	10.572	10.497	10.428	10.269	10.120
		100	19.983	19.934	19.851	19.773	19.591	19.420

1.3.12 Minimum Work Requirement for Reverse Osmosis Desalination Processes

Reverse osmosis systems are conceptually simple. The basic components required for most reverse osmosis systems are pretreatment equipment such as cartridge filters, chemical feeders, high pressure pumps, reverse osmosis modules, and post treatment equipment such as a degasifier, and chemical feeders. The incoming saline water is first filtered to remove any suspended particles. Filters have a mesh size of 10 μm diameter which is satisfactory in most reverse osmosis processes. The filtration process prevents clogging of passages in reverse osmosis modules, and pump damage. The incoming saline water may also contain precipitable salts which can cause membrane fouling. The saline water should therefore be treated with some chemicals (sulfuric acid, ferric sulfide, polyeletrolyte, sodium hypocloride, sodium bisulfate, etc) depending upon the source of feed water, e.g., surface waters, ground water, and seawater. Then, the saline water is deaerated from oxygen to prevent corrosion of the metallic components of the system. It is pressurized by high pressure pumps to a range of 14 atm (≅ 200 psi) to 68 atm (≅ 1000 psi) depending upon the salt content of the incoming saline water, and the membrane type. The pressurized feedwater is introduced to a reverse osmosis membrane element which separates fresh water from the saline water. A pressure regulating valve is mounted on the concentrated stream to maintain pressure within the modules. A number of the modules in parallel can be added to increase the production capacity. The system may be cascaded to provide a higher rejection of salt and good product water quality. The system design, type of pumps, and membranes selected are determined by the salinity of the incoming saline water. The post treatment of the product water may include degasification (to remove H_2S and usually CO_2 formed by saline water acidification), elimination of corrosivity of the product water, and chlorination to prevent bacteria growth.

A conceptual reverse osmosis desalination system is schematically shown in Figure 1.5. The components of the system are a high pressure pump, a membrane module, and turbines on the brine and product water streams. The reverse osmosis system is similar to actual ones except that the turbines are not usually used due to difficulties encountered in reality. However, the turbines are employed in the system, because they allow us to determine the work potential of streams leaving the system and provide a clear view of work interactions throughout the system.

The reverse osmosis desalination process is an isothermal process during which the inlet saline water temperature T_o remains constant. Saline water at atmospheric pressure P_o and molar flow rate $\dot{N}_m$ is drawn into the high pressure pump where its pressure is raised to P_o+dP isothermally. The pressurized saline water then proceeds into the membrane module where it is separated into the brine and the product water at constant temperature. The brine at P_o+dP and $\dot{N}_{\text{brine}}$ is then introduced into the turbine where it expands to atmospheric pressure P_o, thus producing power. The product water emerges at P_o+dP and $\dot{N}_{\text{product}}$, and enters into the other turbine in which it produces power as its pressure is reduced from P_o+dP to P_o. In reality, the turbine on the brine stream is not usually employed due to various practical reasons. Instead, a throttling valve is mostly used to reduce the pressure of the brine, and thus exergy is completely destroyed and no work is produced. It is interesting to note that the reverse osmosis system is a membrane process and does not deal with the phase change phenomena involved in the distillation and freezing processes.

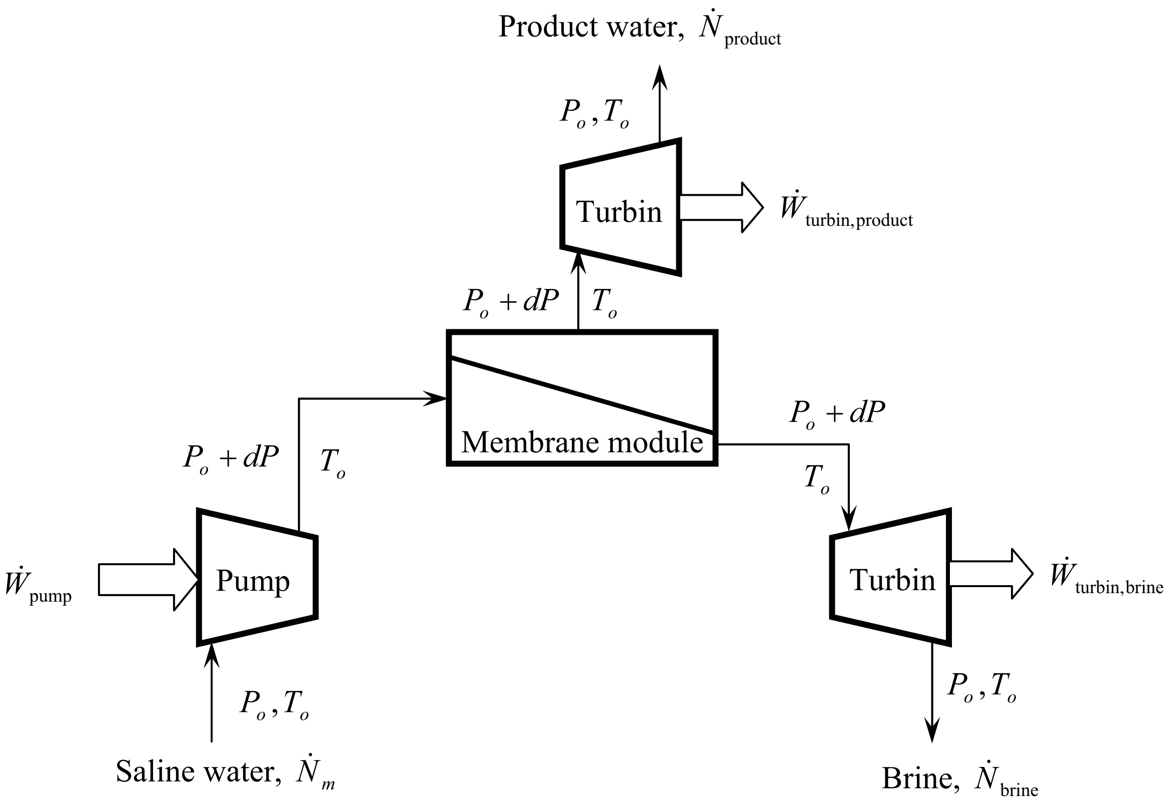

Figure 1.5.—Conceptual design for Reverse Osmosis Desalination Plant.

The minimum work requirement of the reverse osmosis process is developed by utilizing reversible pumps and turbines. The process is analyzed by employing a classical thermodynamic approach, and described in detail. The aim of this approach is to figure out the reversible work input relation for the separation process, and to provide a first approximation to the energy requirement as a basis for dealing with real processes. A number of assumptions must be made to carry out the minimum work analysis of the method. These assumptions not only lead us to the ideal work relation but also provide an easy derivation. The analysis of the minimum work is formulated on the basis of the following assumptions.

(1) Seawater contains a wide variety of salts as well as NaCl, but in the analysis, it is assumed to consist of only NaCl with a percentage of 3.5 percent.

(2) The water-NaCl solution is assumed to be an ideal solution. A solution that obeys Rault's law ($P_i = x_i P_i^{sat}$ where P_i is the partial pressure of component i, x_i is the mole fraction of component i, P_i^{sat} is the saturation pressure of component i in solution) is known as an ideal solution (Klotz, 1994). Actual solutions such as seawater can be approximated closely as ideal solutions depending upon temperature and pressure. Once the assumption of an ideal solution is made for a solution, all extensive properties of the solution become additive. In other words, no change occurs on the properties of components when they are mixed at the same temperature and pressure. Consequently, the enthalpy and volume of mixing are zero for components forming an ideal solution.

For example, the enthalpy of a binary mixture of components A and B can simply be determined to be

$$h_{mixt} = \sum_i x_i h_{i,pure} = x_A h_A + x_B h_B$$

where x_A and x_B are the mole fractions of the components, and h_A and h_B are the enthalpies of components A and B at pure state. However, if the mixture was assumed to be an actual solution, the enthalpies of the components in the pure state would be equal to the partial molar enthalpies at the same temperature and pressure.

(3) The velocity of the incoming saline water is high enough so that there is no concentration polarization at the membrane surface. A build-up of rejected salts, or concentration polarization, close to membrane surface may occur due to insufficient movement of the incoming saline water solution. The concentration of salts becomes higher than that of the saline water, and may clog up the membrane.

(4) Membranes are ideal, and therefore they do not cause any pressure drop as the product water crosses them.

The desalination process mentioned in this work consists of only basic components that are indispensable to operate them. In fact, they are complex and massive in reality. In the analysis, the reverse osmosis process contains only a pump and a membrane module, and turbines. There are no irreversibilities associated with them.

All idealized desalination plants can be considered to be enclosed in a heat insulating barrier through which heat and work are being applied, while the incoming saline water and outgoing product water and brine streams flow at a constant rate, and are at the same temperature and pressure as the environment. In the conceptual design of reverse osmosis, the incoming saline water is pressurized isothermally to a high pressure, and introduced to the membrane unit where it is separated as product water and brine. The product water and the brine leave the unit at the high pressure, and their pressure is reduced to atmospheric pressure by the turbines. The kinetic and potential energy changes of streams are relatively small, and therefore commonly neglected. There is no heat gain/loss associated with the desalting process. The fluid flow is inviscid, and thus there are no pressure drops.

In the derivation of the minimum work, the chemical potential is a very important factor affecting the separation process. It is well-known that the internal energy change, u is a function of specific entropy s and specific volume v for a single component homogeneous system in which only mechanical forces are acting. The internal energy equation of equilibrium as well as other equations can be applied to any homogenous solution of fixed composition. Let us consider a solution containing N_A, N_B …..N_N moles of components A, B, ….N, respectively. The number of moles of any component can be varied independently of any other, and such variations will cause a change in the energy of the mixture or solution. Then, the internal energy also becomes a function of the moles of each of the substance. This is expressed mathematically by

$$du = Tds - Pdv + \frac{\partial u}{\partial N_A} dN_A + \frac{\partial u}{\partial N_B} dN_B + ... + \frac{\partial u}{\partial N_N} dN_N$$

The quantities of $(\partial u/\partial N_i)_{S,V,N_J}$ are called "partial molal quantities" since the internal energy *u* is an extensive property. The importance of these quantities was first realized by J. Willard Gibbs in 1857. They were called "chemical potentials" and represented by the symbol μ. A chemical potential can also be defined in terms of other independent variables as

$$\mu_i = \left(\frac{\partial u}{\partial N_i}\right)_{S,V,N_A} = \left(\frac{\partial h}{\partial N_i}\right)_{S,P,N_A} = \left(\frac{\partial g}{\partial N_i}\right)_{P,T,N_A} = \left(\frac{\partial a}{\partial N_i}\right)_{T,V,N_A}$$

where *u* is the internal energy, *h* the enthalpy, *g* the Gibbs function, and *a* the Helmhotz function.

It can be shown that chemical potentials are intensive properties like pressure and temperature, and thus they are independent of total mass. Let us now attempt to get a better understanding of the meaning of the chemical potential. The well known osmotic pressure occurs due to the difference between the chemical potential of water in the pure liquid state and in the mixture. The water flows in the direction in which its chemical potential decreases, just like heat flows in the direction of decreasing temperature. The membrane only permits water molecules to pass, and does not drive the osmotic pressure. The driving force is, of course, the chemical potential difference between the more concentrated solution and a less concentrated one.

The differential change of the chemical potential of substance *i* in an ideal solution is given by (Cengel et al., 1999)

$$d\mu_i = \mu_i(T,P_i) - \mu_i(T,P) = R_u T \ln x_i \tag{1.73}$$

where R_u is the gas constant, x_i the mole fraction of substance *i* in the solution, *T* the absolute temperature of the solution, $\mu_i(T,P_i)$ the chemical potential of substance *i* in the solution, and $\mu_i(T,P)$ the chemical potential of substance *i* when it exists alone at total mixture temperature and pressure. It can be concluded from Eq. (1.73) that the chemical potential of a substance forming an ideal solution depends on the mole fraction of the substances as well as solution temperature and pressure. Also, the change in the chemical potential of substance *i* in an ideal solution is expressed as (Cengel et al., 1999)

$$d\mu_i = v_i\, dP \tag{1.74}$$

where v_i is the specific volume of substance *i* when it exists alone as a pure substance.

Therefore, a combination of Eq. (1.74) with Eq. (1.73) leads to the following equation that

$$v_i dP = R_u T \ln x_i \tag{1.75}$$

where the specific volume of substance *i* can be related to temperature and mole fraction of that substance. The specific volume of an ideal mixture, on the other hand, is expressed as (Cengel et al., 1999)

$$v_{\text{mixture,ideal}} = \sum_i x_i v_i \tag{1.76}$$

The specific volumes of components forming an ideal solution are additive. The derivation of the minimum work of the reverse osmosis desalting process is quite straight forward, and is derived by employing the reversible steady-flow work relation for incompressible fluids. As can be seen from Figure 1.5, the reverse osmosis system mainly consists of a pump, and two turbines. While the pump requires the minimum possible work input, the turbines produce the maximum possible work outputs in the system. Therefore, the net result of these work inputs and outputs is the minimum work input for the reverse osmosis desalination process.

The reversible amount of work for an incompressible fluid undergoing an adiabatic compression or expansion process may be quantified in the following manner. Since liquids are essentially incompressible, the specific volume remains constant during the process. And, in this case, the reversible work is expressed as

$$w_{\text{rev}} = -v\,\Delta P \tag{1.77a}$$

where v is the specific volume of fluid, and ΔP is the pressure change during compression or expansion. The above equation can also be expressed in the rate form as

$$\dot{W}_{\text{rev}} = -\dot{N}v\,\Delta P \tag{1.77b}$$

where $\dot{N}$ is the molar flow rate of fluid. Note that the equation above can be used to determine the amount of work for compression and expansion processes of liquids. Since the reverse osmosis desalination system deals with the compression and expansion processes of water, Eq. (1.77b) is basically employed to develop the minimum work relation for the system.

The incoming saline water at atmospheric pressure P_o and molar flow rate $\dot{N}_m$ enters the pump and is compressed to the pressure of P_o+dP. Using Eq. (1.77b), the work amount, $\dot{W}_{\text{pump}}$, that needs to be supplied to the pump can be determined to be

$$\dot{W}_{\text{pump}} = -\dot{N}_m\,v_m(P_o + dP - P_o) = -\dot{N}_m v_m dP \tag{1.78}$$

where $\dot{N}_m$ is the molar flow rate of the incoming saline water, and v_m is the specific volume of the saline water. Since the saline water is a mixture of pure water and salt, the specific volume, v_m, as mentioned previously, can be expressed to be

$$v_m = x_s\,v_s + x_w\,v_w \tag{1.79}$$

where x_s and x_w are the mole fractions of the salt and the pure water in the incoming saline water, and v_s and v_w are the specific volumes of the salt and the pure water when they exist alone at mixture temperature and pressure, respectively. Substituting Eq. (1.79) into Eq. (1.78) gives

$$\dot{W}_{\text{pump}} = -\dot{N}_m\left[x_s\,v_s dP + x_w\,v_w dP\right] \tag{1.80}$$

The quantities of vdP in the above equation, as stated with Eq. (1.75), are expressed as a function of the universal gas constant R_u, temperature T, and the mole fraction x. That is,

$$v_s dP = R_u T_o \ln x_s \tag{1.81a}$$

and

$$v_w dP = R_u T_o \ln x_w \tag{1.81b}$$

The molar flow rate of the incoming saline water, $\dot{N}_m$, equals to the sum of the salt and the pure water molar flow rates for incoming and outgoing streams. Therefore, the molar flow rate of the incoming saline water then becomes

$$\dot{N}_m = \dot{N}_s + \dot{N}_w \tag{10}$$

where $\dot{N}_s$ and $\dot{N}_w$ are the molar flow rates of the salt and the pure water in the incoming saline water. Also, from the mass balances of salt and pure water for the entire system,

$$\dot{N}_s = \dot{N}_{s,\text{brine}} + \dot{N}_{s,\text{product}} \tag{11a}$$

and

$$\dot{N}_w = \dot{N}_{w,\text{brine}} + \dot{N}_{w,\text{product}} \tag{11b}$$

where $\dot{N}_{s,\text{brine}}$ and $\dot{N}_{s,\text{product}}$ are the molar flow rates of salt in the brine and product water streams, and $\dot{N}_{w,\text{brine}}$ and $\dot{N}_{w,\text{product}}$ are the molar flow rates of pure water in the brine and product water streams, respectively. Equations (1.83a) and (1.83b) simply come from the conservation of mass principle and mean that the amount of salt and pure water in the incoming saline water equals that of salt and pure water in the outgoing brine and product water streams. Substituting Eqs. (1.81a), (1.81b), (1.82), (1.83a) and (1.83b) into Eq. (1.80) yields

$$\dot{W}_{\text{pump}} = -R_u T_o \left[\dot{N}_{s,\text{brine}} \ln x_s + \dot{N}_{s,\text{product}} \ln x_s + \dot{N}_{w,\text{brine}} \ln x_w + \dot{N}_{w,\text{product}} \ln x_w\right] \tag{1.84}$$

The equation above gives the minimum work requirement for the pump depending on the molar flow rates of salt and pure water content in the outgoing product water and brine streams and the mole fractions of salt and pure water in the incoming saline water.

The pressurized saline water is routed into the membrane modules and is separated into brine and product water. The brine is then introduced into the turbine where it expands and produces work. Using Eq. (1.77b), the amount of work produced is determined to be

$$\dot{W}_{\text{turbine,brine}} = -\dot{N}_{\text{brine}} v_{\text{brine}} dP \tag{1.85}$$

where $\dot{N}_{\text{brine}}$ is the molar flow rate of the brine, and v_{brine} is the specific volume of the brine. The specific volume is expressed as

$$v_{\text{brine}} = x_{s,\text{brine}}\, v_{s,\text{brine}} + x_{w,\text{brine}}\, v_{w,\text{brine}} \tag{1.86}$$

where the subscripts *s* and *w* stand for salt and water content, respectively in the brine stream. Substituting Eq. (1.86) into Eq. (1.85) gives

$$\dot{W}_{\text{turbine, brine}} = -\dot{N}_{\text{brine}} \left[x_{s,\text{brine}}\, v_{s,\text{brine}} dP + x_{w,\text{brine}}\, v_{w,\text{brine}} dP\right] \tag{1.87}$$

Using Eq. (1.75), the terms $v_{s,\text{brine}} dP$ and $v_{w,\text{brine}} dP$ in the above equation are expressed as, respectively,

$$v_{s,\text{brine}} dP = R_u T_o \ln x_{s,\text{brine}} \tag{1.88a}$$

and

$$v_{w,\text{brine}} dP = R_u T_o \ln x_{w,\text{brine}} \tag{1.88b}$$

Substituting Eqs. (16a) and (16b) into Eq. (15) yields

$$\dot{W}_{\text{turbine,brine}} = -\dot{N}_{\text{brine}} R_u T_o \left[x_{s,\text{brine}} \ln x_{s,\text{brine}} + x_{w,\text{brine}} \ln x_{w,\text{brine}} \right] \tag{1.89}$$

Noting that $\dot{N}_{s,\text{brine}} = x_{s,\text{brine}} \dot{N}_{\text{brine}}$ and $\dot{N}_{w,\text{brine}} = x_{w,\text{brine}} \dot{N}_{\text{brine}}$, Eq. (17) becomes

$$\dot{W}_{\text{turbine,brine}} = -R_u T_o \left[\dot{N}_{s,\text{brine}} \ln x_{s,\text{brine}} + \dot{N}_{w,\text{brine}} \ln x_{w,\text{brine}} \right] \tag{1.90}$$

The quantity $\dot{W}_{\text{turbine,brine}}$ is the work output from the turbine as the brine expands from a high pressure of $P_o + dP$ to a low pressure of P_o. It is obvious from Eq. (1.90) that the amount of work production varies with the salinity and the molar flow rate of the brine. The product water, on the other hand, leaves the membrane and enters into the other turbine where its pressure is reduced from $P_o + dP$ to P_o, resulting in the work production. The work produced by the turbine is simply

$$\dot{W}_{\text{turbine,product}} = -\dot{N}_{\text{product}} v_{\text{product}} dP \tag{1.91}$$

where $\dot{N}_{\text{product}}$ is the molar flow rate of the product water and it is equal to the sum of the molar flow rates of the salt and the pure water in the product water, $\dot{N}_{s,\text{product}} + \dot{N}_{w,\text{product}}$, respectively, v_{product} is the specific volume of the product water. The specific volume is

$$v_{\text{product}} = x_{s,\text{product}}\, v_{s,\text{product}} + x_{w,\text{product}}\, v_{w,\text{product}} \tag{1.92}$$

where $x_{s,\text{product}}$ and $x_{w,\text{product}}$ are the mole fractions of the salt and the pure water in the product water, and $v_{s,\text{product}}$ and $v_{w,\text{product}}$ are the specific volumes of the salt and the pure water.

Substituting Eq. (1.92) into Eq. (1.91) gives

$$\dot{W}_{\text{turbine, product}} = -\dot{N}_{\text{product}} \left[x_{s,\text{product}}\, v_{s,\text{product}} dP + x_{w,\text{product}}\, v_{w,\text{product}} dP \right] \tag{1.93}$$

Noting that $v_{s,\text{product}} dP = R_u T_o \ln x_{s,\text{product}}$ and $v_{w,\text{product}} dP = R_u T_o \ln x_{w,\text{product}}$, Eq. (21) is rewritten to be

$$\dot{W}_{\text{turbine,product}} = -\dot{N}_{\text{product}} R_u T_o \left[x_{s,\text{product}} \ln x_{s,\text{product}} + x_{w,\text{product}} \ln x_{w,\text{product}} \right] \tag{1.94}$$

or

$$\dot{W}_{\text{turbine,product}} = -R_u T_o \left[\dot{N}_{s,\text{product}} \ln x_{s,\text{product}} + \dot{N}_{w,\text{product}} \ln x_{w,\text{product}} \right] \tag{1.95}$$

The equation above is similar to Eq. (1.90) and the amount of work produced by the turbine depends on the salinity and the molar flow rate of the product water. This equation completes the determination of all work inputs and outputs associated with the reverse osmosis desalination process. The minimum work input for the entire reverse osmosis desalination process can be found by simply subtracting the work outputs from the work input. It gives,

$$\dot{W}_{\min} = \dot{W}_{\text{pump}} - (\dot{W}_{\text{turbine,brine}} + \dot{W}_{\text{turbine, product}}) \tag{1.96}$$

where $\dot{W}_{\text{pump}}$ is the minimum work requirement to compress the incoming saline water from P_o to P_o+dP, $\dot{W}_{\text{turbine,brine}}$ is the maximum work output as the brine expands from P_o+dP to P_o, and similarly $\dot{W}_{\text{turbine,product}}$ is the maximum work output as the pressure of the product water is reduced from P_o+dP to P_o. Substituting Eqs. (1.84), (1.90), and (1.95) into Eq. (1.96) yields

$$\dot{W}_{\min} = R_u T_o (\dot{N}_{s,\text{brine}} \ln \frac{x_{s,\text{brine}}}{x_s} + \dot{N}_{s,\text{product}} \ln \frac{x_{s,\text{product}}}{x_s} + \dot{N}_{w,\text{brine}} \ln \frac{x_{w,\text{brine}}}{x_w} + \dot{N}_{w,\text{product}} \ln \frac{x_{w,\text{product}}}{x_w}$$

or

$$\begin{aligned}\dot{W}_{\min} = R_u T_o [\dot{N}_{\text{brine}} (x_{s,\text{brine}} \ln \frac{x_{s,\text{brine}}}{x_s} + x_{w,\text{brine}} \ln \frac{x_{w,\text{brine}}}{x_w}) \\ + \dot{N}_{\text{product}} (x_{s,\text{product}} \ln \frac{x_{s,\text{product}}}{x_s} + x_{w,\text{product}} \ln \frac{x_{w,\text{product}}}{x_w})]\end{aligned} \qquad (1.97)$$

The equation above is the net (or minimum) work requirement for the reverse osmosis desalination process and gives the minimum work input required for the separation of incoming saline water into two streams of brine and product water. The minimum work relation can be further simplified. Eqs. (1.83a) and (1.83b) can be expressed in terms of mole fractions and total molar flow rates of incoming and outgoing streams. Thus,

$$x_s \dot{N}_m = x_{s,\text{brine}} \dot{N}_{\text{brine}} + x_{s,\text{product}} \dot{N}_{\text{product}} \qquad (1.98a)$$

and

$$x_w \dot{N}_m = x_{w,\text{brine}} \dot{N}_{\text{brine}} + x_{w,\text{product}} \dot{N}_{\text{product}} \qquad (1.98b)$$

The solution of $\dot{N}_{\text{brine}}$ and $\dot{N}_{\text{product}}$ from these equations above gives

$$\dot{N}_{\text{brine}} = \frac{x_s x_{w,\text{product}} - x_w x_{s,\text{product}}}{x_{s,\text{brine}} x_{w,\text{product}} - x_{w,\text{brine}} x_{s,\text{product}}} \dot{N}_m \text{ and}$$

$$\dot{N}_{\text{product}} = \frac{x_w x_{s,\text{brine}} - x_s x_{w,\text{brine}}}{x_{s,\text{brine}} x_{w,\text{product}} - x_{w,\text{brine}} x_{s,\text{product}}} \dot{N}_m$$

(1.99)

Substituting the $\dot{N}_{\text{brine}}$ and $\dot{N}_{\text{product}}$ relations from Eq. (1.99) and dividing Eq. (1.97) by the molar mass of the product water M_{product} and the molar flow rate of the product water $\dot{N}_{\text{product}}$ yield

$$\begin{aligned}w_{\min} = \frac{R_u T_o}{M_{\text{product}}} [\frac{x_s x_{w,\text{product}} - x_w x_{s,\text{product}}}{x_w x_{s,\text{brine}} - x_s x_{w,\text{brine}}} (x_{s,\text{brine}} \ln \frac{x_{s,\text{brine}}}{x_s} + x_{w,\text{brine}} \ln \frac{x_{w,\text{brine}}}{x_w}) \\ + x_{s,\text{product}} \ln \frac{x_{s,\text{product}}}{x_s} + x_{w,\text{product}} \ln \frac{x_{w,\text{product}}}{x_w}]\end{aligned} \quad \text{(kJ/kg} \qquad (1.100)$$

product)

Note that the above equation is now based on the amount of minimum work per unit mass of product water delivered, and gives the minimum work input required for the separation of incoming saline water of known salinity into brine and product water of known salinities.

It is important to note that Eq. (1.100) is the same as the minimum work input relation found by Cerci et al. (1999) for an incomplete separation of incoming saline water into brine and product water. This is not surprising because the reversible work depends on the end states of a process and it is independent of the process path followed. Therefore, as long as the temperature and the pressure of the incoming and outgoing streams are the same for desalination processes, the same minimum work input relation is expected for each of these processes.

Cerci et al. (1999) also calculated the minimum work input values for different salinities of the incoming and outgoing streams with varying recovery ratios. They also discussed various aspects of the minimum work relation and presented the minimum work figures for the separation of common salinities of water.

1.3.13 Minimum Work Requirement for Distillation Processes

Distillation processes are energy intensive and involve numerous components in varying sizes. Loses in such components have considerable importance both for the design and operation of the plants. The efficiency of the plants is usually expressed in terms of the overall first law efficiency, but it does not show where energy inefficiencies and real energy losses occur and where modifications should be made to improve the overall utilization of energy in the plants. As has been discussed previously, this can be done by the second-law analysis. The first step in such analysis is the determination of the minimum work input requirements by analyzing the "idealized" distillation process. A typical ideal distillation process is proposed and analyzed by employing series of Carnot heat engines and pumps. The distillation process mainly consists of an evaporator, a condenser, and a heat exchanger. The heat interactions of the proposed system are accomplished by Carnot engines and heat pumps, because they give the maximum possible work output or the minimum work input associated with the processes. Therefore, the net result of these inputs and outputs gives the minimum work requirement for the distillation process. It is shown that the minimum work relation for the distillation process depends only on the properties of the incoming saline water and the outgoing pure water and brine, and it is the same as the general minimum work relation found by Cerci et al. (1999) for the production of pure water. Also, certain aspects of the minimum work relation found are discussed. The minimum work relations for the components provide the necessary tools to conduct a second-law analysis of the various components.

Figure 1.6 is a schematic diagram of the distillation process for desalting the saline water, and illustrates the idealized distillation system. As can be seen from the figure, it consists of an evaporator to vaporize the heated saline water, a condenser to liquefy the vapor, and a heat exchanger to recuperate energy from outgoing pure water and brine streams, and a number of Carnot heat engines and heat pumps to determine the minimum work requirement.

The distillation process is an isobaric process during which the inlet saline water pressure P_o remains constant throughout the components. The incoming saline water at T_o and molar flow rate $\dot{N}_m$ flows into a heat exchanger in which it is preheated, and the outgoing brine $\dot{N}_{\text{brine}}$ and the pure water $\dot{N}_{\text{pure}}$ are cooled. Since the molar flow rate of the incoming saline water equals the molar flow rates of the brine and the pure water, the saline water in the heat exchanger is heated from T_o to the saturation temperature of pure water T_L as the outgoing brine and pure water are cooled from T_L to T_o. The saline water at T_L is further heated by a Carnot heat pump where its temperature is raised to its boiling point T_H. Then, the saline water enters into an evaporator where the pure water vapor is formed, and the brine is concentrated. Since all streams entering and leaving the evaporator are in thermal equilibrium, the pure water vapor resulting from the surface of the saline water at T_H becomes superheated (Hawes, 1967). As the pure water vapor at T_H is transferred to the condenser, it is cooled to its saturation temperature T_L by giving off heat to a Carnot heat engine, thus producing power. The pure water vapor at T_L is then introduced into a condenser where it is condensed at the saturation temperature of the pure water T_L. The latent heat of condensation of the pure water is absorbed by another Carnot heat engine connected to the condenser. It should be pointed out that the latent heat of condensation of pure water is different from the latent heat of vaporization of the incoming saline water due to the effect of the salinity on boiling temperature. Therefore, special care must be taken when determining the latent heat of vaporization of the saline water. The pure water at T_L is then routed into the heat exchanger to be cooled by the incoming saline water. The brine, on the other hand, leaves the evaporator at temperature T_H and transfers heat to a Carnot heat engine as it is cooled from T_H to T_L, producing power. It is seen that a unit mass of the vapor is condensed in the condenser, as a unit mass of the pure water is evaporated in the evaporator.

The minimum work requirement for the above distillation process can be determined by representing actual processes by suitable reversible processes. The main assumptions which make the distillation process an idealized distillation process are:

(1) All components of the system operate steadily, and thus there is no change at any point within the system with time.

(2) The heat exchanger is reversible and thus no irreversibilities (such as heat transfer through a finite temperature difference) occur within it.

(3) The components of the system are well insulated and thus there are no direct heat interactions between the system and its surroundings. All heat transfers with the surroundings are through reversible heat engines and heat pumps.

(4) The salinity of the incoming seawater is constant.

(5) No changes in kinetic and potential energies of the fluids occur as they circulate through the system. The fluid flow is inviscid, and thus there are no pressure drops.

(6) Liquid water is an incompressible substance with constant specific heats. The temperature of the incoming saline water and the surroundings is T_o.

(7) The saline water is an ideal solution, and therefore it obeys Rault's law. The assumption of ideal solution is suitable for dilute solutions.

(8) The mole fraction of salt in the 3.5 percent NaCl solution (mass fraction) is about 0.011, and therefore the solution can be considered to be a dilute solution. Note that the enthalpy of an ideal solution is equal to the sum of the enthalpies of pure components that form the solution.

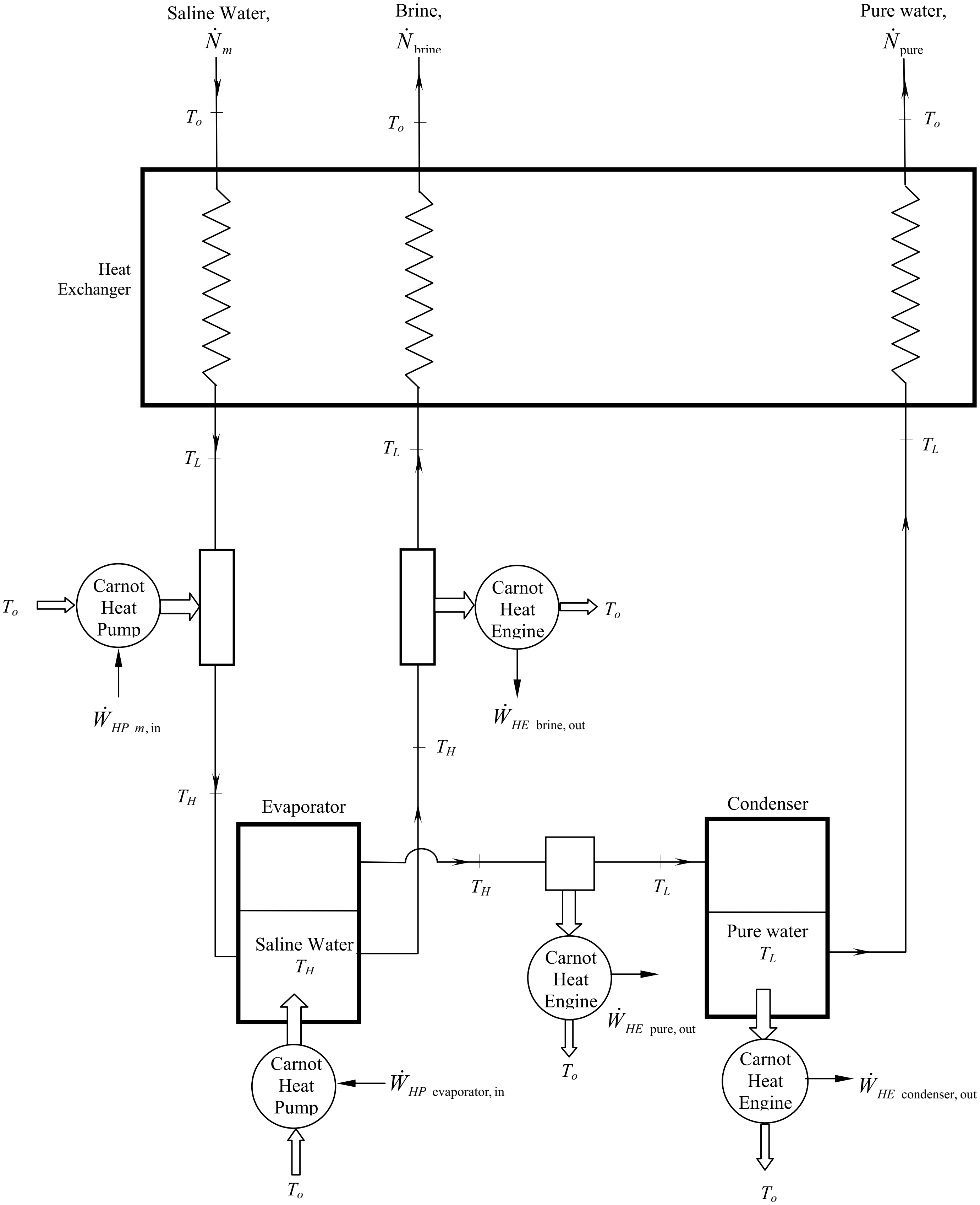

Figure 1.6.—Ideal Distillation Process.

As seen from figure 1.6, heat interactions of the distillation process with the surroundings are accomplished by several Carnot heat engines and pumps. The reversible work in a given environment represents the exergy change of a system in that environment. The minimum possible work input or the maximum possible work output associated with a process occur for the reversible case; it represents the exergy change of a fluid stream as the stream undergoes a process from one state to another. Therefore, in the minimum work analysis of the distillation process, the maximum possible work outputs produced by the Carnot heat engines and the minimum possible work inputs supplied to the Carnot heat pumps can be expressed in terms of the net exergy changes of the streams.

The specific flow exergy of a fluid stream with negligible kinetic and potential energies is given by

$$\psi = h - h_o - T_o(s - s_o) \tag{1.101}$$

where T_o is the dead state temperature, h and s are the enthalpy and the entropy of fluid at a specified state, and h_o and s_o are the corresponding properties of the fluid at the dead state. The proper choice for the dead state is the state of the saline water source. Since the saline water is a mixture of pure water and salt, the properties of salt must be taken into account along with the pure water properties. The molar enthalpy and entropy of a solution can be expressed as (Cengel et al., 1999)

$$h = x_w h_f + x_s h_s \tag{1.102}$$

and

$$s = x_w s_f + x_s s_s - R_u(x_w \ln x_w + x_s \ln x_s) \tag{1.103}$$

where x_w and x_s are the mole fractions of the pure water and the salt in the incoming saline water, h_f and h_s are the enthalpies and, s_f and s_s are the entropies of the pure water and the salt when they exist alone at the mixture temperature and pressure, respectively, and R_u is the universal gas constant. The enthalpy and the entropy values for pure water in the above relations are obtained from thermodynamic tables, and those of salt are calculated by using the thermodynamic relations for solids. These relations, however, require that the reference state of salt be chosen to determine the values of properties at specified states. The state of salt at 0ºC is taken as the reference state, and the values of h and s of salt are assigned a value of zero at that state.

The incoming saline water leaves the heat exchanger at T_L and is heated by the Carnot heat pump. The heat pump receives heat from the heat sink at T_o and supplies it to the saline water as the saline water is heated from T_L to the saline water boiling temperature of T_H. The amount of power, $\dot{W}_{HPm,\text{in}}$, that needs to be supplied to the Carnot heat pump can be determined from (Cengel et al., 1998)

$$\begin{aligned} \dot{W}_{HP\ m,\ \text{in}} &= \dot{N}_m(\psi_{m,H} - \psi_{m,L}) \\ &= \dot{N}_m[h_{m,H} - h_{m.L} - T_o(s_{m,H} - s_{m,L})] \end{aligned} \tag{1.104}$$

where the subscripts m,H and m,L stand for the incoming saline water at temperatures T_H and T_L, respectively, ψ is the molar specific exergy, h is the molar enthalpy, and s is the molar entropy.

From the conservation of mass principle, the molar flow rate of saline water, $\dot{N}_m$, can be expressed as

$$\dot{N}_m = \dot{N}_{\text{pure}} + \dot{N}_{\text{brine}} \tag{1.105}$$

where $\dot{N}_{\text{pure}}$ and $\dot{N}_{\text{brine}}$ are as defined before. Substituting Eq. (1.2) into Eq. (1.1), and expressing the properties in Eq. (1.1) in terms of salt and pure water properties, the power input becomes

$$\begin{aligned} \dot{W}_{HP\ m,\ \text{in}} = (\dot{N}_{\text{brine}} + \dot{N}_{\text{pure}})\{x_w(h_{f,H} - h_{f,L}) + x_s(h_{s,H} - h_{s,L}) \\ - T_o[x_w(s_{f,H} - s_{f,L}) + x_s(s_{s,H} - s_{s.L})]\} \end{aligned} \tag{1.106}$$

where the subscripts *f,H* and *f,L* stand for pure water at temperatures T_H and T_L, and the subscripts *s,H* and *s,L* stand for salt at temperatures T_H and T_L. The quantity $\dot{W}_{HP\ m,\text{in}}$ is the power input to the Carnot heat pump to raise the temperature of the saline water from T_L to T_H. The saline water at T_H is then routed into the evaporator and receives the latent heat of vaporization of the saline water from another Carnot heat pump operating between the boiling point temperature of the saline water and T_o. The power input for the Carnot heat pump is simply the difference between the sum of the exergies of the pure water and the brine leaving the evaporator and the exergy of the saline water entering the evaporator. That is,

$$\dot{W}_{HP\ \text{evaporator,in}} = \dot{N}_{\text{pure}}\psi_{\text{pure},H} + \dot{N}_{\text{brine}}\psi_{\text{brine},H} - \dot{N}_m\psi_{m,H} \tag{1.107}$$

where the subscripts pure,*H* and brine,*H* stand for the pure water and the brine at T_H, respectively. Substitution of exergy relations for the pure water, brine and the saline water streams into Eq. (4), and subsequent rearrangement, yield

$$\begin{aligned} \dot{W}_{HP\ \text{evaporator,in}} = \dot{N}_{\text{pure}}\{h_{g,H} - x_w h_{f,H} - x_s h_{s,H} - T_o[s_{g,H} - x_w s_{f,H} - x_s s_{s,H} \\ + R_u(x_w \ln x_w + x_s \ln x_s)]\} \\ + \dot{N}_{\text{brine}}\{(x_{w,\text{brine}} - x_w)(h_{f,H} - T_o s_{f,H}) + (x_{s,\text{brine}} - x_s)(h_{s,H} - T_o s_{s,H}) \\ - T_o R_u(x_w \ln x_w + x_s \ln x_s - x_{w,\text{brine}} \ln x_{w,\text{brine}} - x_{s,\text{brine}} \ln x_{s,\text{brine}})\} \end{aligned} \tag{1.108}$$

where the subscript *g,H* stands for pure water vapor at T_H, $x_{s,\text{brine}}$ and $x_{w,\text{brine}}$ are the mole fractions of the salt and the pure water in the brine, respectively. Note that the pure water vapor does not contain any salts, and its exergy is expressed in terms of pure water properties only. The power $\dot{W}_{HP\ \text{evaporator,in}}$ supplied to the Carnot heat pump is spent to transfer the latent heat of vaporization of the saline water from the heat sink at T_o to the evaporator at T_H. This results in the production of a unit mass of pure water vapor at T_H. Since the evaporator is maintained at the atmospheric pressure, the pure water vapor is superheated (Hawes, 1967). As the vapor flows from the evaporator to the condenser, it is cooled from T_H to its saturated vapor temperature T_L. The heat given off is transferred to the Carnot heat engine, causing it to produce work. The power output, $\dot{W}_{HE\ \text{pure,out}}$, can be determined from

$$\begin{aligned} \dot{W}_{HE\,\text{pure,out}} &= \dot{N}_{\text{pure}}(\psi_{\text{pure},H} - \psi_{\text{pure},L}) \\ &= \dot{N}_{\text{pure}}[h_{g,H} - h_{g,L} - T_o(s_{g,H} - s_{g,L})] \end{aligned} \tag{1.109}$$

where the subscripts pure,L and g,L stand for pure water vapor at T_L. The above equation includes the properties of the pure water vapor only. This is because the pure water vapor is free of salts. The quantity $\dot{W}_{HE\ \text{pure,out}}$ is the amount of power produced as the pure water vapor is cooled from T_H to T_L at constant pressure. Then, the pure water becomes saturated vapor and enters the condenser at T_L in the vapor phase. The latent heat of condensation of the pure water vapor is transferred to a Carnot heat engine operating between the condenser and the environment at T_o. The power produced by the Carnot heat engine is

$$\begin{aligned}\dot{W}_{HE\ \text{condenser,out}} &= \dot{N}_{\text{pure}}(\psi_{\text{pure},L} - \psi_{\text{pure}(f),L}) \\ &= \dot{N}_{\text{pure}}[h_{g,L} - h_{f,L} - T_o(s_{g,L} - s_{f,L})]\end{aligned} \tag{1.110}$$

where the subscript pure(f),L stands for the pure liquid water at T_L. The quantity $\dot{W}_{HE\ \text{condenser,out}}$ is the amount of power produced as the vapor is condensed in the condenser. The pure water at T_L enters into the heat exchanger where it is cooled from T_L to T_o. The resulting brine, on the other hand, is cooled from T_H to T_L by another Carnot heat engine. During the cooling of the brine, heat is transferred to the Carnot heat engine, causing it to produce work. The power output, $\dot{W}_{HE\ \text{brine,out}}$, can be determined from

$$\begin{aligned}\dot{W}_{HE\,\text{brine,out}} &= \dot{N}_{\text{brine}}(\psi_{\text{brine},H} - \psi_{\text{brine},L}) \\ &= \dot{N}_{\text{brine}}\{x_{w,\text{brine}}[(h_{f,H} - h_{f,L}) - T_o(s_{f,H} - s_{f,L})] \\ &\qquad + x_{s,\text{brine}}[(h_{s,H} - h_{s,L}) - T_o(s_{s,H} - s_{s,L})]\}\end{aligned} \tag{1.111}$$

where the subscript brine,L stands for the brine at T_L. This completes the determination of power inputs and outputs associated with the process. The net power input for the entire distillation process can be found by simply subtracting the power outputs from the power inputs. It gives, after combining some terms,

$$\begin{aligned}\dot{W}_{\text{net,in}} &= \dot{W}_{HP\ m,in} + \dot{W}_{HP\,\text{evaporator, in}} - (\dot{W}_{HE\,\text{pure, out}} + \dot{W}_{HE\,\text{condenser, out}} + \dot{W}_{HE\,\text{brine, out}}) \\ &= \dot{N}_{\text{brine}}[(x_{w,\text{brine}} - x_w)(h_{f,L} - T_o s_{f,L}) + (x_{s,\text{brine}} - x_s)(h_{s,L} - T_o s_{s,L}) \\ &\qquad + T_o R_u(x_{w,\text{brine}} \ln x_{w,\text{brine}} + x_{s,\text{brine}} \ln x_{s,\text{brine}} - x_w \ln x_w - x_s \ln x_s)] \\ &\quad + \dot{N}_{\text{pure}}[(1 - x_w)(h_{f,L} - T_o s_{f,L}) - x_s(h_{s,L} - T_o s_{s,L}) - T_o R_u(x_w \ln x_w + x_s \ln x_s)]\end{aligned} \tag{1.112}$$

Noting that $x_{w,\text{brine}} = 1 - x_{s,\text{brine}}$ and $x_w = 1 - x_s$, Eq. (1.112) becomes

$$\begin{aligned}\dot{W}_{\text{net,in}} &= \dot{N}_{\text{brine}}[(x_s - x_{s,\text{brine}})(h_{f,L} - h_{s,L} + T_o s_{s,L} - T_o s_{f,L}) \\ &\qquad + T_o R_u(x_{w,\text{brine}} \ln x_{w,\text{brine}} + x_{s,\text{brine}} \ln x_{s,\text{brine}} - x_w \ln x_w - x_s \ln x_s)] \\ &\quad + \dot{N}_{\text{pure}}[(x_s)(h_{f,L} - h_{s,L} + T_o s_{s,L} - T_o s_{f,L}) - T_o R_u(x_w \ln x_w + x_s \ln x_s)]\end{aligned} \tag{1.113}$$

A comparison of terms in the above equation reveals that there are two identical quantities associated with the enthalpies and entropies of the pure water and the salt. These are the quantities of $(h_{f,L} - h_{s,L} + T_o s_{s,L} - T_o s_{f,L})$. Also, from the definition of mole fraction and the conservation of mass, we have $\dot{N}_m x_s = \dot{N}_s$, $x_{s,\text{brine}}\dot{N}_\text{brine} = \dot{N}_{s,\text{brine}}$, $\dot{N}_\text{brine} = \dot{N}_m - \dot{N}_\text{pure}$, and $\dot{N}_s = \dot{N}_{s,\text{brine}}$. Note that the molar flow rate of salt in the incoming saline water equals the molar flow rate of salt in the brine since the pure water stream is salt-free. When these equations are substituted into Eq. (1.113), it is found that $\dot{N}_\text{brine}(x_s - x_{s,\text{brine}})$ and $\dot{N}_\text{pure} x_s$ multiplied by the identical quantities are the same but their sign is different. Therefore, these terms in Eq. (1.113) drop out, and the equation becomes independent of the enthalpies and the entropies of the pure water and the salt, and simplifies to

$$\dot{W}_\text{net,in} = R_u T_o[\dot{N}_\text{brine}(x_{w,\text{brine}} \ln x_{w,\text{brine}} + x_{s,\text{brine}} \ln x_{s,\text{brine}} - x_w \ln x_w - x_s \ln x_s) + \dot{N}_\text{pure}(-x_w \ln x_w - x_s \ln x_s)] \tag{1.114}$$

It is obvious from the equation above that the minimum work input requirement for the distillation process depends only on the salinities of the incoming saline water and the brine, even though it is derived from the reversible work relations of the components that make up the distillation process. Eq. (1.114) can be simplified even further by substituting $x_s = 1 - x_w$, $x_w = \dot{N}_w / \dot{N}_m$, $x_s = \dot{N}_s / \dot{N}_m$, $\dot{N}_s = \dot{N}_m - \dot{N}_w$, $\dot{N}_\text{brine} = \dot{N}_m - \dot{N}_\text{pure}$, $\dot{N}_w - \dot{N}_\text{pure} = \dot{N}_{w,\text{brine}}$, $x_{w,\text{brine}}\dot{N}_\text{brine} = \dot{N}_{w,\text{brine}}$, and $1 - x_{w,\text{brine}} = x_{s,\text{brine}}$. It gives, after some manipulations,

$$\dot{W}_\text{net,in} = R_u T_o[\dot{N}_\text{brine}(x_{s,\text{brine}} \ln\frac{x_{s,\text{brine}}}{x_s} + x_{w,\text{brine}} \ln\frac{x_{w,\text{brine}}}{x_w}) + \dot{N}_\text{pure}(-\ln x_w)] \tag{1.115}$$

The minimum work input per unit mass of pure water is obtained by dividing Eq. (12) by the molar mass of the pure water M_water and the molar flow rate of the pure water $\dot{N}_\text{pure}$. It yields

$$w_\text{net,in} = \frac{R_u T_o}{M_\text{water}}[\frac{\dot{N}_\text{brine}}{\dot{N}_\text{pure}}(x_{s,\text{brine}} \ln\frac{x_{s,\text{brine}}}{x_s} + x_{w,\text{brine}} \ln\frac{x_{w,\text{brine}}}{x_w}) - \ln x_w] \tag{1.116}$$

The above equation is the net minimum work input relation for the distillation process and gives the minimum amount of work to extract a unit mass of pure water from the saline water.

It is interesting to note that Eq. (1.116) can also obtained from the general minimum work input relation found by Cerci et al. (1999) by setting $x_{s,\text{product}} = 0$ and $x_{w,\text{product}} = 1$ (since the product water in the distillation process consists of pure water only). Again, this is due to the fact that the reversible work depends on the initial and final states of a process, and it is independent of the process path followed. It is also important to note that the reversible work relations derived for the components can be used to evaluate the performance of actual distillation process components such as evaporators, condensers, and heaters.

1.3.14 Minimum Work Requirement for Freeze Desalination Processes

The minimum work of freeze desalination methods will be analyzed on the basis of an ideal freeze desalination process. The ideal freeze desalination system consists of several Carnot refrigerator and heat engines as shown in Figure 1.7. The Carnot refrigerators and heat engines carry out heat and work interactions, and lead us to the concept of the reversible work for the whole freeze desalination system. The system is representative of the desalination processes described in Section 1.2.3 and includes components which are indispensable to operate it. The heat sink for the system is the saline water source at T_o.

The work requirement of the above freezing process can be calculated if the components operate under ideal conditions. Such a work requirement leads to the minimum work requirement and makes necessary certain assumptions on either processes or components. The main assumptions can be listed as follows:

- The heat exchanger, freezer, and melter are steady operating devices and therefore there is no net accumulation of water or salts in them.
- The temperature at any point in the system does not change with time.
- The components such as the heat exchanger, freezer, and melter are perfect devices such that there are no irreversibilities associated with them.
- There are no heat gain/loss between the system and its surroundings.
- There are no changes in kinetic and potential energies of the fluids circulating through the system.
- The ice crystals frozen from the saline water are perfectly pure such that they do not contain any dissolved salts.
- There are no pressure drops associated with components and connecting pipes.
- Since the fraction of salt is small for most saline waters, they can be assumed to be an ideal solution. Therefore, there are no irreversibilities associated with the saline water itself.

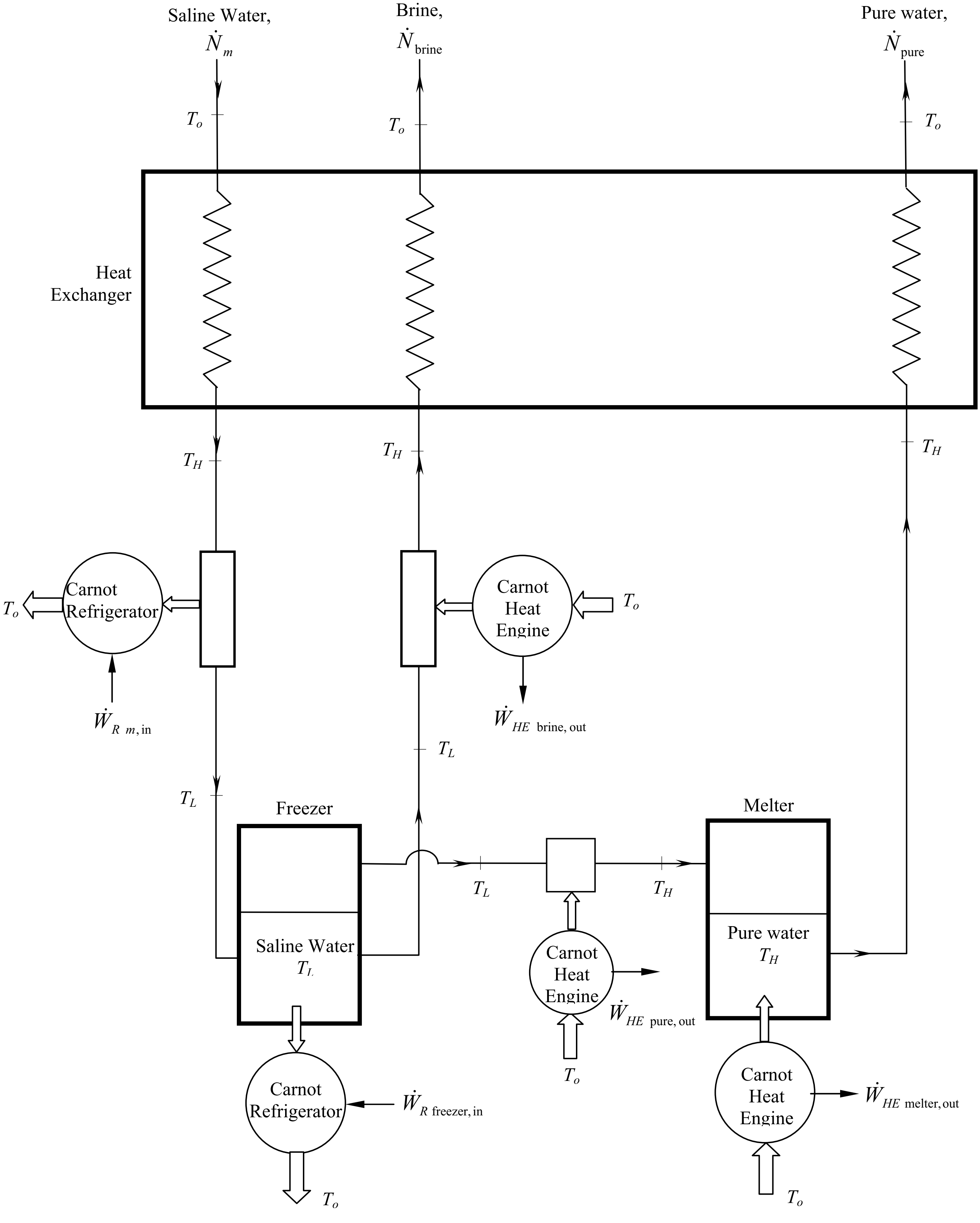

Figure 1.7.—Ideal freeze desalination process.

The ideal freeze desalination process is an isobaric process during which the pressure of the incoming saline water remains constant throughout the entire process. The saline water at temperature T_o and molar flow rate $\dot{N}_m$ enters the heat exchanger to be precooled by heat exchange with the outgoing brine $\dot{N}_{\mathrm{brine}}$ and pure water $\dot{N}_{\mathrm{pure}}$. The pure water and salt contents of the incoming saline water are equal to those of the outgoing brine and pure water streams. Therefore, the saline water is cooled to its freezing point of pure water T_H, and the brine and pure water are heated from T_H to T_o. The saline water at T_H is further cooled by a Carnot refrigerator to its freezing point T_L. The saline water then enters the freezer where the pure ice crystals are formed and separated from the concentrated brine solution. The pure water and the brine streams leave the freezer at the freezing temperature of the saline water, because the freezer is in thermal equilibrium. The latent heat of crystallization of the saline water is removed by another Carnot refrigerator operating between the freezing point temperature of the saline water T_L and the saline water source temperature T_o, causing the pure ice crystals to form. As the ice crystals are transferred from the freezer to the melter, they are allowed to receive heat from a Carnot heat engine, producing work. During this heating process, the temperature of ice crystals is raised to the freezing point of pure water T_H. The ice crystals at T_H, are transferred into the melter in which they are melted by receiving the latent heat of melting of ice from another Carnot heat engine. Note that the latent heat of crystallization is not equal to the latent heat of melting of ice since T_H is not equal to T_L. When the latent heat of melting is absorbed by the ice crystals, they become pure liquid water at T_H. The pure water is then routed into the heat exchanger, and its temperature is raised to T_o by absorbing heat from the incoming saline water. The brine, on the other hand, is heated by a Carnot heat engine, and its temperature is raised to T_H. It is seen that in a broad sense, the incoming saline water at T_o is separated into the pure water and the brine at the same temperature and pressure.

The reversible work for any process equals the exergy change of the system during that process at that environment. The determination of the exergy of a fluid stream at a state requires that the dead state be specified. For desalination processes, the proper choice for the dead state is the state of the saline water source. Since desalination processes deal with different salinities of the incoming saline water and the outgoing brine and product water streams, the properties of salt must be taken into account together with the pure water properties. Therefore, the exergy of the streams at a specified state can be expressed in terms of salt and pure water properties.

The incoming saline water exits the heat exchanger at T_H and is precooled to its freezing temperature by the Carnot refrigerator. The refrigerator absorbs heat as the saline water is cooled from T_H to T_L, and rejects the heat to the heat sink at T_o. The amount of work input to accomplish the cooling can be derived by considering the flow exergy change of the saline water. Therefore, the amount of power input, $\dot{W}_{R\,m,\mathrm{in}}$, is

$$\begin{aligned}\dot{W}_{R\,m,\,\mathrm{in}} &= \dot{N}_m(\psi_{m,L}-\psi_{m,H})\\ &= \dot{N}_m[h_{m,L}-h_{m.H}-T_o(s_{m,L}-s_{m,H})]\end{aligned} \qquad (1.117)$$

where the subscripts *m,L* and *m,H* stand for the incoming saline water at temperatures T_L and T_H, respectively, ψ is the molar specific exergy, h is the molar enthalpy, and s is the molar entropy. In Eq. (1.117) the molar flow rate of the saline water $\dot{N}_m$ equals the sum of the molar flow rate of the pure water $\dot{N}_{\text{pure}}$ and the molar flow rate of brine $\dot{N}_{\text{brine}}$, because the saline water separates into the pure water and the brine. Hence,

$$\dot{N}_m = \dot{N}_{\text{pure}} + \dot{N}_{\text{brine}} \tag{1.118}$$

Combining Eqs. (1.117) and (1.118), and expressing of the enthalpies and the entropies in terms of pure water and salt properties gives

$$\begin{aligned}\dot{W}_{R\ m,in} = (\dot{N}_{\text{brine}} + \dot{N}_{\text{pure}})\{x_w(h_{f,L} - h_{f,H}) + x_s(h_{s,L} - h_{s,H}) \\ - T_o[x_w(s_{f,L} - s_{f,H}) + x_s(s_{s,L} - s_{s.H})]\}\end{aligned} \tag{1.119}$$

where the subscripts *f,L* and *f,H* stand for pure water at temperatures T_L and T_H, and the subscripts *s,L* and *s,H* stand for salt at temperatures T_L and T_H, and x_s and x_w are the mole fractions of the salt and the pure water in the incoming saline water, respectively. The quantity $\dot{W}_{R\ m,\text{in}}$ is the amount of power that is required to supply the Carnot refrigerator to reduce the temperature of the saline water from T_H and T_L. The saline water at T_L then enters the freezer where the latent heat of crystallization of the saline water is removed by another Carnot refrigerator. The Carnot refrigerator operates between the freezing point of the saline water T_L and the heat sink temperature T_o. The required power input to the Carnot refrigerator can readily be expressed as

$$\dot{W}_{R\ \text{freezer,in}} = \dot{N}_{\text{pure}}\psi_{\text{pure},L} + \dot{N}_{\text{brine}}\psi_{\text{brine},L} - \dot{N}_m\psi_{m,L} \tag{1.120}$$

where the subscripts pure,*L* and brine,*L* stand for the pure water and the brine at T_L, respectively. Expressing the flow exergies in Eq. (1.120) in terms of salt and pure water properties and rearranging give

$$\begin{aligned}\dot{W}_{R\ \text{freezer,in}} = \dot{N}_{\text{pure}}\{h_{i,L} - x_w h_{f,L} - x_s h_{s,L} - T_o[s_{i,L} - x_w s_{f,L} - x_s s_{s,L} \\ + R_u(x_w \ln x_w + x_s \ln x_s)]\} \\ + \dot{N}_{\text{brine}}\{(x_{w,\text{brine}} - x_w)(h_{f,L} - T_o s_{f,L}) + (x_{s,\text{brine}} - x_s)(h_{s,L} - T_o s_{s,L}) \\ - T_o R_u(x_w \ln x_w + x_s \ln x_s - x_{w,\text{brine}} \ln x_{w,\text{brine}} - x_{s,\text{brine}} \ln x_{s,\text{brine}})\}\end{aligned} \tag{1.121}$$

where the subscript *i,L* stands for pure ice at T_L, $x_{s,\text{brine}}$ and $x_{w,\text{brine}}$ are the mole fractions of the salt and the pure water in the brine, respectively, and R_u is the universal gas constant. It should be pointed out that the exergy of the pure ice is expressed in terms of the pure ice properties only since it is salt-free. The power $\dot{W}_{R\ \text{freezer,in}}$ is the amount of power required to remove the latent heat of crystallization of the saline water from the freezer. The rejection of the latent heat of crystallization of the saline water from the freezer results in the formation of ice crystals at the solution temperature. As the ice crystals at T_L are transferred from the freezer to the melter, they are heated from T_L to T_H by a Carnot heat engine. The heat engine operates between the temperature at the point of heat rejection and T_o. The power produced by the Carnot heat engine can be determined from

$$\begin{aligned}\dot{W}_{HE\,\text{pure,out}} &= \dot{N}_{\text{pure}}(\psi_{\text{pure},L} - \psi_{\text{pure},H}) \\ &= \dot{N}_{\text{pure}}[h_{i,L} - h_{i,H} - T_o(s_{i,L} - s_{i,H})]\end{aligned} \tag{1.122}$$

where the subscripts pure,*H* and *i*,*H* stand for the pure ice crystals at T_H. It is obvious that the enthalpies and the entropies in Eq. (1.122) are for pure ice crystals only since the pure ice stream does not contain any dissolved salts. Then, the ice crystals at T_H are introduced into the melter where they are melted by another Carnot heat engine operating between T_H and T_o. The Carnot heat engine rejects the latent heat of melting of ice and produces power, $\dot{W}_{HE\ \text{melter,out}}$. The power produced can simply be determined from the exergy change of pure ice crystals during this melting process. That is,

$$\begin{aligned} \dot{W}_{HE\,\text{melter, out}} &= \dot{N}_{\text{pure}}(\psi_{\text{pure},H} - \psi_{\text{pure}(f),H}) \\ &= \dot{N}_{\text{pure}}[h_{i,H} - h_{f,H} - T_o(s_{i,H} - s_{f,H})] \end{aligned} \tag{1.123}$$

where the subscript pure(*f*),*H* stands for the pure liquid water at T_H. The quantity $\dot{W}_{HE\ \text{melter,out}}$ is the amount of power produced as the ice crystals are melted. The pure water at T_H is then routed into the heat exchanger and heated from T_H and T_o by cooling the incoming saline water. The concentrated brine solution, on the other hand, is heated from T_L and T_H by a Carnot heat engine. The Carnot heat engine rejects heat to the brine and produces power $\dot{W}_{HE\ \text{brine,out}}$. The power output can be determined from

$$\begin{aligned} \dot{W}_{HE\,\text{brine, out}} &= \dot{N}_{\text{brine}}(\psi_{\text{brine},L} - \psi_{\text{brine},H}) \\ &= \dot{N}_{\text{brine}}\{x_{w,\text{brine}}[(h_{f,L} - h_{f,H}) - T_o(s_{f,L} - s_{f,H})] \\ &\qquad + x_{s,\text{brine}}[(h_{s,L} - h_{s,H}) - T_o(s_{s,L} - s_{s,H})]\} \end{aligned} \tag{1.124}$$

where the subscript brine,*H* stands for the brine at T_H. The quantity $\dot{W}_{HE\ \text{brine,out}}$ is the amount of power produced as the brine is heated from T_L to T_H. Since all the power inputs and outputs are determined, the net power input that needs to be supplied to the entire freeze desalination process can be carried out by simply subtracting the power outputs from the power inputs. Noting that $x_{w,\text{brine}} = 1 - x_{s,\text{brine}}$ and $x_w = 1 - x_s$, we obtain, after arranging terms,

$$\begin{aligned} \dot{W}_{\text{net,in}} &= \dot{W}_{R\ m,in} + \dot{W}_{R\ \text{freezer, in}} - (\dot{W}_{HE\ \text{pure, out}} + \dot{W}_{HE\ \text{melter, out}} + \dot{W}_{HE\ \text{brine, out}}) \\ &= \dot{N}_{\text{brine}}[(x_s - x_{s,\text{brine}})(h_{f,H} - h_{s,H} + T_o s_{s,H} - T_o s_{f,H}) \\ &\qquad + T_o R_u(x_{w,\text{brine}} \ln x_{w,\text{brine}} + x_{s,\text{brine}} \ln x_{s,\text{brine}} - x_w \ln x_w - x_s \ln x_s)] \\ &\quad + \dot{N}_{\text{pure}}[(x_s)(h_{f,H} - h_{s,H} + T_o s_{s,H} - T_o s_{f,H}) - T_o R_u(x_w \ln x_w + x_s \ln x_s)] \end{aligned} \tag{1.125}$$

The above equation can be further simplified, because there are two identical quantities of $(h_{f,H} - h_{s,H} + T_o s_{s,H} - T_o s_{f,H})$. Also, the conservation of mass and the definition of mole fraction on the streams give $\dot{N}_m x_s = \dot{N}_s$, $x_{s,\text{brine}}\dot{N}_{\text{brine}} = \dot{N}_{s,\text{brine}}$, $\dot{N}_{\text{brine}} = \dot{N}_m - \dot{N}_{\text{pure}}$, and $\dot{N}_s = \dot{N}_{s,\text{brine}}$. The last relation is based on the fact that the pure water stream contains water only and therefore the molar flow rate of salt in the incoming saline water equals the molar flow rate of salt in the brine. Substituting these relations into Eq. (1.125) and then rearranging, we have

$$\dot{W}_{\text{net,in}} = R_u T_o [\dot{N}_{\text{brine}} (x_{w,\text{brine}} \ln x_{w,\text{brine}} + x_{s,\text{brine}} \ln x_{s,\text{brine}} - x_w \ln x_w - x_s \ln x_s) + \dot{N}_{\text{pure}} (-x_w \ln x_w - x_s \ln x_s)] \tag{1.126}$$

It is interesting to note from the above equation that the minimum work input requirement for the freeze desalination process depends on concentration only, and is independent of the enthalpies and the entropies of salt and water. Eq. (1.126) can be simplified further as follows: From the mass balances of salt and water and the definition of mole fraction we also have $x_s = 1 - x_w$, $x_w = \dot{N}_w / \dot{N}_m$, $x_s = \dot{N}_s / \dot{N}_m$, $\dot{N}_s = \dot{N}_m - \dot{N}_w$, $\dot{N}_{\text{brine}} = \dot{N}_m - \dot{N}_{\text{pure}}$, $\dot{N}_w - \dot{N}_{\text{pure}} = \dot{N}_{w,\text{brine}}$, $x_{w,\text{brine}} \dot{N}_{\text{brine}} = \dot{N}_{w,\text{brine}}$, and $1 - x_{w,\text{brine}} = x_{s,\text{brine}}$. When these relations are substituted into Eq. (1.126), it yields, after combining and rearranging,

$$\dot{W}_{\text{net,in}} = R_u T_o [\dot{N}_{\text{brine}} (x_{s,\text{brine}} \ln \frac{x_{s,\text{brine}}}{x_s} + x_{w,\text{brine}} \ln \frac{x_{w,\text{brine}}}{x_w}) + \dot{N}_{\text{pure}} (-\ln x_w)] \tag{1.127}$$

The minimum work input per unit mass of pure water is obtained by dividing Eq. (1.127) by the molar mass M_{water} and the molar flow rate of the pure water $\dot{N}_{\text{pure}}$. It gives

$$w_{\text{net,in}} = \frac{R_u T_o}{M_{\text{water}}} [\frac{\dot{N}_{\text{brine}}}{\dot{N}_{\text{pure}}} (x_{s,\text{brine}} \ln \frac{x_{s,\text{brine}}}{x_s} + x_{w,\text{brine}} \ln \frac{x_{w,\text{brine}}}{x_w}) - \ln x_w] \tag{1.128}$$

where $w_{\text{net, in}}$ is the minimum amount of work to extract a unit mass of pure water from the saline water. The above minimum work relation gives the minimum work values for the freeze desalination process and it depends only on the salinities of the incoming and outgoing streams. The minimum work input becomes zero for pure water undergoing the freeze desalination process due to the absence of salts in it, as expected.

Equation (1.128) gives the minimum work values for separation process in which the incoming saline water is separated into the outgoing brine and pure water streams. The mole fraction of salt in the pure water is zero, and thus the mole fraction of water in the pure water is unity. The general minimum work input relation found by Cerci et al. (1999), on the other hand, is developed for separation processes in which neither stream is pure. However, the general minimum work relation for the case of pure water stream can be derived by setting $x_{s,\text{product}} = 0$ and $x_{w,\text{product}} = 1$, since it is applicable to any separation process. The resulting relation is the same as Eq. (1.128) and gives minimum work values to extract pure water from the saline water. Again this analysis for freeze desalination clearly indicates that the minimum work input is independent of the components utilized in the freeze desalination process and depends only on the salinities of the incoming saline water and the outgoing brine streams. Also, the reversible work relations for the components from which Eq. (1.128) is derived can be used to evaluate the performance of actual freeze desalination components such as freezer, melter, and cooler.

1.4 SUMMARY AND CONCLUSIONS

A detailed analysis of the minimum work for ideal reverse osmosis, distillation, and freeze desalination processes has shown that the minimum work requirement is the same for all desalination processes and is independent of any hardware or process utilized. Relations were obtained for the minimum (or reversible) work input needed for complete separation of mixtures, and presented in various convenient forms. The results obtained can be used for a wide range of separation processes including the desalination of sea or brackish water, and the second-law efficiency of separation processes.

The minimum work input analysis was extended for an incomplete separation process which is the case of all practical desalination processes. Using this relation, the minimum work input can be determined for any salinity of incoming saline water and the recovery ratio. It is shown that lower and upper limits exist for the minimum work, corresponding to recovery ratios of 0 percent and 100 percent, respectively.

We can draw the following conclusions from the minimum work analysis of the incomplete separation process performed and the results presented in the tables and charts:

(1) The minimum work is a strong function of salinity, and increases linearly with salinity at concentrations encountered in practice. For example, the minimum work needed to separate saline water with 2 percent salinity is almost twice as much as that of saline water with 1 percent salinity.

(2) The minimum work input requirement increases with decreasing salinity of the fresh water produced. Therefore, it takes more work to produce water with less salinity.

(3) The minimum work input requirement remains fairly constant for recovery ratios of up to about 80 percent. This is especially true at low salinities. Therefore, operating actual desalination plants at low recovery ratios actually reduces system efficiency and, thereby, increases energy costs per unit of product water.

(4) The minimum work increases drastically at high recovery ratios. Therefore, recovery ratios above about 80 percent should be avoided. This is especially the case for saline waters with high salinities.

(5) An optimum value of recovery ratio exists to minimize the power consumption of actual desalination plants. The optimum recovery ratio decreases with increasing salinity of the incoming saline water. Therefore, particular attention must be paid to the recovery ratios when desalination plants are being designed.

Using the second-law efficiency defined in Section 1.3.10, the overall performance of desalination plants can readily be quantified. In the analysis, the work input to the desalination processes is always mentioned, but there are distillation processes which do not require a work input. In these processes, heat energy is directly applied to the evaporator by burning fuel or other energy sources. A comparison can still be made on the basis of the second law of thermodynamics by considering the exergy (work potential) of the heat through the use of Carnot efficiency. That is,

$$w_{\min} = q_{\min}\left(1 - \frac{T_o}{T}\right)$$

where T is the temperature of the heat source and T_o is the temperature of the heat sink, which can be taken to be the temperature of the incoming seawater. Note that the minimum heat input required depends on the temperature of the heat source as well as the ambient temperature.

It is hoped that the analysis presented in this work helps to understand the thermodynamic aspect of desalination processes better, and guide in identifying the potentials for the improvement of the thermodynamic efficiencies of desalination processes.

2 CASE STUDIES OF FOUR WORKING PLANTS

2.1 INTRODUCTION

To identify where the greatest inefficiencies are, an exergy analyisis was carried out for four different types of operating desalination plants, viz.: two-stage reverse osmosis, two-stage nanofiltration, electrodialysis, and multi-stage flash distillation. The first three plants were housed in the same facility in Port Hueneme, CA. The Port Hueneme Water Agency operates a brackish water research demonstration facility that consists of separate side-by-side full-scale membrane plants of each major type, each producing one million gallons of fresh water per day: The Reverse osmosis (RO) and nanofiltration (NF) plants use a semi permeable membrane that allows water to pass but not salts. The electrodialysis reversal (EDR) plant uses electric current to "withdraw or pull" dissolved ions from the water. The fourth plant is located near the city of Al-Jubail at the Arabian Gulf coast. This Multi-Stage Flash (MSF) plant consists of 40 distillation units and each unit consists of 22 flashing stages. The plant is capable of producing distilled water at a rate of 230 million gallons per day.

The ideal and the actual desalination processes are described, and the exergy change of the major components for the ideal and the actual processes are calculated and illustrated using exergy flow diagrams. The specific objectives of this analysis are:

(1) Develop a procedure to evaluate the minimum work input associated with desalination, and express it in terms of exergy to enable comparison between membrane and thermal processes on an equitable basis,

(2) Develop general procedures to perform a second-law analysis at the systems level as well as for the individual components,

(3) Identify the sources of irreversibility, and consider ways of minimizing them.

(4) Apply the procedure to four operating desalination plants, and determine the second-law efficiency of the components as well as the system,

(5) Identify research areas where the greatest impact on energy use and economics can be achieved to improve the efficacy of desalination technologies.

2.2 EXERGY ANALYSIS OF THREE MEMBRANE PLANTS

2.2.1 Port Hueneme Research Demonstration Facility

The Port Hueneme Water Agency Brackish Water Research Demonstration Facility is located in Port Hueneme, California (North of Los Angeles along the coast). It has a fresh water production capacity of about 2250 gallons per minute (GPM). The facility consists of separate side-by-side full-scale membrane plants of each major type: Reverse osmosis (RO), nano filtration (NF), and electrodialysis reversal (EDR). The RO and NF plants use a semi permeable membrane that allows water to pass but not salts. EDR uses electric current to "withdraw or pull" dissolved ions from the water. The plant started continuous operation in January 3, 1999.

The flow diagrams for the three desalination plants are shown in Figures 2.1, 2.2, and 2.3. General plant operation data are given in Table 2.1. Average monthly data for June 2000 for the RO, NF, and EDR units are given in Tables 2.2, 2.3, and 2.4, respectively. Brackish water with a salinity of about 900 mg/L (parts per million on mass basis or a mass fraction of 0.09 percent for salts) enters the plant at about 15°C and atmospheric pressure. Water is pumped by the main pump to 82 psig (667 kPa absolute), and is filtered and treated.

In the RO unit, a 100-hp booster pump raises raw water pressure to 132 psig (1011 kPa absolute) before it enters the first stage of RO unit that consists of 14 pressure vessels with 84 layers of membranes. The concentrate from the first stage experiences a pressure drop of 30 psi and enters the second stage with 7 pressure vessels and 42 layers of membranes at 102 psig (804 kPa absolute). Permeates from both stages are then combined, and later blended with raw water to raise the salinity of the product water to the desired level of 370 mg/L.

The operation of the NF unit is very similar, except that the pressure of raw water is raised to 119 psig (922 kPa absolute) before the first stage by a 75-hp booster pump, and the pressure is 88 psig (708 kPa) before the second stage. Also, the first stage consists of 15 pressure vessels with 90 elements, and the second stage consists of 7 pressure vessels and 42 elements. The EDR unit does not use a booster pump. Instead, it uses electric current directly to separate salts from water and a smaller pump is used for recirculation.

During a one-year period from February 1, 1999 to January 31, 2000, the power cost per 1000 gallons of treated water was reported to be $0.12 for RO, $0.10 for NF, and $0.09 for EDR unit based on electric utility rate of $0.069/kWh. The total annual operation and maintenance cost per 1000 gallons of treated water, including labor, chemicals, and power were $0.27 for RO, $0.50 for NF, and $0.23 for EDR unit. The construction costs were $724,000 for RO, $721,000 for NF, and $892,000 for EDR facilities for a total of $2.3 million. Each of the three units has a treated water capacity of about 700 GPM. The additional cost for site, building, booster station, and raw and treated water pipelines was a total of $7 million.

2.2.2 Exergy Analysis for Membrane Plants

Salinity is usually expressed in parts per million (MG/L), which is defined as MG/L = $mf_s \times 10^6$. Therefore, a salinity of 1000 mg/L corresponds to a salinity of 0.1 percent, or a salt mass fraction of $mf_s = 0.001$. Then the mole fraction of salt x_s becomes

$$mf_s = \frac{m_s}{m_m} = \frac{N_s M_s}{N_m M_m} = x_s \frac{M_s}{M_m} \quad \text{and} \quad mf_w = x_w \frac{M_w}{M_m} \tag{2.1}$$

Where *m* is mass, *M* is the molar mass, *N* is the number of moles, *and x* is the mole fraction. The subscripts *s*, *w*, and *m* stand for salt, water, and the saline water. The apparent molar mass of the saline water is

$$M_m = \frac{m_m}{N_m} = \frac{N_s M_s + N_w M_w}{N_m} = x_s M_s + x_w M_w \tag{2.2}$$

The molar masses of NaCl and water are 58.5 kg/kmol and 18.0 kg/kmol, respectively. Salinity is usually given in terms of mass fractions, but the minimum work calculations require mole fractions. Combining Eqs. (2.1) and (2.2) and noting that $x_s + x_w = 1$ gives the following convenient relations for converting mass fractions to mole fractions,

$$x_s = \frac{M_w}{M_s(1/mf_s - 1) + M_w} \quad \text{and} \quad x_w = \frac{M_s}{M_w(1/mf_w - 1) + M_s} \tag{2.3}$$

Flow rates and other plant data for the RO, NF, and EDR units are given in Table 2.1. Salinity is usually given in terms of conductivity. There is considerable uncertainty in conductivity measurements, especially in the high range. Therefore, it was necessary to make some adjustments to the data to satisfy mass balances. For the 1-year period from February 1, 1999 to January 31, 2000, the TDS (total dissolved solids) and conductivity are given to be 1000 mg/L and 1390 μS/cm for raw water, and 595 μS/cm and 370 mg/L for the final blend product water. The TDS and conductivity of product water (permeate) for different operations during the same period are given to be 70 mg/L and 23 μS/cm for RO, 90 mg/L and 32 μS/cm for NF, and 320 mg/L and 533 μS/cm for EDR. The TDS and conductivity of rejected brine for different operations during the same period are given to be 3675 mg/L and 4350 uS for RO, 3575 mg/L and 4350 μS/cm for NF, and 5825 mg/L and 5725 μS/cm for EDR.

For June 2000, the conductivity of permeate is given to be 21 μS/cm for RO, 44 μS/cm for NF, and 616 μS/cm for EDR. By interpolation, their corresponding TDS are determined to be 64 mg/L for RO, 124 mg/L for NF, and 370 mg/L for EDR. Using this and brine data from Table 1, the TDS of raw water for June are determined to be 831 mg/L for RO, 903 mg/L for NF, and 793 mg/L for EDR, which is inconsistent and different than the 1000 mg/L value for the 1-year period (they all should be the same since all 3 operations use the same raw water). For consistency, we take the TDS of raw water to be 900 mg/L for all operations. Then the TDS of discharged brine is determined from mass balance for salt for each operation.

The flow rates are given in gallons per minute (GPM), and can be converted to mass flow rates by multiplying them by density. The total mass flow rate $\dot{m}_{\text{total}}$ can simply be determined from

$$\dot{m}_{\text{total}} = (1 + mf_s)\rho_{\text{water}}\dot{V} \tag{2.4}$$

where ρ_{water} = 1 kg/L is the density of water, mf_s = mg/L×10^{-6} is the mass fraction of salt, and $\dot{V}$ is the volume flow rate. For example, the mass flow rate of permeate of RO plant and its salt content are

$$\dot{m}_{\text{total}} = (1 + 64 \times 10^{-6})(1\,\text{kg/L})(476\,\text{gal/min})(3.7854\,\text{L/gal}) = 1802\,\text{kg/min}$$

$$\dot{m}_{\text{salt}} = mf_s \times \dot{m}_{\text{total}} = (64 \times 10^{-6})1802\,\text{kg/min} = 0.1153\,\text{kg/min}$$

When the salinities and flow rates of feedwater and permeate are known, the salinity of brine is determined from mass balance of salt as

$$\dot{m}_{\text{salt, feedwater}} = \dot{m}_{\text{salt, permeate}} + \dot{m}_{\text{salt, brine}} \quad \text{and} \quad mf_{\text{s, brine}} = \dot{m}_{\text{salt, brine}} / \dot{m}_{\text{total, brine}} \tag{2.5}$$

The RO and NF plants involve two-stage desalination in which the brine output from the first stage is further separated into permeate and more concentrated brine in the second stage. The yield of each stage is specified to be roughly the same. Therefore, we take the permeate flow rates from each stage to be equal to half the total permeate mass flow rate, and to have the same salinities. The mass flow rate for product water is determined from the requirement that its salinity is 370 mg/L. Saline water can be considered to be an "ideal solution" with negligible error since the effect of dissimilar molecules (molecules of salt and water) on each other is negligible. Extensive properties of a mixture is the sum of the extensive properties its individual components. The enthalpy and entropy of a mixture, for example, are determined from

$$H = \sum m_i h_i = m_s h_s + m_w h_w \quad \text{and} \quad S = \sum m_i s_i = m_s s_s + m_w s_w \tag{2.6}$$

Dividing by the total mass of the mixture gives the quantities per unit mass of mixture,

$$h = \sum mf_i h_i = mf_s h_s + mf_w h_w \quad \text{and} \quad s = \sum mf_i s_i = mf_s s_s + mf_w s_w \tag{2.7}$$

The enthalpy of mixing of an ideal gas mixture is zero (no heat is released or absorbed during mixing), and thus the enthalpy of the mixture (and thus the enthalpies of its individual components) do not change during mixing. Therefore, the enthalpy an ideal mixture at a specified temperature and pressure is the sum of the enthalpies of its individual components at the same temperature and pressure. Then it follows that the enthalpy of a saline solution can be determined from the relation above by evaluating the enthalpies of individual components at the mixture temperature and pressure.

The average raw brackish water withdrawn for desalination is at about 15°C, 1 atm, and a salinity of 900 mg/L. We take these conditions to be conditions of the environment. Then the properties at the dead state become

$$T_0 = 288.15\text{ K}, \quad P_0 = 1\text{ atm} = 101.\ 325\text{ kPa, and } \text{Sal}_0 = 1000\text{ mg/L} = 0.1\text{ percent} \tag{2.8}$$

The specific heat of salt can be taken to be C_{ps} = 0.8368 kJ/kg·K. Also for consistency with prior work, we take the enthalpy and entropy of salt at T_0 = 15°C to be h_{s0} = 12.552 kJ/kg and s_{s0} = 0.04473 kJ/kg·K (note that for incompressible substances, the enthalpy and entropy are independent of pressure). Then the enthalpy and entropy of salt at temperature T can be determined from

$$h_s = h_{s0} + C_{ps}(T - T_0) \quad \text{and} \quad s_s = s_{s0} + C_{ps}\ln(T / T_0) \tag{2.9}$$

Properties of pure water are readily available in tabulated or computerized forms. We will use water properties evaluated by the built-in functions of the EES (Engineering Equation Solver) software at mixture temperature and pressure. (F-Chart Software, 2002)

Mixing is an irreversible process, and thus the entropy of a mixture at a specified temperature and pressure must be greater than the sum of the entropies of the individual components (prior to mixing) at the same temperature and pressure. Then it follows that the entropies of the components of a mixture are greater than the entropies of their pure counterparts at the same temperature and pressure since the entropy of a mixture is the sum of the entropies of its components. The entropy of a component per unit mole in an ideal solution at a specified temperature T and pressure P is (Cengel et al., 1999)

$$\bar{s}_i = \bar{s}_{i,\text{pure}}(T,P) - R_u \ln x_i \tag{2.10}$$

Note that $\ln x_i$ is a negative quantity since $x_i < 1$, and thus $-R_u \ln x_i$ is always a positive quantity. Therefore, the entropy of a component in a mixture is always greater than the entropy of that component when it existed alone at the mixture temperature and pressure. Then the entropy of a saline solution is the sum of the entropies of salt and water in the saline solutions,

$$\begin{aligned} \bar{s} &= x_s\bar{s}_s + x_w\bar{s}_w \\ &= x_s[\bar{s}_{s,\text{pure}}(T,P) - R_u \ln x_s] + x_w[\bar{s}_{w,\text{pure}}(T,P) - R_u \ln x_w] \\ &= x_s\bar{s}_{s,\text{pure}}(T,P) + x_w\bar{s}_{w,\text{pure}}(T,P) - R_u(x_s \ln x_s + x_w \ln x_w) \end{aligned} \tag{2.11}$$

The entropy of saline water per unit mass is determined by dividing the quantity above (which is per unit mole) by the molar mass of saline water. It gives

$$s = mf_s s_{s,\text{pure}}(T,P) + mf_w s_{w,\text{pure}}(T,P) - R_m(x_s \ln x_s + x_w \ln x_w) \quad (\text{kJ/kg}\cdot\text{K}) \tag{2.12}$$

The exergy of a flow stream is given as (Cengel and Boles, 1998)

$$\psi = h - h_0 - T_0(s - s_0) \tag{2.13}$$

Then the rate of exergy flow associated with a fluid stream becomes

$$\dot{X} = \dot{m}\psi = \dot{m}[h - h_0 - T_0(s - s_0)] \tag{2.14}$$

Using the relations above, the specific exergy and exergy flow rates at various points indicated in Figures 2.1, 2.2, and 2.3 were evaluated. Once exergy flow rates are available, exergy destroyed within any component can be determined from an exergy balance. Note that the exergy of raw brackish water is zero since its state is taken to be the dead state and the exergies of the brine streams are negative due to salinities above the dead state level.

2.2.3 Results and Discussion for Membrane Plants

Using the relations presented above, this desalination plant was analyzed under the following assumptions:

(1) The rates of discharged brine and outgoing product water are taken from plant data. Then the flow rate and salinity of incoming raw water is determined from a mass balance.

(2) The raw water temperature of 15°C is taken as the environment temperature in all calculations.

(3) All components of the system operate at steady state conditions.

(4) The salinity of the incoming raw water is constant.

(5) The kinetic and potential energies of fluid streams are negligible.

(6) The saline water is an ideal solution.

(7) Salt, water, and saline water are incompressible substances.

(8) The electric power supplied is consumed by the pumps and the EDR unit.

The results of analysis were obtained using the EES software (F-Chart Software, 2002), and are given in Tables 2.2, 2.3, 2.4, and 2.5. The exergy input for each operation was taken to be equal to the electric power consumption for that operation, and the average rate of exergy input was determined by dividing the total electricity consumption by the total operating hours for the month. For the RO plant, for example, it is

$$\dot{X}_{\text{in}} = \dot{W}_{\text{electric}} = \frac{W_{\text{electric}}}{\text{No. of hours}} = \frac{52{,}672\ \text{kWh}}{684.5\ \text{h}} = 76.95\ \text{kW}$$

The minimum work input for a steady-flow adiabatic process is the work input required for a reversible adiabatic process, and is equal to the difference between the exergies of the outgoing streams and the exergies of the incoming streams, including the salinity exergy (note that exergy is conserved for reversible processes). The exergy of incoming seawater is zero since its state is taken as the reference state for exergy calculations. Therefore, the minimum work input for the separation of 3442.1 kg/min brackish water at 15°C, 1 atm, and a salinity of 900 mg/L by the RO plant into 2842 kg/min fresh water with a salinity of 370 mg/L and 600.1 kg/min saline water with a salinity of 3410.4 mg/L at the same temperature and pressure is

$$\begin{aligned}\dot{W}_{\min} &= \dot{X}_{\text{outgoing brine and product water}} - \dot{X}_{\text{incoming seawater}} = \dot{X}_{18} + \dot{X}_{12} - \dot{X}_{0} \\ &= 8.78 + (-7.56) - 0 = 1.22\ \text{kW}\end{aligned}$$

Note that the inlet and exit streams are at the same temperature and pressure, and thus this work is entirely due to the composition of incoming and outgoing streams. The minimum work of separation can also be determined independently using the relation developed by Cerci, et al. (Cerci, 1999). It also gives 1.22 kW, which is identical to the result obtained above.

The real value of second-law analysis becomes more evident when the analysis is performed at the component level, and the sites of maximum exergy destruction are identified. Exergy balance for any system undergoing any process is expressed as (Cengel and Boles, 1998)

$$\underbrace{X_{\text{in}} - X_{\text{out}}}_{\text{by heat, work, and mass}} - X_{\text{destroyed}} = \Delta X_{\text{system}}$$

For a system that does not involve any work interaction (no exergy transfer by work) and undergoes a process that is steady (no change in the exergy of the system) and adiabatic (no exergy transfer by heat), the relation above simplifies to

$$\dot{X}_{\text{destroyed}} = \dot{X}_{\text{in, by mass}} - \dot{X}_{\text{out, by mass}}$$

The product water is typically pumped to higher pressures to serve communities, and thus the mechanical exergy of product water is also utilized. Its value in the RO plant is

$$\dot{X}_{\text{mech, product}} = \dot{X}_{17} - \dot{X}_{18} = 13.68 - 8.78 = 4.90\ \text{kW}$$

The exergy supplied other than the minimum work and the mechanical exergy of product water is wasted. Then the rate of total exergy destruction in the RO plant is

$$\dot{X}_{\text{destroyed, total}} = \dot{X}_{\text{in}} - (\dot{W}_{\text{min}} + \dot{X}_{\text{mech, product}}) = 76.95 - (1.22 + 4.90) = 70.83\ \text{kW}$$

The fraction of exergy destruction within a component in the RO plant is determined from

$$f_{\text{destroyed}} = \frac{\dot{X}_{\text{destroyed, component}}}{\dot{X}_{\text{destroyed, total}}} = \frac{\dot{X}_{\text{destroyed, component}}}{70.83\ \text{kW}}$$

The exergy supplied by the pumps of the RO plant, the exergy destruction (and its percentage) by the pumps and their motors, and the combined pump-motor efficiency is

$$\begin{aligned}\Delta\dot{X}_{\text{pumps}} &= \Delta\dot{X}_{\text{main pump}} + \Delta\dot{X}_{\text{booster pump}} = (\dot{X}_1 - \dot{X}_0) + (\dot{X}_9 - \dot{X}_8)\\ &= (33.33 - 0) + (36.36 - 20.85) = 48.84\ \text{kW}\end{aligned}$$

$$\eta_{\text{pumps}} = \frac{\Delta\dot{X}_{\text{pump}}}{X_{\text{in}}} = \frac{48.84\ \text{kW}}{76.95\ \text{kW}} = 63.5\%$$

$$\dot{X}_{\text{destroyed, pumps}} = \dot{X}_{\text{in}} - \Delta\dot{X}_{\text{pumps}} = 76.95 - 48.84 = 28.11\ \text{kW} \quad \text{(39.7 percent of total)}$$

The amount and fraction of exergy destroyed in various components are determined to be

RO unit (1st stage):

$$\dot{X}_{\text{destroyed, RO1}} = \dot{X}_9 - \dot{X}_{10} - \dot{X}_{14} = 36.36 - 13.47 - 6.16 = 16.73\ \text{kW} \quad (23.6\%)$$

RO unit (2nd stage):

$$\dot{X}_{\text{destroyed, RO2}} = \dot{X}_{10} - \dot{X}_{11} - \dot{X}_{13} = 13.47 - (-1.58) - 6.16 = 8.89\ \text{kW} \quad (12.5\%)$$

Bypass water during throttling:

$$\dot{X}_{\text{destroyed, bypass}} = \dot{X}_6 - \dot{X}_{16} = 9.29 - 1.79 = 7.49\ \text{kW} \quad (10.6\%)$$

Discharged raw water:

$$\dot{X}_{\text{destroyed, discharge}} = \dot{X}_2 - \dot{X}_3 = 0.93 - 0 = 0.93\ \text{kW} \quad (1.3\%)$$

Discharged brine (mechanical):

$$\dot{X}_{\text{destroyed, brine}} = \dot{X}_{11} - \dot{X}_{12} = -1.58 - (-7.56) = 5.97\ \text{kW} \quad (8.4\%)$$

Bag filters:

$$\dot{X}_{\text{destroyed, filter}} = \dot{X}_4 - \dot{X}_5 = 32.40 - 30.74 = 1.66\ \text{kW} \quad (2.3\%)$$

Static mixer:

$$\dot{X}_{\text{static mixer}} = \dot{X}_7 - \dot{X}_8 = 21.45 - 20.85 = 0.60\ \text{kW} \quad (0.8\%)$$

Blending with bypass water:

$$\dot{X}_{\text{destroyed,blending}} = \dot{X}_{15} + \dot{X}_{16} - \dot{X}_{17} = 12.32 + 1.79 - 13.69 = 0.43\,\text{kW} \quad (0.6\%)$$

The second-law efficiency of this RO plant is determined by subtracting the ratio of the total exergy destruction to the total exergy input from one. It gives

$$\eta_{\text{II}} = 1 - \frac{\dot{X}_{\text{destroyed}}}{\dot{X}_{\text{in}}} = 1 - \frac{70.83\,\text{kW}}{76.95\,\text{kW}} = 8.0\%$$

which is low. It indicates that this desalination process at specified rates could be accomplished using only 6.13 kW of exergy (or work input) instead of 76.95 kW. Note that the pump-motor units are responsible for the largest fraction of exergy destruction (about 39.7 percent), followed by the two stages of the RO unit (36.2 percent), as expected.

The next largest exergy destructions occur in the throttling valve of the bypass water (10.6 percent). The remaining 13.5 percent of exergy destruction occurs during discharging of brine, bag filters, static mixer, and discharged raw water.

The NF and EDR plants were analyzed similarly, and the results are summarized in Table 2.5. Exergy flow diagrams that indicate the exergy destruction at various components are given for all 3 operations in Figures 2.5, 2.6, and 2.7.

2.3 EXERGY ANALYSIS OF A MSF DISTILLATION PLANT

2.3.1 MSF Plant Description

The data analyzed in this work was obtained from the integrated Al-Jubail MSF plant with a water production capacity of 230 MGD (0.871 million m^3/day), and an installed power generation capacity of 1295 MW. The plant is located near the city of Al-Jubail at the Arabian Gulf coast. The MSF unit consists of 40 distillation units, and each unit consists of 22 flashing stages and is capable of producing distilled water at a rate of 272 kg/s or 23,500 m^3/day.

The flow diagram describing this plant is shown in Figure 2.4. Seawater with a salinity of 46,500 mg/L (parts per million on mass basis or a mass fraction of 4.65 percent for salts) enters the plant at 35°C (308 K) at atmospheric pressure at a rate of 2397 kg/s. Most of this water serves as a coolant in the later stages of flashing (its temperature rises from 308 to 316.3 K), and is discharged back to the sea, while 808 kg/s of it is supplied into the flashing chamber after it is treated with chemicals. The mixture in the flashing chamber at 316.3 K with a salinity of 64,828 mg/L is pumped back into a cooling line through the flashing chamber, and its temperature rises to 358 K as it cools and condenses the water vapor in the flashing stages. The saline water is then heated by steam to 363.8 K in a heat exchanger while steam at 98.9°C condenses at a rate of 37.02 kg/s. The saline water is then flashed successively to lower pressures in the flashing cells as its pressure drops from 635 kPa to about 8 kPa absolute. Vacuum in the lowest stages is maintained by steam injection. The condensed vapor is collected, and discharged as distilled water at a rate 272 kg/s while saline water is discharged partially at a rate of 536 kg/s and a salinity of 70,093 mg/L.

The properties at various points throughout the plant are also given on the diagram and in Table 2.6.

2.3.2 MSF Plant Exergy Analysis

Salinity is usually expressed in parts per million (MG/L), which is defined as MG/L = $mf_s \times 10^6$. Therefore, a salinity of 46,500 mg/L (as encountered in the gulf) corresponds to a salinity of 4.65 percent, or a salt mass fraction of $mf_s = 0.0465$. Then the mole fraction of salt x_s becomes

$$mf_s = \frac{m_s}{m_m} = \frac{N_s M_s}{N_m M_m} = x_s \frac{M_s}{M_m} \quad \text{and} \quad mf_w = x_w \frac{M_w}{M_m} \tag{2.15}$$

Where m is mass, M is the molar mass, N is the number of moles, *and* x is the mole fraction. The subscripts s, w, and m stand for salt, water, and the saline water. The apparent molar mass of the saline water is

$$M_m = \frac{m_m}{N_m} = \frac{N_s M_s + N_w M_w}{N_m} = x_s M_s + x_w M_w \tag{2.16}$$

The molar masses of NaCl and water are 58.5 kg/kmol and 18.0 kg/kmol, respectively. Salinity is usually given in terms of mass fractions, but the minimum work calculations require mole fractions. Combining Eqs. (2.1) and (2.2) and noting that $x_s + x_w = 1$ gives the following convenient relations for converting mass fractions to mole fractions,

$$x_s = \frac{M_w}{M_s(1/mf_s - 1) + M_w} = \frac{18}{58.5(1/mf_s - 1) + 18} \tag{2.17a}$$

and

$$x_w = \frac{M_s}{M_w(1/mf_w - 1) + M_s} = \frac{58.5}{18(1/mf_w - 1) + 58.5} = 1 - x_s \tag{2.17b}$$

For example, the average salinity of seawater is 3.5 percent, and thus the mass fractions are mf_s =0.035 are $mf_w = 0.965$. The mole fractions are determined from the relations above to be are x_s =0.011 are x_w =0.989. Therefore, the average molar salinity of seawater is about 1.1 percent.

Saline water can be considered to be an "ideal solution" with negligible error since the effect of dissimilar molecules (molecules of salt and water) on each other is negligible. Extensive properties of a mixture are the sum of the extensive properties of its individual components. The enthalpy and entropy of a mixture, for example, are determined from

$$H = \sum m_i h_i = m_s h_s + m_w h_w \quad \text{and} \quad S = \sum m_i s_i = m_s s_s + m_w s_w \tag{2.18}$$

Dividing by the total mass of the mixture gives the quantities per unit mass of mixture,

$$h = \sum mf_i h_i = mf_s h_s + mf_w h_w \quad \text{and} \quad s = \sum mf_i s_i = mf_s s_s + mf_w s_w \tag{2.19}$$

The enthalpy of mixing of an ideal gas mixture is zero (no heat is released or absorbed during mixing), and thus the enthalpy of the mixture (and thus the enthalpies of its individual components) do not change during mixing. Therefore, the enthalpy of an ideal mixture at a specified temperature and pressure is the sum of the enthalpies of its individual components at the same temperature and pressure. Then it follows that the enthalpy of a saline solution can be determined from the relation above by evaluating the enthalpies of individual components at the mixture temperature and pressure.

The seawater withdrawn for desalination is given to be at 308 K, 1 atm, and a salinity of 46,500 mg/L. We take these conditions to be conditions of the environment. Then the properties at the dead state becomes

$$T_0 = 308 \text{ K}, \quad P_0 = 1 \text{ atm} = 101.325 \text{ kPa, and } \text{Sal}_0 = 46{,}500 \text{ mg/L} = 4.65 \text{ percent} \tag{2.20}$$

The specific heat of salt can be taken to be $C_{ps} = 0.8368$ kJ/kg·K. Also for consistency with prior work, we take the enthalpy and entropy of salt at $T_0 = 308$ K to be $h_{s0} = 29.288$ kJ/kg and $s_{s0} = 0.1009175$ kJ/kg·K (note that for incompressible substances, enthalpy and entropy are independent of pressure). Then the enthalpy and entropy of salt at temperature T can be determined from

$$h_s = h_{s0} + C_{ps}(T - T_0) \quad \text{and} \quad s_s = s_{s0} + C_{ps}\ln(T/T_0) \tag{2.21}$$

Properties of pure water are readily available in tabulated or computerized forms. We will use water properties evaluated by the built-in functions of the EES software at mixture temperature and pressure.

Mixing is an irreversible process, and thus the entropy of a mixture at a specified temperature and pressure must be greater than the sum of the entropies of the individual components (prior to mixing) at the same temperature and pressure. Then it follows that the entropies of the components of a mixture are greater than the entropies of their pure counterparts at the same temperature and pressure since the entropy of a mixture is the sum of the entropies of its components. The entropy of a component per unit mole in an ideal solution at a specified temperature T and pressure P is (Cengel et al., 1999)

$$\bar{s}_i = \bar{s}_{i,\text{pure}}(T,P) - R_u \ln x_i \tag{2.22}$$

Note that $\ln x_i$ is a negative quantity since $x_i < 1$, and thus $-R_u \ln x_i$ is always a positive quantity. Therefore, the entropy of component in a mixture is always greater than the entropy of that component when it existed alone at the mixture temperature and pressure. Then the entropy of a saline solution is the sum of the entropies of salt and water in the saline solutions,

$$\begin{aligned} \bar{s} &= x_s\bar{s}_s + x_w\bar{s}_w \\ &= x_s[\bar{s}_{s,\text{pure}}(T,P) - R_u \ln x_s] + x_w[\bar{s}_{w,\text{pure}}(T,P) - R_u \ln x_w] \\ &= x_s\bar{s}_{s,\text{pure}}(T,P) + x_w\bar{s}_{w,\text{pure}}(T,P) - R_u(x_s \ln x_s + x_w \ln x_w) \end{aligned} \tag{2.23}$$

The entropy of saline water per unit mass is determined by dividing the quantity above (which is per unit mole) by the molar mass of saline water. It gives

$$s = mf_s s_{s,\text{pure}}(T,P) + mf_w s_{w,\text{pure}}(T,P) - R_m(x_s \ln x_s + x_w \ln x_w) \quad \text{(kJ/kg·K)} \tag{2.24}$$

The exergy of a flow stream is given as (Cengel and Boles, 1998)

$$\psi = h - h_0 - T_0(s - s_0) \tag{2.25}$$

Then the rate of exergy flow associated with a fluid stream becomes

$$\dot{X} = \dot{m}\psi = \dot{m}[h - h_0 - T_0(s - s_0)] \tag{2.26}$$

Using the relations above, the specific exergy and exergy flow rates at various points indicated in Figure 4 were evaluated. Once exergy flow rates are available, exergy destroyed within any component can be determined from exergy balance.

Note that the exergy of incoming seawater is zero since its state is taken to be the dead state. Also, some exergies are negative, which can be explained as follows: the work potential (exergy) of a fluid stream is due to the temperature, pressure, and chemical potential of the fluid relative to the dead state (assuming kinetic and potential energies are negligible, and the chemical and nuclear effects are not considered). Therefore, the thermo mechanical exergy of a substance (due to temperature and pressure) is zero when it is at dead state temperature and pressure, but its salinity exergy due to concentration is not zero. When the salinity of a fluid stream is above the salinity of incoming seawater, it requires a net "work input" to reduce its salinity to the dead state level, and thus its salinity exergy is negative. But when the salinity of a fluid stream is below the salinity of incoming seawater (such as the pure water), it can produce work as it is allowed to mix with salt until its salinity rises to the dead sate level, and thus its salinity is positive. A comprehensive second-law analysis of distillation processes is given in a recent paper by Cerci et al. (2000).

2.3.3 Results and Discussion for MSF Plant

Using the relations presented above, this MSF desalination plant was analyzed under the following assumptions:

(1) The rates of incoming seawater and outgoing product water are taken from plant data, but the flow rate and salinity of discharged brine are adjusted to satisfy mass balances.

(2) The flow rate of steam is adjusted to satisfy the energy balance in the HX.

(3) The steam evacuated by the barometric condenser that provides vacuum in the MSF system is disregarded.

(4) The combined pump-motor efficiency is taken to be 75 percent.

(5) The incoming seawater temperature of 308 K is taken as the environment temperature in all calculations.

(6) All components of the system operate steadily.

(7) The salinity of the incoming saline water is constant.

(8) The kinetic and potential energies of fluid streams are negligible.

(9) The saline water is an ideal solution.

(10) Salt, water, and saline water are incompressible substances.

The results were obtained using the EES software, and are given in Table 2.6. Saline water is heated from 358 K to 363.8 K at a rate of 3621 kg/s by saturated steam at 98.9°C in a heat exchanger. Steam leaves the heat exchanger at the same temperature as saturated liquid. An energy balance on the heat exchanger gives the condensation rate of steam to be 37.02 kg/s. Also, the rate of heat transfer to the saline water from steam is

$$\dot{Q}_{\text{in, steam}} = \dot{m}_{\text{steam}} h_{fg\,@\,98.9\,\text{C}} = (37.02\ \text{kg/s})(2260\ \text{kJ/kg}) = 83{,}665\ \text{kJ/s}$$

Taking the dead-state temperature to be $T_o = 35°\text{C} = 308\ \text{K}$, the rate of exergy supply by the steam is

$$\begin{aligned}\dot{X}_{\text{in, steam}} &= \dot{m}_{\text{steam}}(\Delta h - T_o \Delta s = h_{fg} - T_o s_{fg}) \\ &= (37.02\ \text{kg/s})[2260\ \text{kJ/kg - }(308\ \text{K})(6.076\ \text{kJ/K})] = 13{,}559\ \text{kJ/s}\end{aligned}$$

The plant involves 4 pumps at locations indicated in Figure 2.4. The combined pump-motor efficiency can be defined as the ratio of the mechanical energy transferred to the fluid (which is the increase in the exergy of the fluid in this case) to the electrical energy consumed. The total rate of exergy increase of various fluid streams is the sum of the exergy change across the pumps, and is determined to be

$$\begin{aligned}\Delta\dot{X}_{\text{pumps}} &= \Delta\dot{X}_{\text{seawater pump}} + \Delta\dot{X}_{\text{productwater pump}} + \Delta\dot{X}_{\text{brine pump}} + \Delta\dot{X}_{\text{recirculating pump}} \\ &= (\dot{X}_1 - \dot{X}_0) + (\dot{X}_{13} - \dot{X}_5) + (\dot{X}_{14} - \dot{X}_6) + (\dot{X}_8 - \dot{X}_7) \\ &= (153.41 - 0) + (3008.76 - 2852.90) + [-1735.30 - (-1877.23)] + [-7540.01 - (-9676.76)] \\ &= 2587.95\ \text{kW}\end{aligned}$$

For a combined pump-motor efficiency of 75 percent, the exergy supplied in the form of electric power is

$$\dot{X}_{\text{in, pumps}} = \Delta\dot{X}_{\text{pumps}} / \eta_{\text{pump-motor}} = 2587.95 / 0.75 = 3450\ \text{kW}$$

Then the total exergy supplied to this desalination plant becomes

$$\dot{X}_{\text{in, total}} = \dot{X}_{\text{in, steam}} + \dot{X}_{\text{in, pumps}} = 13{,}559 + 3450 = 17{,}009\ \text{kW}$$

Next we determine the minimum work input for the separation of 808 kg/s seawater at 35°C, 1 atm, and a salinity of 46,550 mg/L into 272 kg/s fresh water with zero salinity and 536 kg/s saline water with a salinity of 70,093 mg/L at the same temperature and pressure. The minimum work input for a steady-flow adiabatic process is the work input required for a reversible adiabatic process, and is equal to the difference between the exergies of the outgoing streams and the exergies of the incoming streams, including the salinity exergy (note that exergy is conserved for reversible processes). The exergy of incoming seawater is zero since its state is taken as the reference state for exergy calculations. Therefore,

$$\begin{aligned}\dot{W}_{\text{min}} &= \dot{X}_{\text{outgoing brine and product water}} - \dot{X}_{\text{incoming seawater}} \\ &= \dot{X}_{15} + \dot{X}_{16} - \dot{X}_0 \\ &= (-2083.16) + 2792.87 - 0 = 709.70\ \text{kW}\end{aligned}$$

Note that the inlet and exit streams are at the same temperature and pressure, and thus this work is entirely due to the composition of incoming and outgoing streams.

The minimum work of separation can also be determined independently using the relation developed by Cerci et al. (1999). It gives 709 kW, which gives essentially the same result obtained above.

The second-law efficiency of this MSF distillation plant is the ratio of the minimum exergy input required (which is equivalent to the minimum work of separation) to the total actual exergy input. It gives

$$\eta_{\mathrm{II}} = \frac{\dot{X}_{\text{in, min}}}{\dot{X}_{\text{in, total}}} = \frac{\dot{W}_{\min}}{\dot{X}_{\text{in, total}}} = \frac{709.7\ \mathrm{kW}}{17{,}009\ \mathrm{kW}} = 4.2\%$$

which is quite low. It indicates that this desalination process at the specified rates could be accomplished ideally using only 710 kW of exergy (or work input) instead of 17,009 kW. Then the rate of exergy destruction (wasted exergy) during this process becomes

$$\begin{aligned}\dot{X}_{\text{destroyed, total}} &= \dot{X}_{\text{in, total}} - \dot{X}_{\text{in, min}} = \dot{X}_{\text{in, total}} - \dot{W}_{\min} \\ &= 17{,}009 - 709.70 \\ &= 16{,}299\ \mathrm{kW}\end{aligned}$$

The real value of second-law analysis becomes more evident when the analysis is performed at the component level, and the sites of maximum exergy destruction are identified. For example, the rate of exergy destruction by the pumps is

$$\dot{X}_{\text{destroyed,pumps}} = \dot{X}_{\text{in, pumps}} - \Delta\dot{X}_{\text{pumps}} = 3450 - 2587.95 = 862\ \mathrm{kW} \quad \text{(5.3 percent of total)}$$

Exergy balance for any system undergoing any process is expressed as (Cengel and Boles, 1998)

$$\underbrace{X_{\text{in}} - X_{\text{out}}}_{\text{by heat, work, and mass}} - X_{\text{destroyed}} = \Delta X_{\text{system}}$$

For a system that does not involve any work interaction (no exergy transfer by work) and undergoes a process that is steady (no change in the exergy of the system) and adiabatic (no exergy transfer by heat), the relation above simplifies to

$$\dot{X}_{\text{destroyed}} = \dot{X}_{\text{in, by mass}} - \dot{X}_{\text{out, by mass}}$$

The fraction of exergy destruction within a component is determined from

$$f_{\text{destroyed}} = \frac{\dot{X}_{\text{destroyed, component}}}{\dot{X}_{\text{destroyed, total}}} = \frac{\dot{X}_{\text{destroyed, component}}}{16{,}299\ \mathrm{kW}}$$

Then the amount and fraction of exergy destroyed in various components are determined to be

The MSF unit:

$$\begin{aligned}\dot{X}_{\text{destroyed, MSF}} &= (\dot{X}_1 + \dot{X}_4 + \dot{X}_8 + \dot{X}_{10}) - (\dot{X}_2 + \dot{X}_5 + \dot{X}_6 + \dot{X}_7 + \dot{X}_9) \\ &= [153.41 + 316.41 + (-7540.01) + 56{,}107.03] \\ &\quad - [1181 + 2852.90 + (-1877.23) + (-9676.76) + 43{,}896.30] \\ &= 12{,}660.64\ \mathrm{kW} \qquad (77.7\%)\end{aligned}$$

The Steam-brine HX:

$$\dot{X}_{\text{destroyed,HX}} = (\dot{X}_9 + \dot{X}_{11}) - (\dot{X}_{10} + \dot{X}_{12})$$

$$= [43{,}896.30 + 13{,}559.02] - [56{,}107.03 + 0] = 1348.29\ \text{kW} \quad (8.3\%)$$

Feedwater during throttling:

$$\dot{X}_{\text{destroyed,throttling}} = \dot{X}_3 - \dot{X}_4 = 398.10 - 316.41 = 81.69\ \text{kW} \quad (0.5\%)$$

Discharged seawater used for cooling (thermal):

$$\dot{X}_{\text{destroyed,cooling}} = \dot{X}_2 - (\dot{X}_{17} + \dot{X}_3) = 1181 - (0 + 398) = 783\ \text{kW} \quad (4.8\%)$$

Discharged brine (thermal):

$$\dot{X}_{\text{destroyed,brine}} = \dot{X}_{14} - \dot{X}_{15} = -1735.30 - (-2083.16) = 347.86\ \text{kW} \qquad (2.1\%)$$

Product water (thermal):

$$\dot{X}_{\text{destroyed,product}} = \dot{X}_{13} - \dot{X}_{16} = 3008.76 - 2792.87 = 215.89\ \text{kW} \quad (1.3\%)$$

Note that largest exergy destruction (about 77.8 percent) occurs within the MSF unit, as expected. The next largest exergy destructions occur in the heat exchanger (8.3 percent), the pumps and their motors (5.3 percent), and the discharge of cooling water back into the sea (4.8 percent). The remaining 3.8 percent of exergy destruction occurs during throttling, discharge of brine, and discharge of product water.

Table 1.1.—Average plant data for June 2000

Quantity	**RO**	**NF**	**EDR**
Electricity consumption, kWh	52,672	39,658	39,325
Operating hours, h	684.5	685.6	685.5
Average power input, kW[1]	76.95	57.84	57.37
Raw water flow rate, GPM	660	689	793
Brine flow rate, GPM	158	168	87
Permeate flow rate, GPM	476	502	658
1st stage pressure, psig	132	119	50
2nd stage pressure, psig	102	88	--
Permeate pressure, psig	15	14	8
Brine pressure, psig	87	65	8
Pressure drop across bag filters, psi	4.2	4.2	4.2
Raw water TDS (total dissolved solids), mg/L[2]	900	900	900
Brine conductivity, uS	3710	3810	4632
Brine TDS, mg/L[3]	3410.4	3211.6	4889.7
Permeate conductivity, uS	21	44	616
Permeate TDS, mg/L[4]	64	124	370
Product water TDS, after blending with bypass water	370	370	370

[1] Calculated from values above.

[2] Approximate average value.
[3] Calculated from mass balance of salt.
[4] Calculated from conductivity data.

Table 2.2.—Properties and exergy flow rates at various locations throughout the RO plant

Location	Temperature T, K	Pressure P, kPa	Salinity, mg/L	Mass flow rate, kg/min	Specific exergy, ψ, kJ/kg	Exergy flow rate, X, kW
0	288.15	101.325	900	3540.6	0	0
1	288.15	667	900	3540.6	0.5648	33.328
2	288.15	667	900	98.5	0.5648	0.927
3	288.15	101.325	900	98.5	0	0
4	288.15	667	900	3442.1	0.5648	32.400
5	288.15	638	900	3442.1	0.5359	30.742
6	288.15	638	900	1040	0.5359	9.289
7	288.15	638	900	2402.1	0.5359	21.454
8	288.15	623	900	2402.1	0.5209	20.853
9	288.15	1011	900	2402.1	0.9083	36.362
10	288.15	804	1401.8	1501.1	0.5385	13.472
11	288.15	701	3410.4	600.1	-0.1581	-1.581
12	288.15	205	3410.4	600.1	-0.7554	-7.555
13	288.15	205	64	901	0.4103	6.161
14	288.15	205	64	901	0.4103	6.161
15	288.15	205	64	1802	0.4103	12.322
16	288.15	205	900	1040	0.1035	1.794
17	288.15	101.325	370	2842	0.2889	13.684
18	288.15	101.325	370	2842	0.1853	8.777

Table 2.3.—Properties and exergy flow rates at various locations throughout the NF plant

Location	Temperature *T*, K	Pressure *P*, kPa	Salinity, mg/L	Mass flow rate, kg/min	Specific exergy, ψ, kJ/kg	Exergy flow rate, *X*, kW
0	288.15	101.325	900	3492.6	0	0
1	288.15	667	900	3492.6	0.5648	32.876
2	288.15	667	900	72.0	0.5648	0.678
3	288.15	101.325	900	72.0	0	0
4	288.15	667	900	3420.6	0.5648	32.198
5	288.15	638	900	3420.6	0.5359	30.550
6	288.15	638	900	882.1	0.5359	7.878
7	288.15	638	900	2538.5	0.5359	22.672
8	288.15	623	900	2538.5	0.5209	22.038
9	288.15	922	900	2538.5	0.8195	34.670
10	288.15	708	1364.3	1588.3	0.4546	12.034
11	288.15	550	3211.6	638.0	-0.2526	-2.686
12	288.15	101.325	3211.6	638.0	-0.6996	-7.439
13	288.15	198	124	950.3	0.3776	5.980
14	288.15	198	124	950.3	0.3776	5.980
15	288.15	198	124	1900.5	0.3776	11.960
16	288.15	198	900	882.1	0.0965	1.419
17	288.15	198	370	2782.6	0.2819	13.073
18	288.15	101.325	370	2782.6	0.1853	8.593

Table 2.4.—Properties and exergy flow rates at various locations throughout the EDR plant

Location	Temperature T, K	Pressure P, kPa	Salinity, mg/L	Mass flow rate, kg/min	Specific exergy, ψ, kJ/kg	Exergy flow rate, X, kW
0	288.15	101.325	900	3004.5	0	0.00
1	288.15	667	900	3004.5	0.5648	28.28
2	288.15	667	900	181.8	0.5648	1.71
3	288.15	101.325	900	181.8	0	0.00
4	288.15	667	900	2822.7	0.5648	26.57
5	288.15	638	900	2822.7	0.5359	25.21
6	288.15	638	900	2822.7	0.5359	25.21
7	288.15	638	900	0	0.5359	0.00
8	288.15	157	900	0	0.0556	0.00
9	288.15	157	4889.7	331.0	-1.1017	-6.08
10	288.15	101.325	4889.7	331.0	-1.1571	-6.38
11	288.15	157	370	2491.7	0.2410	10.01
12	288.15	157	370	2491.7	0.2410	10.01
13	288.15	101.325	370	2491.7	0.1853	7.70

Table 2.5.—Results of exergy analysis for June 2000

Quantity	RO	NF	EDR
Exergy input, kW[1]	76.95	57.84	57.37
Min work of separation, kW	1.224	1.157	1.314
Total exergy destruction, kW	70.82	52.21	53.74
Mechanical energy of product water, kW	4.91	4.48	2.31
2nd-law efficiency[1]	8.0 percent	9.7 percent	6.3 percent
Exergy destruction in various components and its percentage:			
Discharged raw water	0.93 (1.3 percent)	0.68 (1.3 percent)	1.71 (3.2 percent)
Bag filters	1.66 (2.4 percent)	1.65 (3.2 percent)	1.36 (2.5 percent)
Static mixer	0.60 (0.8 percent)	0.63 (1.2 percent)	--
Separation unit (RO, NF, EDR)[2]	25.62 (36.2 percent)	25.4 (48.6 percent)	21.28 (39.6 percent)
Throttling of bypass water	7.49 (10.6 percent)	6.46 (12.4 percent)	0 (0 percent)
Blending with bypass water	0.43 (0.6 percent)	0.31 (0.6 percent)	0 (0 percent)
Mech. exergy of discharged brine	5.97 (8.4 percent)	4.75 (9.1 percent)	0.31 (0.6 percent)
Pumps and piping system	28.11 (39.7 percent)	12.33 (23.6 percent)	28.28 (54.1 percent)

[1] Accounts for the mechanical energy of product water.

[2] For RO plant 16.73 kW (23.6 percent) in first stage, and 8.89 kW (12.6 percent) in second stage. For NF plant, 16.66 kW (31.9 percent) in first stage, and 8.74 kW (16.7 percent) in second stage

Table 2.6.—Properties and exergy flow rates at various locations throughout the MSF plant

Location	Temperature T, K	Pressure P, kPa	Salinity, mg/L	Mass flow rate, kg/s	Specific exergy, ψ, kJ/kg	Exergy flow rate, X, kW
0	308	101.325	46,500	2397	0	0.00
1	308	168	46,500	2397	0.0640	153.41
2	316.3	115	46,500	2397	0.4927	1181.00
3	316.3	115	46,500	808	0.4927	398.10
4	316.3	7.96	46,500	808	0.3916	316.41
5	314.4	7.96	0	272	10.4886	2852.90
6	316.3	7.96	70,093	536	-3.5023	-1877.23
7	316.3	7.96	64,828	3621	-2.6724	-9676.76
8	316.3	635	64,828	3621	-2.0823	-7540.01
9	358	635	64,828	3621	12.1227	43896.30
10	363.8	635	64,828	3621	15.4949	56107.03
11	371.9	97.4	-	34.93	388.1770	13559.02
12	371.9	97.4	-	34.93	0	0.00
13	314.5	578	0	272	11.0616	3008.76
14	316.3	292	70,093	536	-3.2375	-1735.30
15	308	101.325	70.093	536	-3.8865	-2083.16
16	308	101.325	0	272	10.2679	2792.87
17	308	101.325	46,500	1589	0	0.00

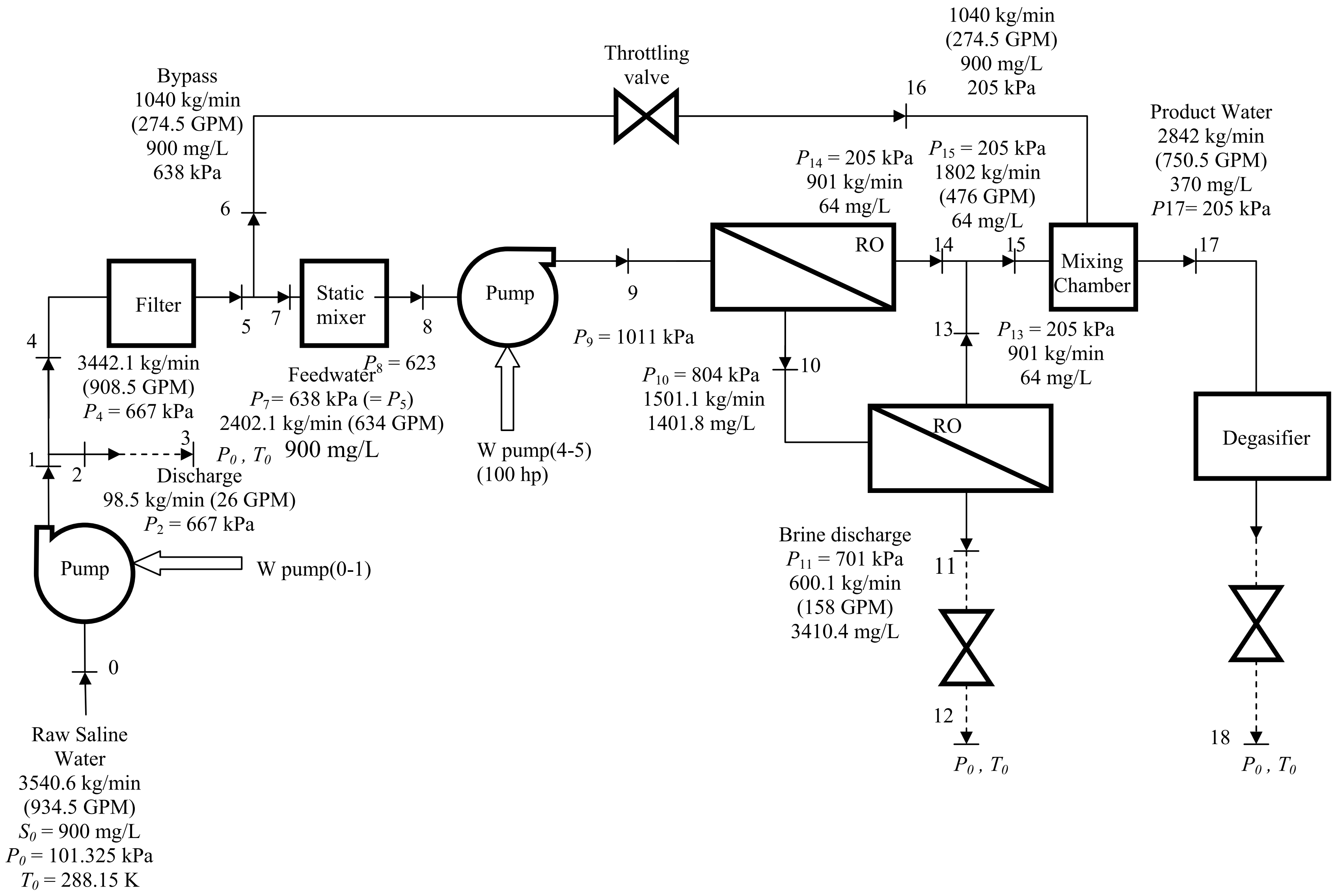

Figure 2.1.—Schematic of the two-stage RO portion of the desalination plant

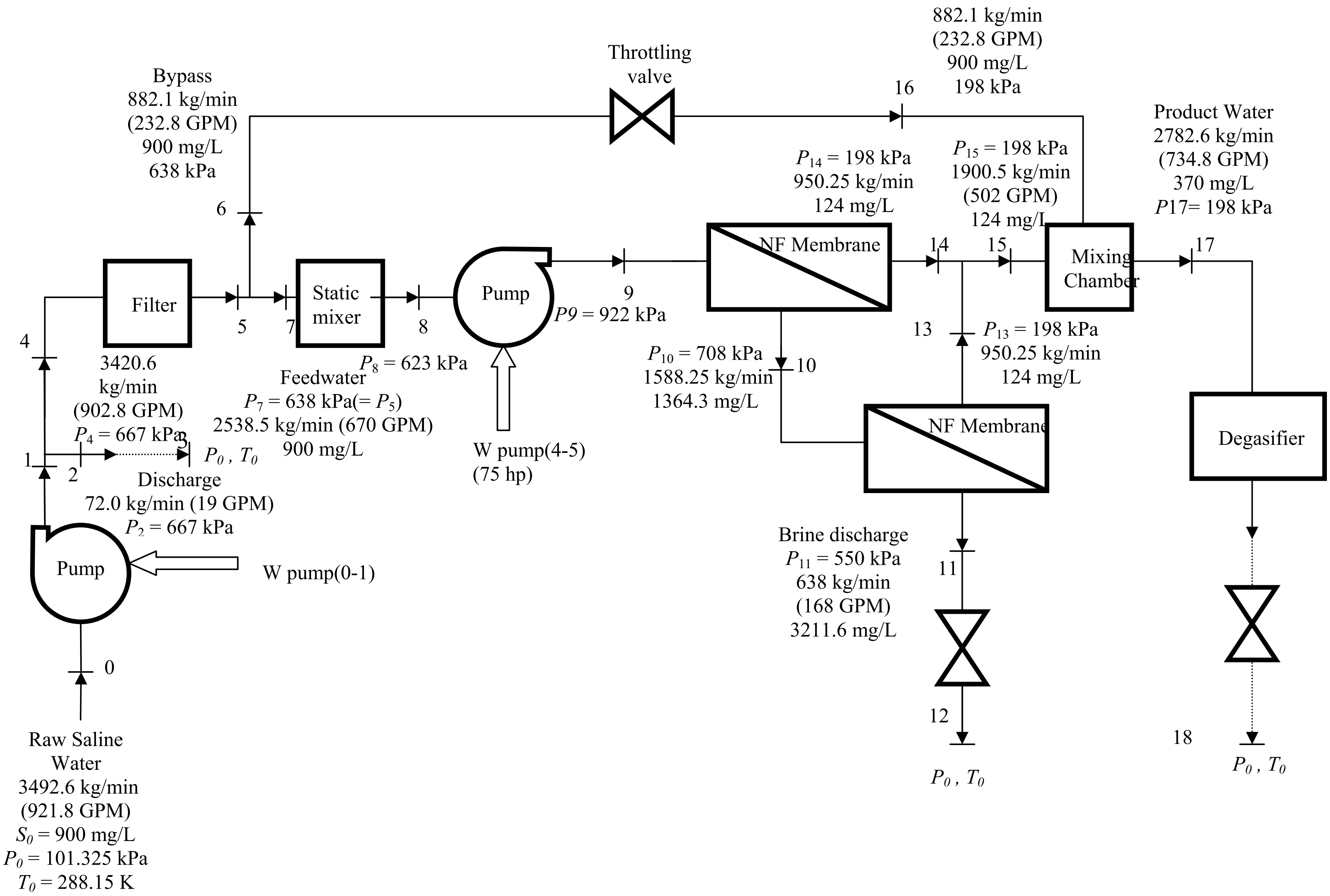

Figure 2.2.—Schematic of the two-stage NF portion of the desalination plant

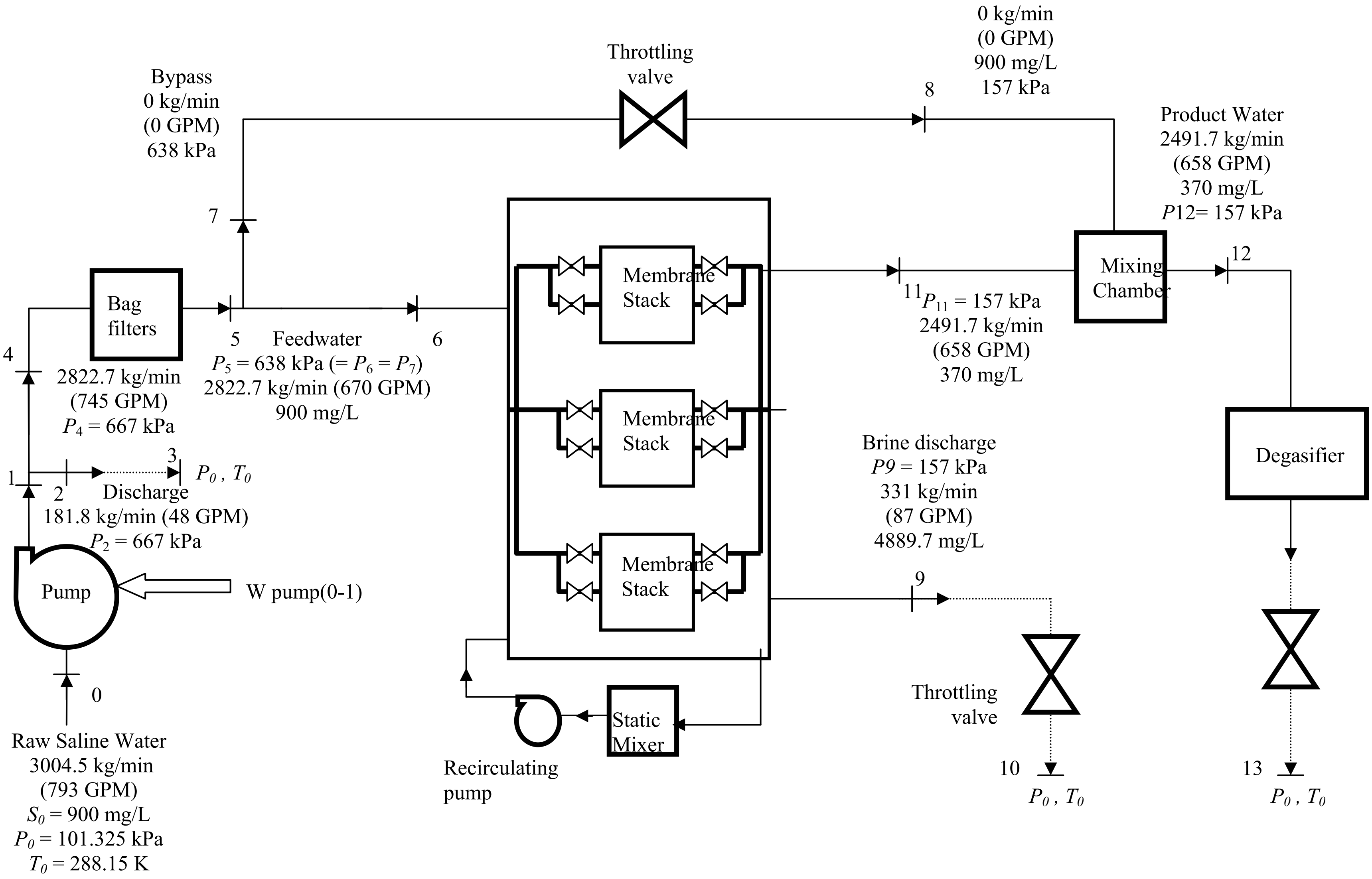

Figure 2.3.—Schematic of the EDR portion of the desalination plant

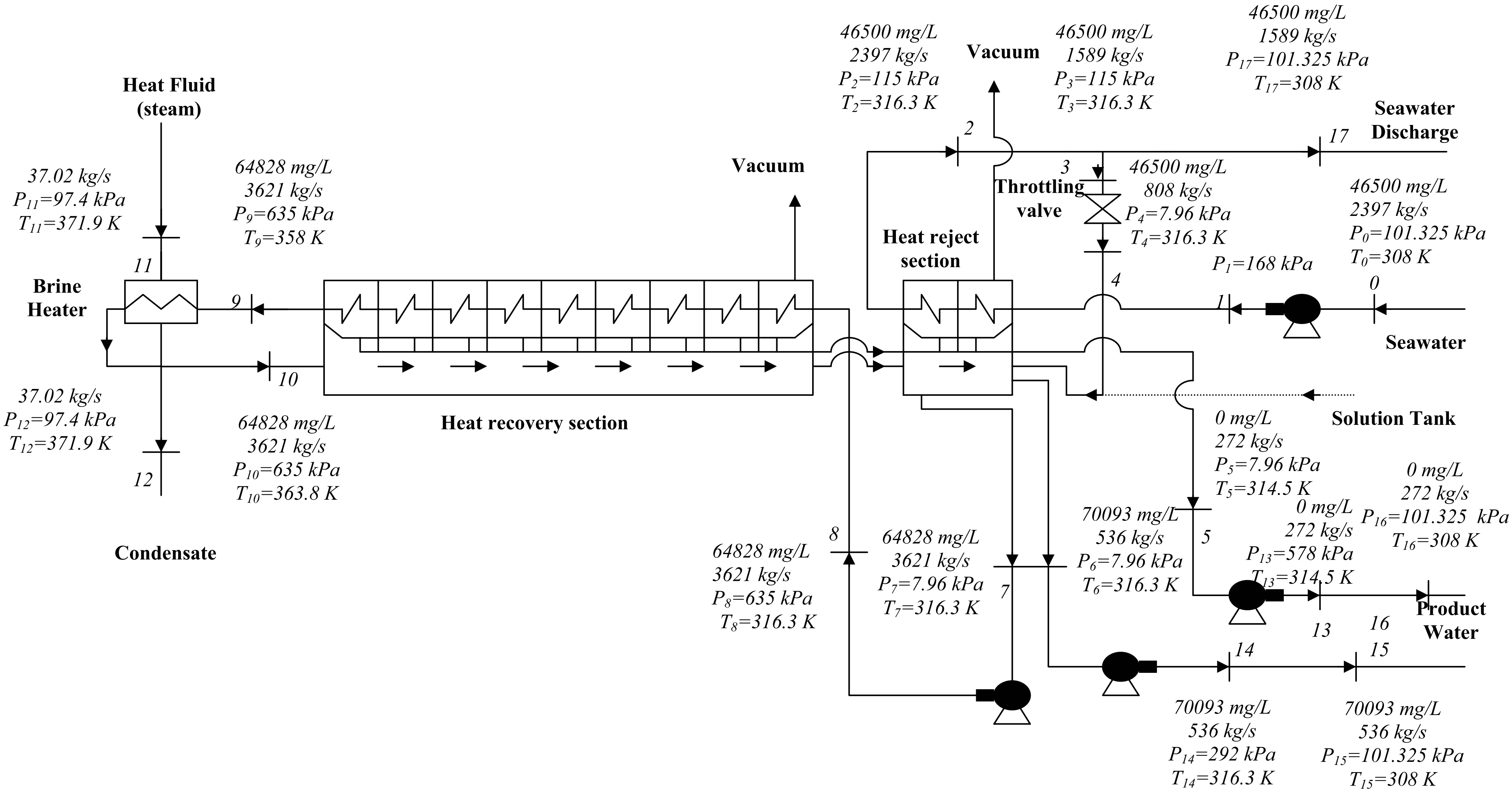

Figure 2.4.—Schematic of the MSF Distillation Plant

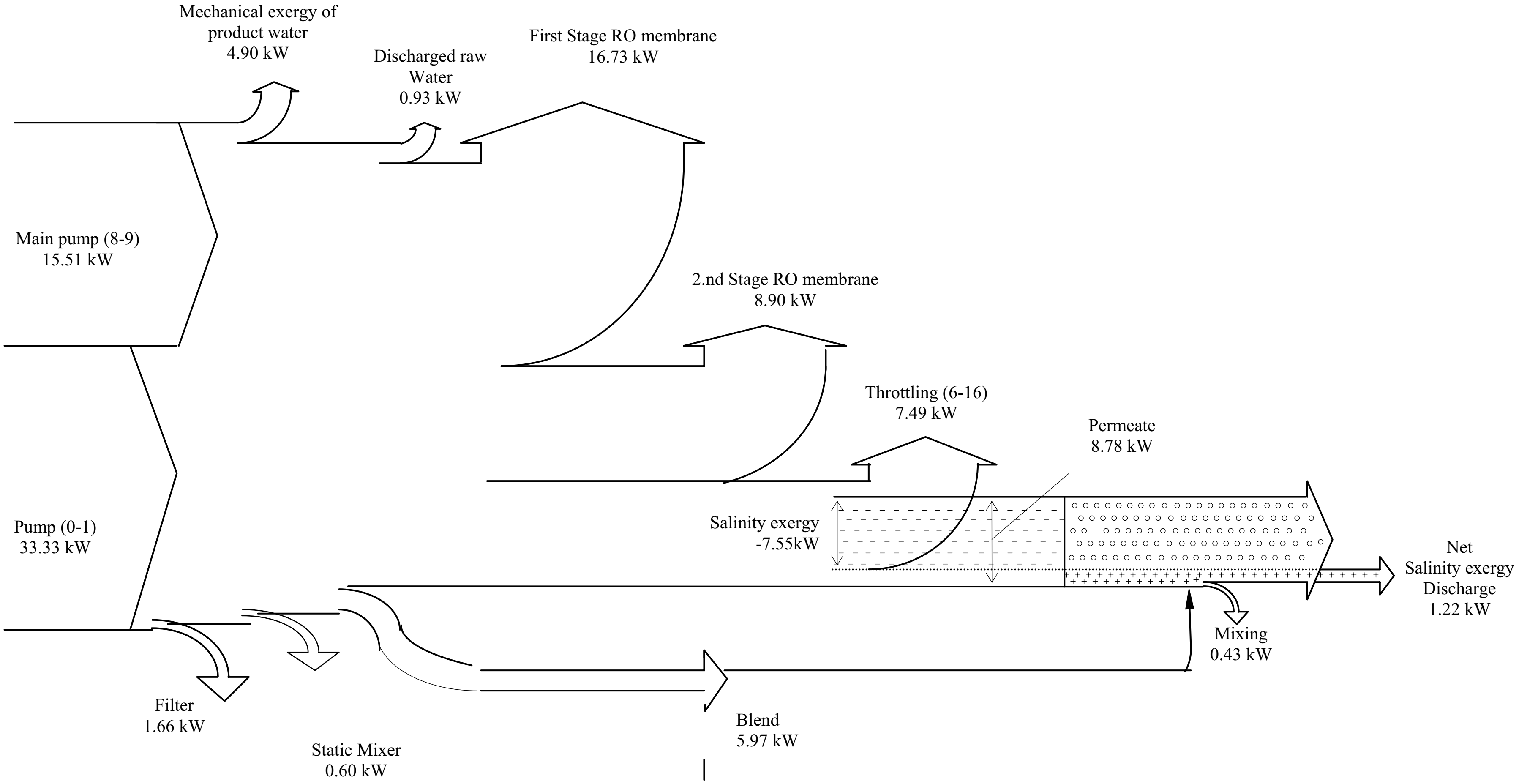

Figure 2.5.—Exergy balance for an actual reverse osmosis desalination process

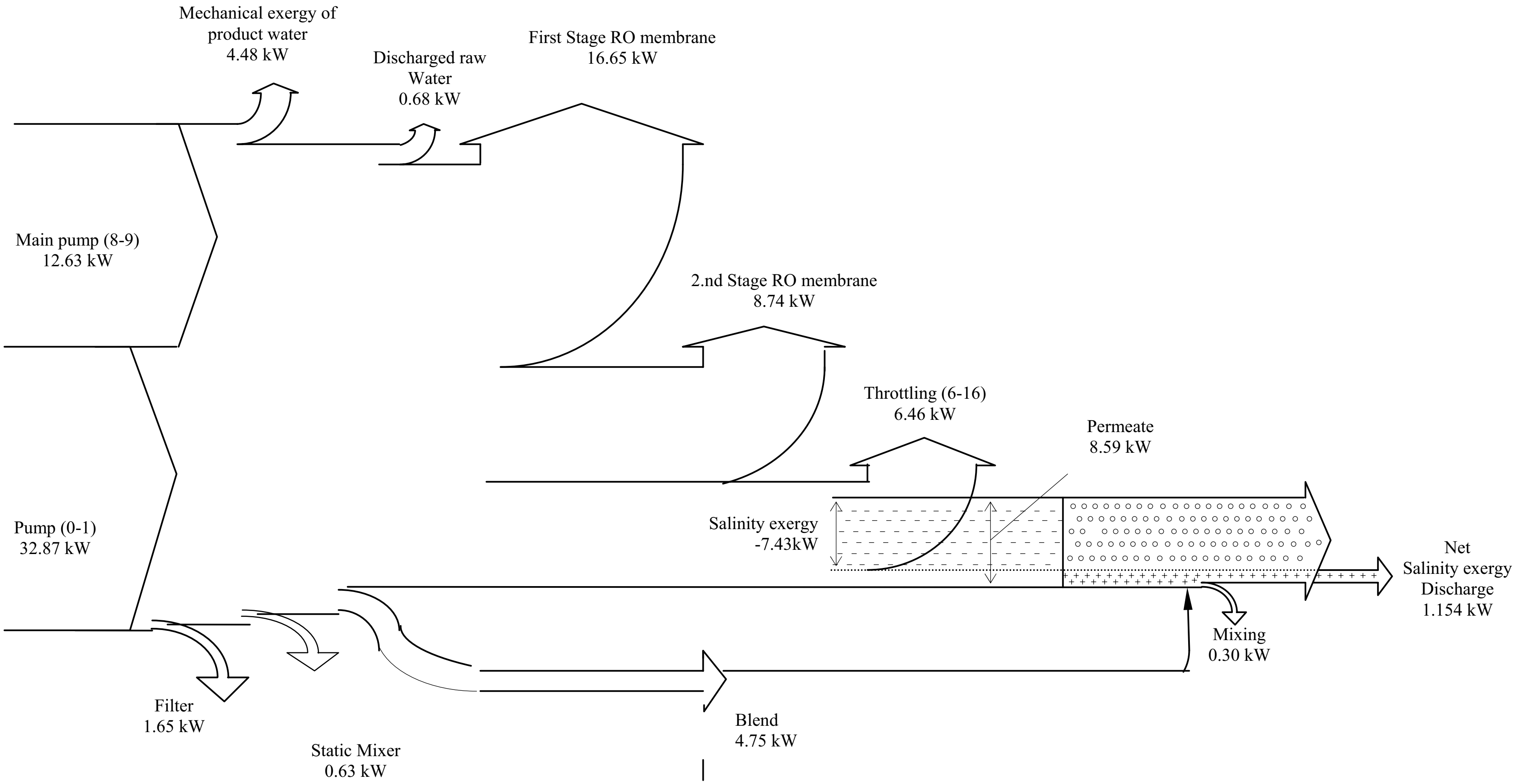

Figure 2.6.—Exergy balance for an actual nanofiltration (NF) desalination process.

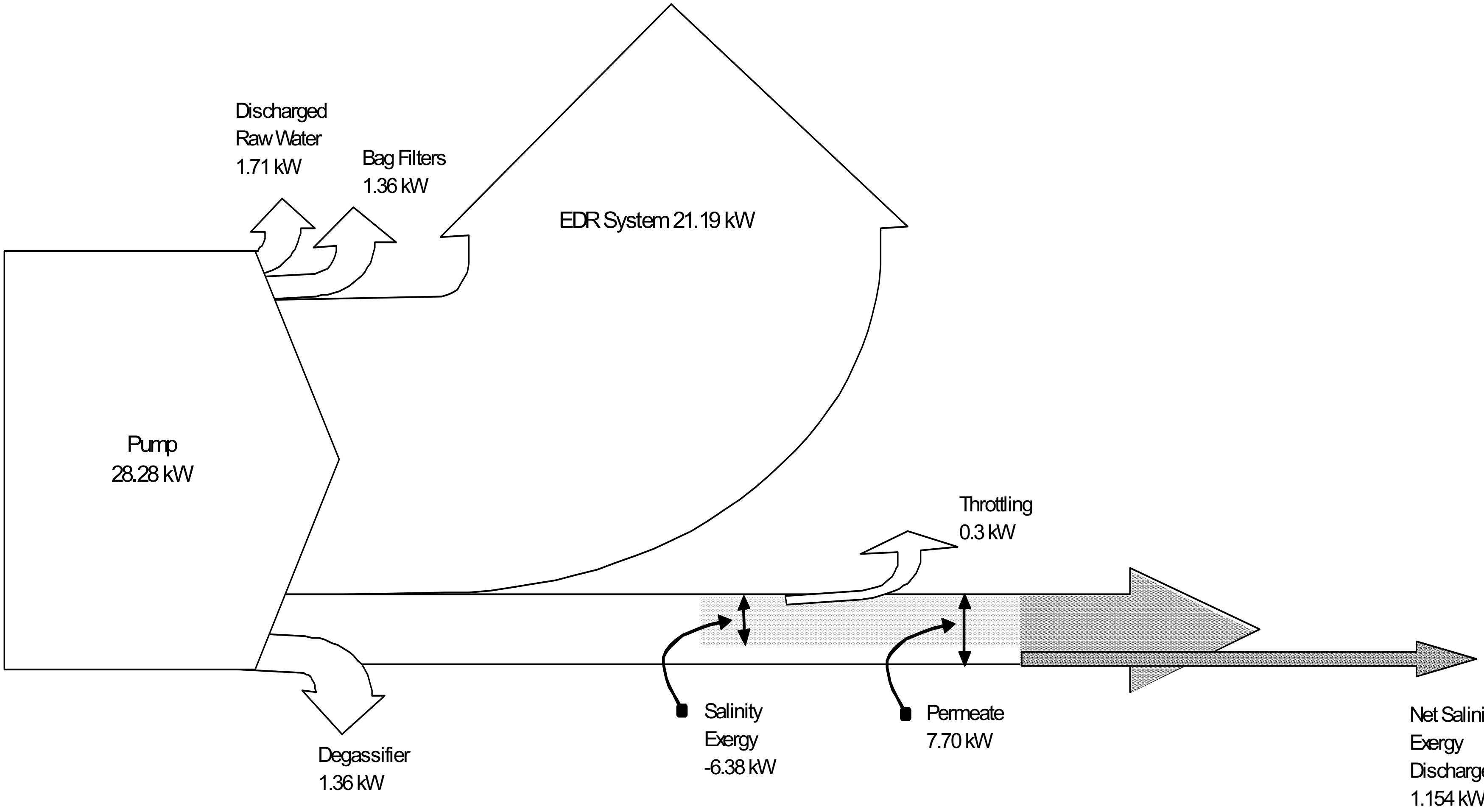

Figure 2.7.—Exergy balance for an actual EDR desalination process.

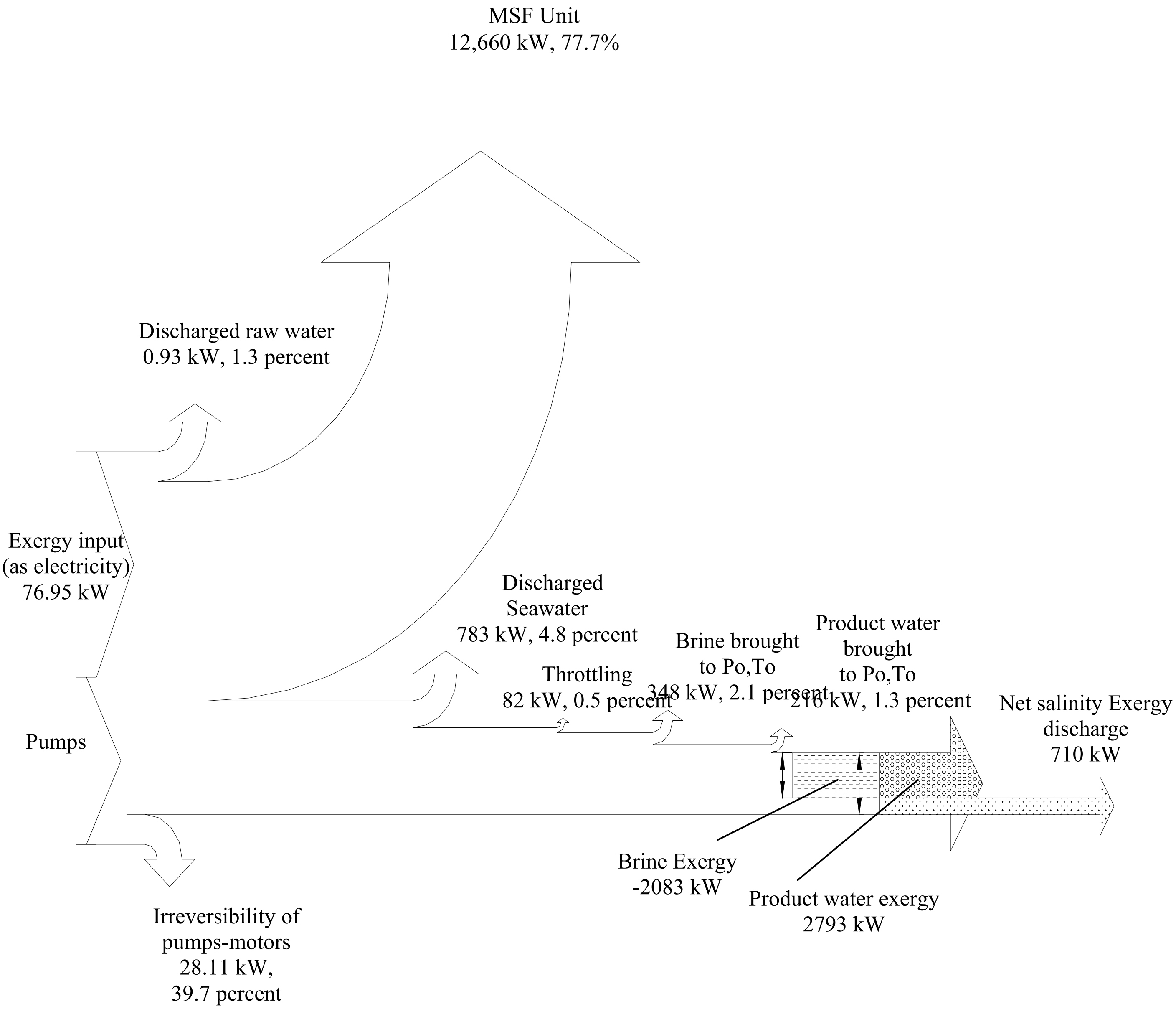

Figure 2.8—Exergy flow diagram for MSF plant with exergy destruction amounts and percentages

2.4 SUMMARY AND CONCLUSIONS

The second-law efficiencies of 8.0 percent for the RO unit, 9.7 percent for the NF unit, and 6.3 percent for the EDR unit, and 4 percent for the MSF unit were very low compared to the second-law efficiency of a modern power plant of over 50 percent. Therefore, significant opportunities exist to improve the thermodynamic performance of the plant. The analysis showed that most exergy destruction occurs in the pump/motor and the separation units. The fraction of exergy destruction in the pump/motor units is 39.7 percent for the RO unit, 23.6 percent for the NF unit, and 54.1 percent for the EDR unit. Therefore, using high-efficiency pumps and motors equipped with VFD drives can reduce the cost of desalination significantly.

The fraction of exergy destruction in the separation units is 36.2 percent for the RO unit, 48.6 percent for the NF unit, and 39.6 percent for the EDR unit. These values indicated that current designs of all separation units are highly inefficient and far from ideal, and large amounts of energy can be saved by improving the designs. Therefore, modifications and improvements to the processes should be considered. Minimizing the pressure drop across the membranes is an obvious way of decreasing exergy destruction, and this can be accomplished by allowing the salinity of permeate to be higher. From a thermodynamic point of view, it makes no sense to produce nearly pure water by forcing saline water through many layers of membranes with fine pores and consuming a large amount of electric power in the process, and then mixing it with saline water to raise the salinity to the desired level of 370 mg/L. A better way is to design the system such that the permeate leaves at the desired salinity.

The throttling of the bypass water is also responsible for significant exergy destruction (10.6 percent for RO and 12.4 percent for the NF units). This exergy can be saved by pressurizing the bypass water to the pressure of permeate stream rather than the higher levels. A small amount (1 to 3 percent) of exergy is also lost by the discharged raw water. This loss can be eliminated by using better controls, sealing, and VFD pumps.

The wasted mechanical exergy of discharged brine for the RO and NF units is also very significant (8.4 percent for RO, 9.1 percent for NF, but only 0.6 percent for EDR unit). If this mechanical energy in the form of high pressure is not needed to move the brine long distances, it can be used to recuperate some of the power consumed by running a turbine with it before it is discharged. There are commercial units on the market to do this.

For the MSF plant, the analysis shows that 78 percent of exergy destruction occurs within the Multistage flash distillation unit, which indicates that the flashing process itself is highly inefficient. Therefore, modifications and improvements to the process should be considered. Increasing the number of flashing stages is one way of decreasing exergy destruction, but its cost effectiveness must be considered.

Also, about 20 percent of total exergy is supplied by the pumps in the form of electrical energy, which is a very significant amount. Therefore, using high-efficiency pumps and motors can reduce the cost of distilled water significantly.

Finally, the plant requires steam at only about 100°C. Therefore, low-temperature sources are ideally suited as heat sources for distillation plants. If thermal energy is obtained by burning fuel, this will result in a tremendous amount of additional exergy destruction. If burning a fuel is the only available source of thermal energy, then a cogeneration plant could be considered where electric power is generated by high temperature steam, and the heat exchanger of the MSF unit serves as the condenser.

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