# Chapter 13

# Refrigeration and Cryogenics*

## INTRODUCTION

Refrigeration and cryogenics have aroused considerable interest among workers in the fields of engineering and science. All refrigeration processes involve work, specifically, the extraction of heat from a body of low temperature and the rejection of this heat to a body willing to accept it. Refrigeration generally refers to operations in the temperature range of 120 to 273 K, while cryogenics usually deals with temperatures below 120 K where gases, including methane, oxygen, argon, nitrogen, hydrogen, and helium, can be liquefied.

In addition to being employed for domestic purposes (when a small "portable" refrigerator is required), refrigeration and cryogenic units have been used for the storage of materials such as antibiotics, other medical supplies, specialty foods, etc. Much larger cooling capacities than this are needed in air conditioning equipment. Some of these units, both small and large, are especially useful in applications that require the accurate control of temperature. Most temperature-controlled enclosures are provided with a unit that can maintain a space below ambient temperature (or at precisely ambient temperature) as required. The implementation of such devices led to the recognition that cooling units would be well suited to the refrigeration of electronic components and to applications in the field of instrumentation. Such applications usually require small compact refrigerators, with a relatively low cooling power, where economy of operation is often unimportant.

One of the main cost considerations when dealing with refrigeration and cryogenics is the cost of building and powering the equipment. This is a costly element in the process, so it is important to efficiently transfer heat so that money is not wasted in lost heat in the refrigeration and cryogenic processes. Since the cost of equipment can be expensive, there are a number of factors to be considered when choosing equipment. Equipment details are discussed in later sections.

Cryogenics plays a major role in the chemical processing industry. Its importance lies in the recovery of valuable feedstocks from natural gas streams, upgrading the heat

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content of fuel gas, purifying many process and waste streams, producing ethylene, as well as other chemical processes.

Cryogenic air separation provides gases (nitrogen, oxygen, and argon) used in

1. the manufacturing of metals such as steel,
2. chemical processing and manufacturing industries,
3. electronic industries,
4. enhanced oil recovery, and
5. partial oxidation and coal gasification processes.

Other cryogenic gases, including hydrogen and carbon monoxide, are used in chemical and metal industries while helium is used in welding, medicine, and gas chromatography.

Cryogenic liquids have their own applications. Liquid nitrogen is commonly used to freeze food, while cryogenic cooling techniques are used to reclaim rubber tires and scrap metal from old cars. Cryogenic freezing and storage is essential in the preservation of biological materials that include blood, bone marrow, skin, tumor cells, tissue cultures, and animal semen. Magnetic resonance imaging (MRI) also employs cryogenics to cool the highly conductive magnets that are used for these types of nonintrusive body diagnostics.(1)

As will become apparent throughout this chapter, there is a wide variety of applications, uses, and methods to produce and to utilize the systems of refrigeration and cryogenics. Multiple factors must be considered when dealing with these practices, including the choice of refrigerant or cryogen, the choice of equipment and methods of insulation, and all hazards and risks must be accounted for to ensure the safest environment possible.

Topics covered in this chapter include:

1. Background material
2. Equipment
3. Materials of construction
4. Insulation and heat loss
5. Storage and transportation
6. Hazards, risks, and safety (see also Chapter 24)
7. Basic principles and applications

## BACKGROUND MATERIAL

### Refrigeration

The development of refrigeration systems was rapid and continuous at the turn of the 20th century, leading to a history of steady growth. The purpose of refrigeration, in a general sense, is to make materials colder by extracting heat from the material. As described in earlier chapters, heat moves in the direction of decreasing temperature (i.e., it is transferred from a region of high temperature to one of a lower temperature). When the opposite process needs to occur, it cannot do so by itself, and a refrigeration system (or its equivalent) is required.(2)

Refrigeration, in a commercial setting, usually refers to food preservation and air conditioning. When food is kept at colder temperatures, the growth of bacteria and the accompanying spoiling of food is prevented. People learned early on that certain foods had to be kept cold to maintain freshness and many kept these foods in ice boxes where melting ice usually absorbed the heat from the foods. Household refrigerators became popular in the early 1900s and only the wealthy could afford them at the time. Freezers did not become a staple part of the refrigerator until after World War II when frozen foods became popular.

The equipment necessary in refrigeration is dependent upon many factors, including the substances and fluids working in the system. One very important part of refrigeration is the choice of refrigerant being employed and the refrigerant choice obviously depends on the system in which it will be used. The following criteria are usually considered in refrigerant selection:

1. practical evaporation and condensation pressures
2. high critical and low freezing temperatures
3. low liquid and vapor densities
4. low liquid heat capacity
5. high latent heat of evaporation
6. high vapor heat capacity.

Ideally, a refrigerant should also have a low viscosity and a high coefficient of performance (to be defined later in this chapter). Practically, a refrigerant should have:

1. a low cost,
2. chemical and physical inertness at operating conditions,
3. no corrosiveness toward materials of construction,
4. low explosion hazard, and
5. be non-poisonous and non-irritating.

Solid refrigerants are not impossible to use but liquid refrigerants are most often used in practice. These liquid refrigerants include hydrocarbon and non-hydrocarbon refrigerants. The most commonly used hydrocarbon refrigerants include:

1. propane,
2. ethane,
3. propylene, and
4. ethylene.

Non-hydrocarbon liquid refrigerants include:

1. nitrogen,
2. oxygen,
3. neon,
4. hydrogen, and
5. helium.

## Cryogenics

Cryogenics is not, in itself, an integral field. It is merely the extension of many other fields of science that delve into the realm of the thermodynamic variable of temperature. When compared to room temperature, the properties of most substances change dramatically at extremely low temperatures. From a molecular perspective, the atoms in any substance at a lower temperature, while still vibrating, are compressed closer and closer together. Depending on the phase of the substance, various phenomena and changes to physical and chemical characteristics occur at these lower temperatures.

There are many accepted definitions of cryogenics. Some classify it simply as a "temperature range below −240°F." Another more elaborate explanation defines it as: "is the unusual and unexpected property variations appearing at low temperatures and which make extrapolations from ambient to low temperature reliable."(3) Webster's dictionary defines cryogenics as "the branch of physics that deals with the production and effects of very low temperatures."(4) Cryogenics has also been referred to as: "all phenomena, processes, techniques, or apparatus occurring or using temperatures below 120 K."(5) Combining all of these definitions, the contributing author of this chapter(6) has provided the all-purpose definition that "cryogenics is the study of the production and effects of materials at low temperatures."

There have been uses for cryogenic technologies as far back as the latter part of the 19th century. It became common knowledge in the 1840s that in order to store food at low temperatures for long periods of time, it needed to be frozen, a technology that is still utilized today.

At the beginning of the 20th century, the scientist Carl von Linde produced a double distillation column process that separated air into pure streams of its basic components of 78% nitrogen, 21% oxygen, and 1% argon. By 1912, it was discovered that minor modifications to the double distillation column process could separate many other gases from the input stream. Since there are trace amounts of neon, krypton, and xenon in air, the aforementioned distillation process, with minor modifications, was found capable of separating these gases into relatively pure streams. In the 1930s, the development of the sieve tray brought changes in cryogenic technology. A sieve tray is a plate, utilized in distillation columns, with perforated holes about 5–6 mm in diameter, which enhances mass transfer.(7) These trays were highly popular in cryogenics due to their simplicity, versatility, capacity, and cost effectiveness.

When the "Space Race" hit the United States in the 1960s, cryogenic technologies were utilized to develop a process known as cryopumping which is based on the freezing of gases on a cold surface. This process helped produce an ultrahigh vacuum here on Earth that would be similar to what was to be experienced in outer space. This led to many other discoveries, including rocket propulsion technologies which enabled astronauts to better prepare for their voyage(s) into space. Unfortunately, the space race initialized the Cold War and the subsequent development of missiles and nuclear weapons.

The *cryopreservation* process is based on the same principles as food storage (i.e., using extremely low temperatures to preserve a perishable item). Cryopreservation has become more and more popular because of its appeal in preserving living cells. Whole cells and tissue can be preserved by this technique by stopping biological activity at extremely low temperatures. The preservation of organs by cryogenics has been a stepping stone for *cryosurgery* which relies on the cold temperatures to insure clean and precise incisions. More recently, *cryobiology* has been applied well below freezing temperatures to living organisms to observe how they "react." Cryobiology has also provided developing technologies in order to help cure such fatal illnesses as Parkinson's disease.(8) Most recently, incorporating electronic systems with cryo-technologies has provided valuable information on superconductivity. Extremely low temperatures have also led to systems that contain near-zero resistance throughout the wires.

## Liquefaction

Liquefaction is the process for converting a gaseous substance to a liquid. Depending on the liquefied material, various steps are employed in an industrial process. Common to each is the use of the Joule–Thomson effect(9) (where the temperature changes as a fluid flows through a valve), heat exchangers, and refrigerants to achieve the cryogenic temperatures. Generally, the methods of refrigeration and liquefaction used include:

1. vaporization of a liquid,
2. application of the Joule–Thomson effect (a throttling process), and
3. expansion of a gas in a work producing engine.

Liquid nitrogen is the best refrigerant for hydrogen and neon liquefaction systems while liquid hydrogen is usually used for helium liquefaction.

The largest and most commonly used liquefaction process involves the separation of air into nitrogen and oxygen. The process starts by taking air compressed initially to 1500 psia through a four-stage compressor with intercoolers.(10) The air is then compressed again to 2000 psia and cooled down to about the freezing point of water in a precooler. The high-pressure air is then further cooled by ammonia to about −70°F. The air is then split into two streams after this cooling stage. One stream leads to heat exchangers that cool most of the air by recycled cold gaseous nitrogen. This proceeds to an expansion valve which condenses most of the air, absorbing heat in the process.

The other stream goes to a booster expansion engine which compresses the air and then allows for expansion to further cool and then condense it (by means of the aforementioned Joule–Thomson effect). This liquid air is mixed and filtered and then introduced to the first of two fractional distillation columns. 100% nitrogen exits the top of the first column, and when condensed, contains less than 7 ppm oxygen. The oxygen rich mixture is pumped out of the bottom of the first column and is introduced to the second column. The oxygen leaving the bottom of the second column is usually 99.6% oxygen or higher. The remaining 0.4% is argon and requires a subsequent separation process. The columns implemented are similar to distillation columns and function to separate the nitrogen and oxygen.(7)

The major application of these liquefied gases is that they can act as refrigerants for other substances.

## Cryogens

The most widely used cryogenic liquids include oxygen, nitrogen, air, hydrogen, and helium. There are multiple sources that contain reference and thermodynamic data for these cryogens. Table 13.1(11) shows typical data for a select number of cryogenic liquids and some details are discussed below for the most common of these. Most of the fluids, excluding helium, may be considered “classical” fluids in that their behavior can be predicted using accepted mechanical and thermodynamic principles.(1)

Liquid oxygen presents some safety problems not characteristic of some of the other cryogens (i.e., it is slightly magnetic, is extremely reactive, and may be a contributing factor to fire and explosions). Additional details are provided in a later section. Liquid nitrogen is more often used as a refrigerant in cryogenic laboratories than oxygen because it has a lower cost, is easily produced, and has an ease of handling that is certainly not the case with oxygen. Liquid nitrogen is often used in industrial and laboratory settings to:

1. maintain an intermediate heat sink between room temperature and lower temperature areas,
2. provide precooling in liquefiers and refrigerators,
3. precool equipment for use at low temperatures, and
4. cool adsorbents used in gas purification.

While liquid air was once the most commonly used cryogen due to it being the principal product of liquefiers, this is not the case anymore. The ease of producing liquid nitrogen from air has gradually decreased the use of this particular cryogen. Liquid hydrogen, which exists in its *ortho* and *para* states, is also widely used, especially as a rocket fuel, although, like oxygen, it is flammable. Hydrogen is slightly less hazardous because it is only necessary to isolate it from oxygen, while liquid oxygen must be isolated from a number of substances. Liquid helium is a unique cryogen and is available in two isotopes (helium-3 and helium-4), with helium 4 being the more

**Table 13.1** Properties of Cryogenic Fluids

| | Boiling point at 1 atm, K | Critical temperature, K | Critical pressure, atm | Freezing point, K | Density | | Heat of vaporization, cal/g |
|---|---|---|---|---|---|---|---|
| | | | | | Liquid,[a] g/L | Gas,[b] g/L | |
| Helium 4 | 4.26 | 5.29 | 2.26 | <0.80 | 0.125 | 0.178 | 5.20 |
| Hydrogen | 20.43 | 33.22 | 12.80 | 13.99 | 0.071 | 0.090 | 107.00 |
| Deuterium | 23.60 | 38.30 | 16.30 | – | – | – | 75.60 |
| Neon | 27.21 | 44.42 | 26.85 | 24.44 | 1.202 | 0.900 | 20.70 |
| Nitrogen | 77.35 | 126.00 | 33.50 | 63.27 | 0.807 | 1.250 | 47.00 |
| Carbon monoxide | 81.10 | 134.00 | 35.00 | 74.00 | 0.803 | 1.250 | 51.56 |
| Fluorine | 85.02 | 144.00 | 55.00 | 53.54 | 1.100 | 1.700 | 41.20 |
| Argon | 87.40 | 150.70 | 48.00 | 83.83 | 1.390 | 1.780 | 37.90 |
| Oxygen | 90.13 | 154.31 | 49.71 | 54.73 | 1.140 | 1.430 | 51.00 |
| Methane | 111.70 | 190.60 | 45.80 | 89.90 | 0.420 | 0.720 | – |
| Krypton | 120.20 | 210.50 | 54.30 | 116.50 | 2.400 | 3.730 | – |
| Ozone | 161.00 | 285.30 | 54.60 | – | – | – | 71.00 |
| Xenon | 166.00 | 289.60 | 58.20 | 161.60 | 3.060 | 5.890 | – |
| Ethylene | 169.40 | 282.80 | 50.90 | 103.70 | 0.570 | 1.260 | – |

[a] Liquid density at boiling point.

[b] Gas density at 273 K.

common choice because of the rarity of helium 3. It is most commonly used in systems that work with temperatures lower than liquid nitrogen.

## EQUIPMENT

Highly specialized equipment is used to achieve the extremely low temperatures necessary for refrigeration and cryogenic processes. Compressors, expanders, heat exchangers, storage containers, and transportation devices (as a means of moving materials and end products) are just a few of the specialty pieces of equipment that are required in these processes. Since the drastically cold temperatures that are reached can damage most equipment, it is important for all devices to be made of materials that are durable and that can withstand any massive temperature and pressure excursions. In addition, it is also essential to incorporate temperature, pressure, and density measurement devices/gauges.

Compressor power makes up approximately 80% of the total energy used in processes involving the production of industrial gases and the liquefaction of natural gases. Therefore, in order to operate a cryogenic facility at optimum efficiency, the compressor choice is an important factor. Selection of a compressor relies on the cost of the equipment and the cost of installation, the energy and fuel costs associated with the equipment, and the cost of maintenance. There are several different types of compressors, including reciprocating compressors and centrifugal compressors. Reciprocating compressors adapt to a wide range of volumes and pressures and operate with high efficiency. Centrifugal compressors are ideal for high-speed compression; these compressors are highly efficient and reliable, especially when dealing with low pressure cryogenics.(10)

In refrigeration and cryogenics, expansion valves, often referred to as expanders, serve to reduce the temperature of a gas being expanded to provide refrigeration. Fluid expansion to produce refrigeration is performed by two unique methods: in an expansion valve where work is produced, or by a Joule–Thomson valve where no work is produced. Mechanical expansion valves generally work very much like a reciprocating compressor, while a Joule–Thomson valve provides constant enthalpy (isenthalpic) cooling of the flowing gas.(2)

There are a number of different methods used to measure temperature when dealing with refrigerants and cryogens. Gas, vapor pressure, metallic resistance, and nonmetallic resistance thermometry are among a few of the methods used. Each of the thermometry techniques requires a number of specific equipment parts but all include a measurement of temperature across a wide range. When choosing a type of equipment for a refrigeration or cryogenic process, it is important to select a unit that can withstand not only the variety of temperatures but also the pressures that are experienced when expanding and compressing a gas into a liquid.

### Typical Heat Exchangers

Low-temperature operation has varied effects on equipment; therefore, sophisticated heat exchangers must be implemented for optimum efficiency in heat transfer. The following guidelines should be followed when designing low-temperature heat exchangers:

1. small temperature differences between the inlet and exit streams
2. large surface area to volume ratio
3. high heat transfer
4. low mass flow rates
5. multichannel capability
6. high pressure potential
7. minimal pressure drop
8. minimal maintenance.

Some of the most common heat exchanger designs (see Part III for details) used for cryogenic processes include:

1. coiled tube exchangers,
2. plate-fin exchangers,
3. reversing exchangers, and
4. regenerators.

Again, these units are primarily used because of their high efficiency in extremely low temperatures. Details on each of these follows.

A coiled tube heat exchanger is especially important to the cryogenic process because of its unique abilities. The large number of tubes that are wound in helices around a core tube can have varying spacing patterns that allow for equalized pressure drops in any stream. Systems that desire simultaneous heat transfer between multiple streams employ the coiled tube heat exchanger. The coiled tube heat exchanger is specifically useful in cryogenic processes because of the typically high demand of heat transfer and high operating pressures that are required.

Plate-fin exchangers, reversing exchangers, and regenerators are all second in popularity to the coiled tube heat exchanger. However, each of these exchangers has its own advantages and can be used for a number of the same reasons that a coiled tube exchanger would be employed. The plate-fin exchanger is compact and light-weight and allows for large temperature and pressure excursions. The primary purpose for a reversing exchanger is to remove impurities in a stream before it is cooled and condensed. Similar to the previously mentioned heat exchangers, a regenerator uses a method to simultaneously cool and purify any given stream. Calculation details on heat exchangers are provided in the next Part of this book.

## MATERIALS OF CONSTRUCTION

It is common for basic construction materials to contract and become distorted as temperature decreases. This can result in unnecessary stresses on accompanying equipment including expanders, pumps, piping, etc. Many materials have temperature limitations and because of this, when it comes to these concerns, more exotic materials must be considered and possibly implemented. It is important to know the properties and behavior of the various materials for proper design considerations. Some combinations of materials, with each other as well as with the refrigerant or cryogen, can be hazardous to the fluid in question or the outside environment.

Equipment considerations that are taken into account when choosing a construction material are thermal conductivity, thermal expansivity, and density. Some materials exhibit the effect of superconductivity at very low temperatures. This phenomenon affects the heat capacity, thermal conductivity, electrical resistance, magnetic permeability, and thermoelectric effect of the material. These superconductive materials need to be strictly analyzed before use in these systems because high temperature superconductors usually have a brittle ceramic structure.

Plastics actually increase in strength as temperature decreases but decrease in impact resistance, which is not a desirable property. Teflon and glass-reinforced plastics retain impact resistance upon decreasing temperature but for some situations, these materials may not be ideal. Usually, for the double-walled vessel to be discussed later, carbon steel or aluminum is used for the outer shell but it should be thick enough to withstand collapsing or buckling.

About 9% nickel steels are often utilized for high boiling cryogens ($>75$ K) while many aluminum alloys and austenitic steels are structurally suitable for the entire cryogenic temperature range. While aluminum alloys are acceptable, pure aluminum is not recommended across the insulation space because of its high thermal conductivity.(12)

## INSULATION AND HEAT LOSS

Insulation must certainly be considered an integral part of any refrigeration or cryogenic unit. The extent of the problem of keeping heat out of a storage vessel containing a liquid refrigerant or a cryogenic liquid varies widely. Generally, one must decide on the permissible and/or allowable heat losses (leaks) since insulation costs money, and an economic analysis must be performed. Thus, the main purpose of insulation is to minimize radiative and convective heat transfer and to use as little material as possible in providing the optimal insulation. When choosing appropriate insulation, the following factors are taken into consideration:

1. ruggedness
2. convenience
3. volume and weight
4. ease of handling
5. thermal effectiveness
6. cost.

The thermal conductivity ($k$) of a material is a major consideration in determining the thermal effectiveness of the insulation material. Different types of insulation obviously have different $k$ values and there are five categories of insulation. These include:

1. vacuum insulation which employs an evacuated space that reduces radiant heat transfer
2. multilayer insulation, referred to by some as superinsulation, which consists of alternating layers of highly reflective material and low conductivity insulation in a high vacuum
3. powder insulation which utilizes finely divided particulate material packed between surfaces
4. foam insulation which employs non-homogeneous foam whose thermal conductivity depends on the amount of insulation
5. special insulation which includes composite insulation that incorporates many of the advantageous qualities of the other types of insulation.

It should also be noted that multilayer insulation has revolutionized the design of cryogenic refrigerant vessels.

In a double-walled vessel, typical of cryogen storage to be discussed in the next section, heat is usually transferred to the inner vessel by three methods:

1. conduction through the vessel's "jacket" by gases present in this space
2. conduction along solid materials touching both the inner and outer containers
3. radiation from the outer vessel.

It was discovered in 1898, that the optimum material to place inside the space created by the double-walled vessel is "nothing" (i.e., a vacuum). This Dewar vessel, named after Sir James Dewar, is still one of the most widely used insulation techniques for cryogenic purposes.

Insulation practices and techniques can be applied to all types of insulation, whether it is to keep heat in or to prevent heat from entering a system. The following three illustrative examples, although based on a furnace, are applicable to any problem where insulation is employed. In a very real sense, they involve extensions of the illustrative examples presented in Chapter 7 of this Part. Also note that a separate Chapter (19) in Part Three is devoted to insulation and refractory.

## ILLUSTRATIVE EXAMPLE 13.1

The vertical flat walls of the combustion chamber of a furnace consist of 7.5 in of refractory, $k_R = 0.75$; 3 in of insulation, $k_I = 0.08$; and 0.25 in of steel, $k_S = 26.0$. The units of $k$ are Btu/h·ft·°F. The average surface temperature of the inner face of the refractory and the outer face of the steel are 2000°F and 220°F, respectively.

Calculate the heat loss expressed as Btu/h·ft$^2$.

***SOLUTION*:** Figure 13.1 depicts the system described in the problem statement. The heat loss per hour can be calculated using the following equation, presented in Chapter 7.

$$\frac{\dot{Q}}{A} = \frac{\sum \Delta T}{\left(\frac{L}{k_R}\right)_R + \left(\frac{L}{k_I}\right)_I + \left(\frac{L}{k_S}\right)_S} \tag{13.1}$$

The thicknesses of the wall components must first be converted to feet before this calculation can proceed. Therefore,

$$L_R = 0.625 \text{ ft}$$
$$L_I = 0.25 \text{ ft}$$
$$L_S = 0.021 \text{ ft}$$

$\Delta T$ is defined as

$$\Delta T = T_R - T_S = 2000 - 220 = 1780$$

Substituting,

$$\frac{\dot{Q}}{A} = \frac{1780}{\left[\left(\frac{0.625}{0.75}\right) + \left(\frac{0.25}{0.08}\right) + \left(\frac{0.021}{26.0}\right)\right]}$$
$$= 450 \,\text{Btu/h} \cdot \text{ft}^2$$

■

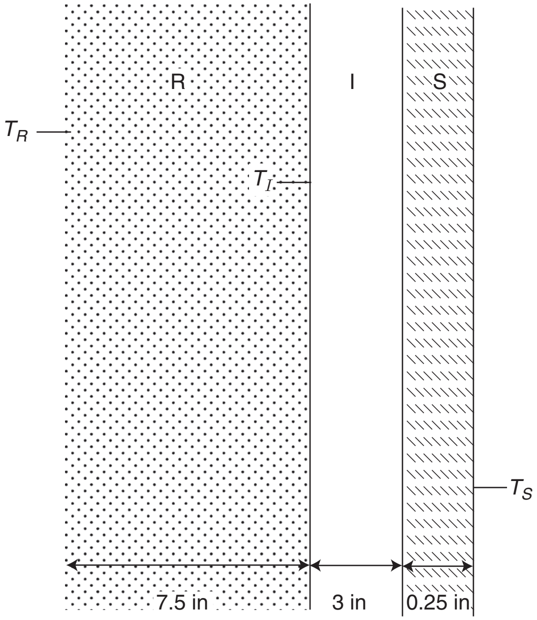

**Figure 13.1** Insulation on furnace wall; Illustrative Example 13.1.

## ILLUSTRATIVE EXAMPLE 13.2

For the combustion chamber of the furnace in the previous example, calculate the temperature of the boundary where the refractory meets the insulation, $T_I$.

***SOLUTION*:** The heat transferred across all three components is equal to that across each individual material. Therefore, since

$$\dot{Q} = \frac{\Delta T}{\sum R}$$

and the resistance in a solid is defined as

$$R = \frac{L}{kA} \tag{13.2}$$

apply the equation from Illustrative Example 13.1 to calculate $T_I$.

$$\frac{\dot{Q}}{A} = \frac{T_R - T_S}{\left(\frac{L}{k_{\text{av}}}\right)_R + \left(\frac{L}{k_{\text{av}}}\right)_I + \left(\frac{L}{k_{\text{av}}}\right)} = \frac{T_R - T_I}{\left(\frac{L}{k_{\text{av}}}\right)_R}$$

Substituting,

$$450 = \frac{2000 - T_I}{\frac{0.625}{0.75}}$$

$$T_I = 1625°\text{F}$$

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## ILLUSTRATIVE EXAMPLE 13.3

Using the scenario described in Illustrative Examples 13.1 and 13.2, calculate the area available for heat transfer if the total heat loss is 70,000 Btu/h.

***SOLUTION*:** The heat loss, $\dot{Q}$, is provided in the problem statement.

$$\dot{Q} = 70,000 \text{ Btu/h}$$

From the two previous examples,

$$\frac{\dot{Q}}{A} = 450 = \frac{70,000}{A}$$

$$A = 155.6 \text{ ft}^2$$

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## STORAGE AND TRANSPORTATION

Storage and transportation needs must also be considered in order to use cryogenic processes in food production. As noted in the previous section, the storage and transfer of these products is dependent on the storage tanks and how they are insulated; the heat gain in a storage tank could jeopardize the cryogenic state and could potentially ruin any product that was contained in the tank. Therefore, to safely store a product in a tank, the structure of the tank needs to be protected against any heat gain in the form of radiation and conduction through the insulation itself, as well as conduction though the inner shell, the supports, and the other openings and valves in the storage tank. Furthermore, the material that the storage tank is made out of needs to be non-reactive to the material being stored.

The choice of storage vessel(s) is dependent on the material being kept in the vessel and they range in type from low performance containers with minimal insulation to high performance vessels with multilayer insulation. When storing liquid refrigerants, caution must be exercised. It is crucial to avoid overpressure inside the vessel, which manufacturers try to account for by providing "bursting disks" that prevent actual disasters from occurring (see following Hazards, Risks, and Safety section).(13) Superinsulated vessels normally have an inner stainless steel vessel and are kept at the temperature of the stored material. The outer vessel, or vacuum jacket, for these units maintain a vacuum necessary for effective insulation and prevents the condensation of water or other materials on the inner vessel's cold surface.

Three major processes are employed to transport a cryogen, i.e., a cryogenic liquid:

1. a self-pressurized container
2. an external gas pressurization
3. a mechanical pumping system.

*Self-pressurization* is a process in which some of the fluid is removed from a container, vaporized, and then the vapor is reintroduced to the excess space and displaces the contents. *External gas pressurization* uses an external gas to displace the contents of a vessel. In *mechanical pumping*, a cryogenic pump, located at the liquid drain line, removes the contents of a container.

The use of trucks, railroad cars, and airplanes has been utilized to transport cryogens. More recently, there have been barges used to transport the cryogens via waterways. Specialized equipment is also used to measure the temperature and pressure of the cryogen while stored in these tanks and transporting units. For pressure measurements, a gauge line is run from the point of interest to a point with ambient pressure, and thus the two pressures are compared using a device such as a Bourdon gauge.(10) This procedure is not void of thermal oscillations which make it less than perfect; however, these problems can be avoided by insulating pressure transducers at the point of measurement.

## HAZARDS, RISKS, AND SAFETY

While there are many risks and hazards associated with refrigerant and cryogenic fluids, time and experience has proven that under proper conditions, these materials can be used safely in industrial and laboratory applications. In these environments, all facilities and equipment, as previously discussed, must be properly designed and maintained; and, the personnel in these areas must be sufficiently trained and supervised. The primary hazards associated with cryogenic fluids are those dealing with human response to the fluids, as well as risks related to the interaction of cryogenic fluids and their surroundings. Constant attention and care must be exercised in order to avoid most, if not all, conceivable hazards that may be encountered in this field (see also Chapter 24, Part Four).(14)

### Physiological Hazards

There are a few sources of personal hazard in the field of cryogenics. If the human body were to come in contact with a cryogenic fluid or a surface cooled by a cryogenic fluid, severe "cold burns" could result. Cold burns inflict damage similar to a regular burn, causing stinging sensations and accompanying pain. But, with cryogenics, the skin and/or tissue is essentially frozen, significantly damaging or destroying it. As with any typical burn or injury, the extent and "brutality" of a cold burn depends on the area and time of contact; medical assistance is strongly advised when one receives a burn of this type.

Protective insulated clothing should be worn during work with low temperature atmospheres to prevent "frost bite" when dealing with cryogenic liquids. Safety goggles (or in some cases, face shields), gloves and boots are integral parts of these uniforms. The objective of these precautions is to prevent any direct contact of the skin with the cryogenic fluid itself or with surfaces in contact with the cryogenic liquid. All areas in which cryogenic liquids are either stored or used should be clean and organized in a manner to prevent any avoidable accidents or fires and explosions that could result; this is especially true when working with systems using oxygen.

#### ILLUSTRATIVE EXAMPLE 13.4

Briefly discuss the routes by which a chemical, specifically a hazardous cryogen, can enter the body.(15)

***SOLUTION*:** To protect the body from hazardous cryogens, one must know the route of entry into the body. All chemical forms, including cryogens and refrigerants, may be inhaled. After a cryogen is inhaled into the nose or mouth, it may be ingested, absorbed into the bloodstream, or remain in the lungs. Various types of personal protective equipment (PPE) such as dust (particulate) masks and respirators prevent hazardous chemicals from entering the body through inhalation. Ingestion of cryogens can also be prevented by observing basic housekeeping rules, such

**Table 13.2** Chemical Routes of Entry into the Body

| Chemical form | Principal danger |
|---|---|
| Solids and fumes | Inhalation, ingestion, and skin absorption |
| Dusts and gases | Inhalation into lungs |
| Liquids, vapors, and mists | Inhalation of vapors and skin absorption |

as maintaining separate areas for eating and chemical use or storage, washing hands before handling food products, and removing gloves when handling food products. Wearing gloves and protective clothing prevent hazardous chemicals from entering the body through skin absorption.

The route of entry of a chemical is often determined by the physical form of the chemical. After a chemical has entered the body, the body may decompose it, excrete it, or the chemical may remain deposited in the body. Most cryogens are liquids. Their chemical forms and the routes of entry are summarized in Table 13.2. ■

## Physical Hazards

There are multiple possible hazards associated with high pressure gases in cryogenic situations because their stored energy may be considerable. During gas compression in liquefaction and refrigeration, liquids are pumped to high pressure and then evaporated. These high pressure liquids and gases are eventually stored. When these materials are stored, they could experience breaks or ruptures in the line that can cause significant force upon storage vessels and their environments, or spills that could have disastrous effects. If a spill of a cryogenic fluid occurs, the heat in a room will readily vaporize the fluid into a gas. The primary hazard that occurs when dealing with non-oxygen cryogenic fluids is asphyxiation. The rapidly expanding gas can fill the room or area and displace the oxygen that was in the room. With a lack of oxygen in the room, the environment is extremely dangerous for humans.

### ILLUSTRATIVE EXAMPLE 13.5

Briefly describe the role that respirators can play in the health risk management of cryogens and refrigerants.(16)

***SOLUTION*:** Respirators provide protection against inhaling harmful materials. Different types of respirators may be used depending in the level of protection desired. For example, supplied-air respirators (e.g., a self-contained breathing apparatus) may be required in situations where the presence of highly toxic substances is known or suspected and/or in confined spaces where it is likely that toxic vapors may accumulate. On the other hand, a full-face or half-face air-purifying respirator may be used in situations where measured air concentrations of identified substances will be reduced (by the respirator) below the substance's threshold limit value (TLV) and the concentration is within the service limit of the respirator.(13)

Other sources of hazard include the use of portable high pressure storage cylinders, which if knocked over or not handled correctly, can result in serious accidents. Manufacturers recommend inspection and testing of high pressure storage cylinders every five years to prevent the previously stated dangerous consequences. All storage cylinders should also be adequately secured (e.g., with chains, etc.) even if they are empty. Simply put, it is necessary to give considerable thought and energy to the design and implementation of all storage containers for refrigerants and cryogens. Designers must also attempt to foresee all possible consequences(13) from leaks and blockages and take the appropriate steps to avoid them. ■

## ILLUSTRATIVE EXAMPLE 13.6

List the types of process events that can result in a plant accident and discuss the various kinds of equipment failure that can occur in a process plant where cryogenic substances are implemented.

***SOLUTION*:** The types of process events that can result in a plant accident are:

Abnormal temperatures
Abnormal pressures
Material flow stoppage

Equipment failures that can occur in a process plant implementing cryogens may be described within the major equipment categories of heat exchangers, vessels, pipes and valves, pumps and compressors. The failures associated with these categories are discussed below:

Heat Exchangers

- **(a)** *Fouling*: Heat transfer is reduced when deposited materials accumulate in the heat exchanger and foul the heat exchanger.
- **(b)** *Tube rupture*: Tube rupture may be caused by fouling, which leads to high fluid velocities, tube vibration, corrosion, or erosion.
- **(c)** *Leakage*: Leakage is usually caused by corrosion of baffles in the heat exchanger.

Vessels

- **(a)** *Pressure/temperature excursions*: High pressure and temperature in a vessel may result in tank rupture, especially when the condition repeats itself.
- **(b)** *Stability*: Vessels, tanks, and phase separators(7) are designed according to specifications. Factors such as fabrication, construction, and corrosion must be considered when selecting a vessel for a particular service.

Pipes and Valves

- **(a)** Insufficient or ineffective supports
- **(b)** Poor weld quality
- **(c)** Temperature stress
- **(d)** Overpressure
- **(e)** Dead ends
- **(f)** Material compatibility

Pumps

**(a)** Gland failure

**(b)** *Dead-heading*: Dead-heading in a pump is a condition where the pump is allowed to run against a closed valve. When this occurs, the temperature rise may lead to seal damage and process fluid leakage compressors.

Compressors

See pumps above. ■

## Chemical Hazards

Hazards associated with the chemical properties of cryogenic fluids can give rise to fires or explosions. In order for a fire or explosion to occur, there must be a fuel and/or an oxidant, and an ignition source. Because oxygen and air are prime candidates for cryogenic fluids, and are present in high concentrations, the chances of disasters occurring dramatically increases, as oxygen will obviously act as the oxidizer. A source of fuel can range from a noncompatible material to a flammable gas, or even a compatible material under extreme heat. An ignition source could be any electrical or mechanical spark or flame, any undesired thermodynamic event, or even a chemical reaction.(14–16)

### ILLUSTRATIVE EXAMPLE 13.7

What is the difference between a hazardous chemical and a toxic chemical?(13)

***SOLUTION*:** The term hazardous chemicals encompasses a broad category of terms that includes chemicals that may be (according to the EPA) toxic, flammable, corrosive, explosive, or harmful to the environment. A toxic chemical is one type of a hazardous chemical. Toxic chemicals cause adverse health effects, including severe illness or death when ingested, inhaled, or absorbed by a living organism. ■

## BASIC PRINCIPLES AND APPLICATIONS

As noted earlier, refrigeration systems are cyclic and operate using the following main components: a compressor, condenser, expander, and evaporator (see Figure 13.2). If the object to be refrigerated is a reservoir of heat at some low temperature and the object or reservoir where the heat is rejected is at a higher temperature, the continuous refrigeration cycle depicted in Figure 13.2 is a simplistic representation of the process.

### ILLUSTRATIVE EXAMPLE 13.8

Discuss the details of a basic refrigeration cycle as seen in Figure 13.2.(17)

***SOLUTION*:** The cycle begins when a refrigerant enters the compressor as a low pressure gas (1). Once compressed, it leaves as a hot high pressure gas. Upon entering the condenser (2), the

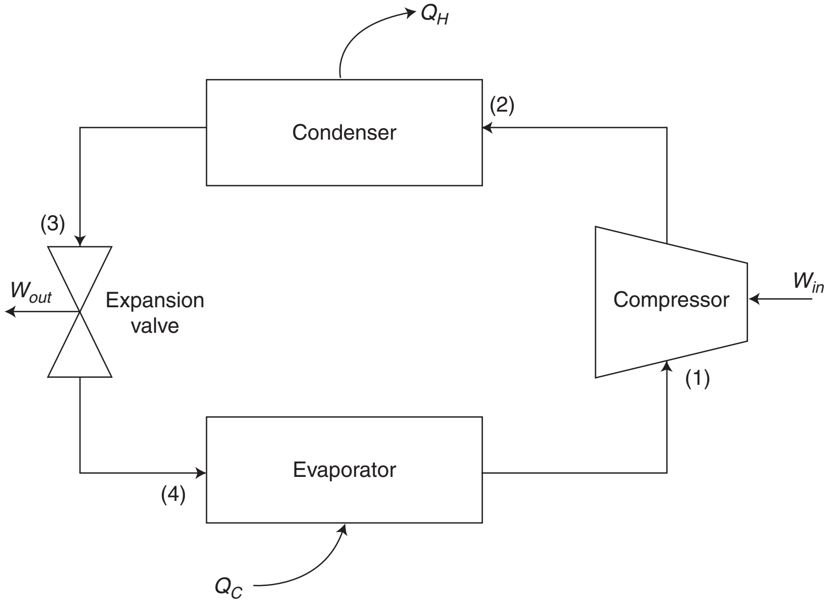

**Figure 13.2** Basic Components of a Refrigeration System.

gas condenses to a liquid and releases heat to the outside environment, which may be air or water. The cool liquid then enters the expansion valve at a high pressure (3); the flow is restricted and the pressure is lowered. In the evaporator (4), heat from the source to be cooled is absorbed and the liquid becomes a gas. The refrigerant then repeats the process (i.e., the cycle continues).

In a refrigerator, the working fluid enters the evaporator in a wet condition and leaves dry and saturated (or slightly superheated). The heat absorbed, $Q_C$, by the evaporator can therefore be estimated by multiplying the change in the fluid's entropy, $\Delta s$, as it passes through the evaporator by the fluid's saturation temperature, $T_S$, at the evaporator pressure since the fluid's temperature will be constant while it is in a wet condition at constant pressure. Thus,

$$Q_C = T_S \Delta s \tag{13.2}$$

where $Q_C$ = heat absorbed by the evaporator (e.g., kJ/kg)
$T_S$ = fluid saturation temperature at evaporator temperature (e.g., K)
$\Delta s$ = fluid entropy change (e.g., kJ/kg·K)

■

## ILLUSTRATIVE EXAMPLE 13.9

A refrigerator's evaporator is at 0.2 MPa and has a working fluid that enters the unit as liquid with an enthalpy, $h_{\text{in}}$, of 230 kJ/kg. If the refrigerator's working fluid (see Table 13.3) exits the evaporator as dry and saturated vapor, calculate the heat absorbed by the evaporator, $Q_C$.

**Table 13.3** Fluid Data for Illustrative Example 13.9

| $P$, MPa | $T_{\text{sat}}$, °C | $h_f$, kJ/kg | $h_g$, kJ/kg | $h$ at 20°C superheated, kJ/kg |
|---|---|---|---|---|
| 0.2 | −10 | 190 | 390 | 410 |
| 0.6 | 20 | 230 | 410 | 430 |

***SOLUTION*:** Determine the enthalpy of the fluid that exits from the evaporator, $h_{\text{out}}$. From the problem statement and data,

$$\begin{aligned} h_{\text{out}} &= h_g \text{ at } 0.2\text{ MPa} \\ &= 390\text{ kJ/kg} \end{aligned}$$

Calculate the heat absorbed by the evaporator, $Q_C$, using the change in enthalpy across the evaporator:

$$\begin{aligned} Q_C &= h_{\text{out}} - h_{\text{in}};\ h_{\text{in}} = h_l \\ &= 390 - 230 \\ &= 160\,\text{kJ/kg} \end{aligned}$$

■

## ILLUSTRATIVE EXAMPLE 13.10

As a follow-up to Illustrative Example 13.9, what is the fluid's change in entropy across the evaporator?

***SOLUTION*:** Determine the fluid's saturation temperature expressed in Kelvin (K). From the problem statement and data,

$$T_S = -10°\text{C} = 263\,\text{K}$$

Calculate the fluid's change in entropy from Equation (13.2) and using the solution in the previous example.

$$\begin{aligned} \Delta s &= \frac{Q_C}{T_S} = \frac{160}{263} \\ &= 0.61\,\text{kJ/kg}\cdot\text{K} \end{aligned}$$

■

## Coefficient of Performance

The performance and energy saving ability of a refrigerator is measured in terms of the system's Coefficient of Performance (C.O.P.). This is defined as the heat removed at a low temperature, i.e., the cooling effect, $Q_C$, divided by the work input, $W_{\text{in}}$, into the system:

$$\text{C.O.P.} = \frac{Q_C}{W_{\text{in}}} \tag{13.3}$$

where C.O.P. = coefficient of performance, dimensionless
$Q_C$ = cooling effect (e.g., kJ/kg)
$W_{\text{in}}$ = work input (e.g., kJ/kg)

The traditional system of units used in refrigeration are English units (i.e., Btu, etc.) but SI units are also acceptable and are used in the following two illustrative examples. The cooling effect, $Q_C$, is equal to the change in enthalpy of the working fluid as it passes through the evaporator, and the work input ($W_{\text{in}}$) is equal to the increase in the working fluid's enthalpy as it passes through the compressor.

## ILLUSTRATIVE EXAMPLE 13.11

The working fluid in a refrigerator enters a compressor at dry-saturated conditions at a pressure of 0.2 MPa and exits the compressor 20°C superheated at a pressure of 0.6 MPa. Given the fluid data from Illustrative Example 13.9, and given that the fluid leaves the condenser wet-saturated, what is the heat absorbed by the evaporator of the refrigerator?

***SOLUTION*:** Employ the subscripts associated with Figure 13.2. Determine the fluid enthalpy on entering the compressor, $h_1$. From the problem statement and data,

$$h_1 = 390 \text{ kJ/kg}$$

Determine the fluid enthalpy on leaving the compressor, $h_2$. From the problem statement and data,

$$h_2 = 430 \text{ kJ/kg}$$

Finally, determine the fluid enthalpy on leaving the condenser, $h_3$. From the problem statement and data, and noting that the enthalpy change across the expansion value is approximately zero,(2)

$$h_4 = h_3 = 230 \text{ kJ/kg}$$

Calculate the heat rejected from the condenser, $Q_H$, using the change in enthalpy across the condenser:

$$\begin{aligned} Q_H &= h_2 - h_3 \\ &= 430 - 230 \\ &= 200 \text{ kJ/kg} \end{aligned}$$

Calculate the work input, $W_{\text{in}}$, using the change in enthalpy across the compressor:

$$\begin{aligned} W_{\text{in}} &= h_2 - h_1 \\ &= 430 - 390 \\ &= 40 \text{ kJ/kg} \end{aligned}$$

Calculate the heat absorbed by the evaporator, $Q_C$, using the first law of thermodynamics:(2)

$$\begin{aligned} Q_C &= Q_H - W_{\text{in}} \\ &= 200 - 40 \\ &= 160 \text{ kJ/kg} \end{aligned}$$

■

## ILLUSTRATIVE EXAMPLE 13.12

From Illustrative Example 13.11, what is the refrigerator's C.O.P.?

***SOLUTION*:** Determine the C.O.P using Equation (13.3) and the values of $Q_C$ and $W_{\text{in}}$ from the previous example:

$$\begin{aligned} \text{C.O.P.} &= \frac{Q_C}{W_{\text{in}}} \\ &= \frac{160}{40} \\ &= 4.0 \end{aligned}$$

*Comment*: The C.O.P. for a refrigerator is defined in terms of the cooling load, $Q_C$; however, the C.O.P. for a heat pump is defined in terms of the heating load, $Q_H$. ■

## Thermal Efficiency

The performance of a steam power plant process can be measured in a manner somewhat analogous to the C.O.P. for a refrigeration system. The thermal efficiency, $\eta_{\text{th}}$, of a work-producing cycle is defined as the ratio of work produced to heat added. Thus,

$$\eta_{\text{th}} = \frac{W_{\text{net}}}{Q_{\text{in}}} \tag{13.4}$$

where $\eta_{\text{th}}$ = thermal efficiency, dimensionless

$W_{\text{net}}$ = net work produced by the cycle (e.g., J/kg)

$Q_{\text{in}}$ = heat added to the cycle (e.g., J/kg)

This can be rewritten as:

$$\eta_{\text{th}} = \frac{W_{\text{out}} - W_{\text{in}}}{Q_{\text{in}}} \tag{13.5}$$

where $W_{\text{out}}$ = work produced by the cycle (e.g., J/kg)
$W_{\text{in}}$ = work consumed by the cycle (e.g., J/kg)

For this type of cycle, the compressor, evaporator, and expansion value in Figure 13.2 are replaced by a turbine, boiler, and pump, respectively, with both $Q_C$ and $Q_H$ as well as $W_{in}$ and $W_{out}$ reversed. See Figure 13.3. When no velocity information is provided, velocity effects can be neglected and this equation can be expressed in terms of enthalpies at points on entry and exit to the boiler, turbine, and pump, which for a simple power cycle is:

$$\eta_{\text{th}} = \frac{(h_2 - h_3) - (h_1 - h_4)}{(h_2 - h_1)} \tag{13.6}$$

where $h_1$ = enthalpy on entry to the boiler (e.g., J/kg)
$h_2$ = enthalpy on exit from the boiler, on entry to the turbine (e.g., J/kg)
$h_3$ = enthalpy on exit from the turbine (e.g., J/kg)
$h_4$ = enthalpy on entry to the pump (e.g., J/kg)

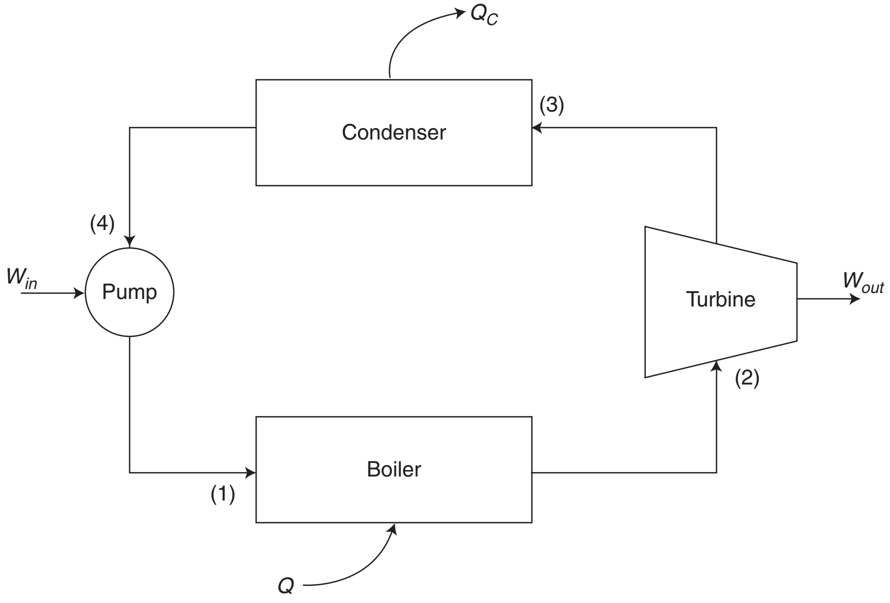

**Figure 13.3** Basic Components of a Steam Power System.

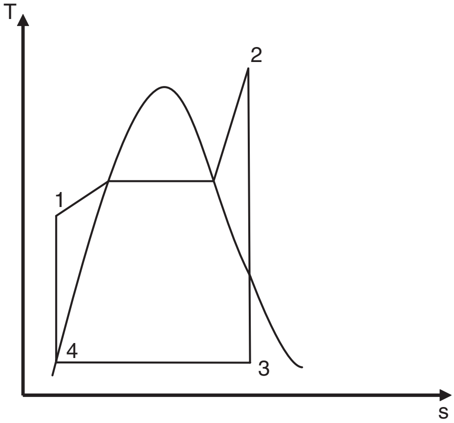

**Figure 13.4** Rankine Cycle T-s Diagram.

Note that the change in enthalpy across the pump is often neglected since it is close to zero relative to the other enthalpy changes. In effect, $h_1 - h_4 \approx 0$.

## ILLUSTRATIVE EXAMPLE 13.13

A Rankine cycle has a T-S diagram as shown in Figure 13.4, and rejects 2043 kJ/kg of heat during the constant pressure process between points 3 and 4. The data provided in Table 13.4 is also associated with this cycle. Calculate the enthalpy change across the boiler.

Properties associated with the condenser are as follows:

$P = 0.1235$ bar
$h_f = 209$ kJ/kg
$h_g = 2592$ kJ/kg
$s_f = 0.7038$ kJ/kg · K
$s_g = 8.0763$ kJ/kg · K

**Table 13.4** T-S Data for Illustrative Example 13.13

| Point | $x$ | $h$, kJ/kg | $s$, kJ/kg·K |
|---|---|---|---|
| 1 | | 548 | |
| 2 | | 3989 | 7.5190 |
| 3 | 0.9575 | 2491 | 7.7630 |
| 4 | | | 1.4410 |

Note: $x$ = mass fraction vapor.

***SOLUTION*:** Determine the steam enthalpy at the entry and exit to the boiler (points 1 and 2), turbine (points 2 and 3), and pump (points 4 and 1) from the problem statement and data:

$$h_1 = 548 \text{ kJ/kg}$$
$$h_2 = 3989 \text{ kJ/kg}$$
$$h_3 = 2491 \text{ kJ/kg}$$

In addition,

$$h_4 = h_3 - Q_H$$

where $Q_H$ = heat rejected by the condenser

Thus:

$$\begin{aligned} h_4 &= 2491 - 2043 \\ &= 448 \text{ kJ/kg} \end{aligned}$$

Calculate the heat added to the boiler (which is equal to the enthalpy change across the boiler):

$$\begin{aligned} Q_{\text{boiler}} &= h_2 - h_1 \\ &= 3989 - 548 \\ &= 3441 \text{ kJ/kg} \end{aligned}$$

■

## ILLUSTRATIVE EXAMPLE 13.14

What is the thermal efficiency of the cycle in Illustrative Example 13.13?

***SOLUTION*:** Calculate the work produced by the turbine by determining the enthalpy change across the turbine:

$$\begin{aligned} W_{\text{turbine}} &= h_2 - h_3 \\ &= 3989 - 2491 \\ &= 1498 \text{ kJ/kg} \end{aligned}$$

Calculate the work used by the pump, which is equal to the enthalpy change across the pump:

$$\begin{aligned} W_{\text{pump}} &= h_1 - h_4 \\ &= 548 - 448 \\ &= 100 \text{ kJ/kg} \end{aligned}$$

Calculate the net work by subtracting the pump work from the turbine work:

$$\begin{aligned} W_{\text{net}} &= W_{\text{turbine}} - W_{\text{pump}} \\ &= 1498 - 100 \\ &= 1398 \text{ kJ/kg} \end{aligned}$$

Calculate the thermal efficiency, $\eta_{\text{th}}$, from Equation (13.4):

$$\begin{aligned}\eta_{\text{th}} &= \frac{W_{\text{net}}}{Q_{\text{in}}} = \frac{W_{\text{net}}}{Q_{\text{boiler}}}\\ &= \frac{1398}{3441}\\ &= 0.406 = 40.6\%\end{aligned}$$

*Comment*: Unless otherwise specified, it is assumed that the turbine and pump operate adiabatically. ■

## Entropy and Heat

The Clausius inequality states that, for a reversible process, the entropy change associated with the process is equal to the integral of the heat transferred divided by the temperature. Thus,

$$\Delta s = \int \frac{dQ_{\text{rev}}}{T} \tag{13.7}$$

where $\Delta s$ = process change in entropy (e.g., J/kg)
$dQ_{\text{rev}}$ = total heat transferred (e.g., J/kg)
$T$ = temperature (e.g., K)

Consequently, for a constant temperature process,

$$\int dQ_{\text{rev}} = Q_{\text{rev}} = T\Delta s \tag{13.8}$$

### ILLUSTRATIVE EXAMPLE 13.15

Using the Rankine cycle T-s diagram, in Figure 13.4, and the data from Illustrative Example 13.13, calculate the temperature at point 3.

***SOLUTION***: Identify the known properties at point 3, which are $x$, $h$, and $s$ from Table 13.4:

$$\begin{aligned}x_3 &= 0.9575\\ h_3 &= 2491 \text{ kJ/kg}\\ s_3 &= 7.7630 \text{ kJ/kg}\cdot\text{K}\end{aligned}$$

Identify a process that is associated with point 3, which is inside the vapor dome and therefore will be a constant pressure process. The heat rejection of

$$h_3 - h_4 = Q_{\text{out}} = 2043 \text{ kJ/kg} \approx Q_{\text{rev}}$$

is associated with a constant temperature, constant pressure condensation process.

Determine the relationship between the process and the point in question. Since the entropy and the heat transfer associated with the condenser are known, a relationship therefore exists that allows the temperature to be determined by rearranging Equation (13.8).

$$T_3 = \frac{Q_{\text{out}}}{\Delta s} = \frac{Q_{\text{out}}}{s_3 - s_4}$$

Substitute the known values.

$$\begin{aligned} T_3 &= \frac{2043}{7.7630 - 1.4410} \\ &= 323\,\text{K} = 50^\circ\text{C} \end{aligned}$$

*Comment*: The Clausius inequality is only applicable to *reversible* processes. Therefore, it does not apply to *irreversible* processes. ■

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