# CRYOGENIC MIXED REFRIGERANT PROCESSES

# INTERNATIONAL CRYOGENICS MONOGRAPH SERIES

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Springer

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Dedicated to the loving memory of my father

G. V. Narasimham

# Preface

This monograph deals with mixed refrigerant processes that operate at temperatures less than 123 K. Most conventional cryogenic refrigerators and liquefiers operate with pure fluids, the major exception being natural gas liquefiers that use mixed refrigerant processes. The fundamental aspects of mixed refrigerant processes, though very innovative, have not received the due attention in the open literature in view of commercial interests. Hundreds of patents exist on different aspects of mixed refrigerant processes for the liquefaction of natural gas and the composition of mixtures for Joule–Thomson (Linde–Hampson) and other refrigerators. It is difficult to piece together the existing information to choose an appropriate process and an optimum composition for a given application. The main purpose of this monograph is to explain all the aspects of mixed refrigerant processes and the methods for choosing the composition of refrigerants using robust analytical methods based on sound thermodynamic principles.

All concepts required to design and evaluate mixed refrigerant processes including exergy are introduced from first principles in the first chapter. The performance of traditional cryogenic processes that operate with pure fluids such as Linde–Hampson and Kapitza and the reasons for the low exergy efficiency of these processes are also presented in the first chapter.

Cryogenic processes differ from general chemical processes in several ways. The use of multistream heat exchangers with internal pinch points makes it necessary to use somewhat different approaches to simulate mixed refrigerant processes. The methods for simulating and optimizing cryogenic processes using a process simulator are presented in the second chapter.

The need for using refrigerant mixtures over pure fluids is presented in the third chapter with reference to simple refrigeration and gas cooling processes. The more complex refrigeration processes are presented in the fourth chapter. A unified design approach has been evolved for optimizing mixed refrigerant process refrigerators and liquefiers and is presented in the fifth chapter. The different natural gas and nitrogen liquefaction processes are presented in the sixth and seventh chapters, respectively.

Optimum operating pressures and mixture compositions have been determined for a variety of mixed refrigerant process refrigerators and natural gas/nitrogen liquefiers. In some cases, the performance of processes with different alternate mixture

compositions and operating pressures has been presented to help understand these processes thoroughly. The performance of different processes is evaluated in terms of exergy losses in different components. Most of the examples and case studies presented are largely unpublished.

The examples presented in this monograph were solved using Aspen Plus, a commercial process simulator, and CRYOSIM, a cryogenic process simulator developed in-house. It should be possible, however, to use any process simulator with optimization capabilities to solve the examples independently. The reader can also use the data presented in the examples as the starting values (estimates) in his or her own optimization studies. Those who are familiar with process optimization will appreciate the value of good estimates that allow the optimizer to start from a feasible point and converge rapidly. Many of the examples provided are nearly optimal solutions. However, students and practicing engineers are encouraged to find even better solutions as a part of their learning exercise. Practicing refrigeration and cryogenic engineers will benefit from this monograph and would be able to apply the methods presented to design optimum mixed refrigerant processes. This monograph can also be used as a textbook for a graduate course on advanced refrigeration or cryogenic processes. No prior knowledge of refrigeration/cryogenic processes is required to read this monograph. Some knowledge of thermodynamics and optimization is helpful, but not necessary. Access to a process simulator is, however, necessary to design mixed refrigerant processes.

The material covered in this monograph has been drawn largely from my research on refrigerant mixtures for over 15 years. I used the material presented in a graduate course on advanced cryogenic systems at IIT Madras.

# Contents

# Nomenclature

| | |
|---|---|
| $A$ | Heat transfer area ($m^2$) |
| $a_i$ | Constant in Eq. (3.15) |
| $b_i$ | Constant in Eq. (3.16) |
| C | Clearance ratio of compressor |
| COP | Coefficient of performance ($-$) |
| $c$ | Constant in Eq. (5.1) |
| $c_p$ | Specific heat at constant pressure (J/mol·K) |
| $c_v$ | Specific heat at constant volume (J/mol·K) |
| ex | Specific exergy of a stream = $[(h - h_o) - T_o(s - s_o)]$ (J/mol) |
| $f$ | Fugacity (bar) |
| HX | Heat exchanger |
| $h$ | Specific enthalpy at pressure $p$, temperature $T$ (J/mol) |
| $h_o$ | Specific enthalpy at ambient pressure and temperature (J/mol) |
| $i$ | Iteration number |
| LNG | Liquefied natural gas |
| LPG | Liquefied petroleum gas |
| MRC | Mixed refrigerant cascade |
| $n$ | Moles (mol) |
| $\dot{n}$ | Mole flow rate (mol/s) |
| $\dot{n}_i$ | Mole flow rate of the $i$th component (mol/s) |
| $p$ | Pressure (bar) |
| $p_c$ | Critical pressure (bar) |
| $Q$ | Heat transferred (J) |
| $\dot{Q}$ | Heat transfer rate (W) |
| $\dot{Q}_o$ | Heat transfer rate to ambient (W) ($\dot{Q}_o < 0$) |
| $Q_v$ | Volumetric cooling capacity (J/mol) |
| $R$ | Universal gas constant (bar·$m^3$/mol·K) |
| $s$ | Specific entropy at pressure $p$, temperature $T$ (J/mol·K) |
| $s_o$ | Specific entropy at ambient pressure and temperature (J/mol-K) |

| | |
|---|---|
| $T$ | Temperature (K) |
| $T_{c,\,in}$ | Temperature of cold stream at heat exchanger inlet (K) |
| $T_{c,\,out}$ | Temperature of cold stream at heat exchanger outlet (K) |
| $T_{h,\,in}$ | Temperature of hot stream at heat exchanger inlet (K) |
| $T_{h,\,out}$ | Temperature of hot stream at heat exchanger outlet (K) |
| $T_o$ | Ambient temperature (K) |
| $t_o$ | Ambient temperature (°C) |
| $U$ | Overall heat transfer coefficient (W/m²·K) |
| $\dot{V}$ | Volume flow rate (m³/s) |
| $\dot{V}_c$ | Displacement rate of compressor (m³/s) |
| VLE | Vapor liquid equilibria |
| VLLE | Vapor-liquid-liquid-equilibria |
| $v$ | Specific volume (m³/mol) |
| $W$ | Work (J) |
| $\dot{W}$ | Power (W) |
| $\dot{W}_c$ | Compressor power (W) ($\dot{W}_c < 0$) |
| $\dot{W}_e$ | Power extracted from an expander (W) ($\dot{W}_e > 0$) |
| $x$ | Vapor fraction |
| $Y$ | Liquid yield (flow rate of liquid product/flow rate through compressor, also the fraction of the gas that gets liquefied on expansion) |

## Greek letters

| | |
|---|---|
| $\alpha$ | Constant in Eq. (4.10) |
| $\beta$ | Constant in Eq. (4.10) |
| $\Delta c_{p,\,fusion}$ | $c_{p,\,liq} - c_{p,\,solid}$ at triple point (J/mol·K) |
| $\Delta Ex_{loss}$ | Ratio of exergy loss to power input (-) |
| $\Delta h_{fusion}$ | Enthalpy of fusion (J/mol) |
| $\Delta h_{min}$ | Specific refrigeration effect (J/mol) |
| $\Delta s$ | Specific entropy change (J/mol·K) |
| $\Delta T$ | Temperature difference, temperature approach between hot and cold streams of a heat exchanger (K) |
| $\Delta T_{min}$ | Minimum temperature approach between the hot and cold streams in the heat exchanger (K) |
| $\Delta v_{fusion}$ | $v_{liq} - v_{solid}$ at triple point (m³/mol) |
| $\varepsilon$ | Effectiveness of the heat exchanger |
| $\gamma$ | Adiabatic index $= c_p/c_v$ |
| $\eta_{ad}$ | Adiabatic efficiency (-) |
| $\eta_{ex}$ | Exergy efficiency (-) |
| $\eta_{fc}$ | Frictional efficiency of compressor (-) |
| $\eta_m$ | Efficiency of motor (-) |
| $\eta_v$ | Volumetric efficiency (-) |
| $\Lambda$ | Ratio of the length of a part of heat exchanger to the total length of the heat exchanger |

| | |
|---|---|
| $\mu_{\text{J–T}}$ | Joule–Thomson coefficient (K/bar) |
| $\Theta$ | Ratio of the heat transfer over a part of the heat exchanger to the heat transfer over the entire heat exchanger |
| $\tau$ | Dimensionless temperature of streams in a heat exchanger $= (T - T_{c,\,\text{in}})/(T_{h,\,\text{in}} - T_{c,\,\text{in}})$ |
| $\rho$ | Density (mol/l) |
| $\xi$ | Mole fraction (-) |

**Subscripts**

| | |
|---|---|
| ad | Adiabatic |
| c | Compressor, cold stream |
| comp | Compressor |
| cb | Cold box |
| ce | Cold end of heat exchanger |
| cs | Compressor section (compressor and aftercooler/condenser) |
| cv | Control volume |
| e | Expander |
| ex | Exergy |
| gas | Process gas being cooled |
| h | Constant enthalpy, hot stream, high temperature |
| hp | High-pressure stream |
| hx | Heat exchanger |
| i | $i$th component |
| ideal | Ideal system |
| l | Liquefier, gas cooler, low temperature |
| liq | Liquid phase |
| lm | LMTD |
| lp | Low-pressure stream |
| max | Maximum |
| min | Minimum |
| $N_2$ | Nitrogen |
| o | Ambient, surroundings |
| p | Constant pressure |
| pre | Precooler |
| ps | Phase separator |
| r | Refrigerator |
| ref | Refrigerant |
| rev | Reversible |
| solid | Solid phase |
| specified | Specified |
| T | Constant temperature |
| t | Turbine |
| tp | Triple point |
| vp | Vapor pressure |
| we | Warm end of heat exchanger |

# 1

# Fundamental principles and processes

Single-stage mixed refrigerant processes that can provide refrigeration at very low temperatures were first proposed nearly 70 years ago by Podbielniak [69] and were adopted for large-scale liquefaction of natural gas after the pioneering work of Kleemenko [50] of the former Soviet Union in the 1960s. Today most base-load natural gas liquefaction plants operate on mixed refrigerant processes. Mixed refrigerant processes have also been adopted for peak-shaving natural gas liquefaction plants.

Mixed refrigerant processes were also studied in the early 1970s in the former Soviet Union by Brodyanskii and his colleagues for small cryocooler applications [17]. The interest in mixed refrigerant cryocoolers was revived about 10 years ago when DARPA funded projects for the development of low-cost cryocoolers [62].

Currently, there's worldwide interest in using mixed refrigerant processes for the liquefaction of nitrogen and separation of air [25]. Several U.S. patents have been granted during the last five years on the liquefaction of nitrogen using mixed refrigerant processes and two large plants have been built and tested [25].

Refrigeration processes can be divided into two broad groups based on the variation of pressure with time at any location of the process as follows [72]:

- periodic refrigerators in which the pressure at any point of the cycle varies with time, and
- steady-state refrigerators in which the pressure at any point of the cycle is constant and does not vary with time.

Cycles such as the Stirling, Gifford–McMahon, and Pulse-Tube belong to the first group, whereas cycles such as the Linde–Hampson (Joule–Thomson), Kapitza, etc. belong to the second group. The classification is analogous to alternating- and direct-current electrical machines. The theory and fundamental principles of these two groups are different enough to be treated separately. This monograph deals with mixed refrigerant processes in which the pressure at any part of the process is steady and does not vary with time. The flow is also unidirectional and steady in these processes.

Steady-state processes have been used in cryogenic liquefiers and refrigerators for over a century. Pure (single-component) fluids have traditionally been used in cryogenic refrigerators, whereas the fluid being liquefied is itself used as the refrigerant in the traditional liquefaction processes, the exception being the liquefaction of natural gas using mixed refrigerant processes. There are several advantages in using zeotropic refrigerant mixtures in cryogenic refrigerators and liquefaction systems:

- The exergy efficiency (figure of merit) of refrigeration and liquefaction systems operating with refrigerant mixtures is many times that of systems operating with pure fluids.
- The operating pressure is much lower when refrigerant mixtures are used, compared to pure fluids.
- Refrigeration and liquefaction systems operating with pure fluids operate largely in the superheated vapor region, whereas those operating with refrigerant mixtures operate largely in the two-phase region. Consequently, the heat transfer coefficients in the heat exchangers are much larger in systems operating with refrigerant mixtures compared to those operating with pure fluids, resulting in smaller heat exchangers.
- The degradation of heat exchanger performance due to longitudinal (axial) heat conduction is much smaller due to higher apparent specific heat [$(\partial h/\partial T)_p$] of refrigerant mixtures in the two-phase region compared to the specific heat at constant pressure ($c_p$) of pure fluids in the superheated (single-phase) region.

It will be advantageous to replace many traditional processes operating with pure fluids with those operating with refrigerant mixtures.

## 1.1 Applications

Mixed refrigerant processes are used in numerous applications. Some of them are listed below

**Liquefiers**

- Liquefaction of natural gas in base-load and peak-shaving plants
- Liquefaction of natural gas derived from capped wells, biogas from landfills, municipal wastes, etc. on a small scale
- Liquefaction of nitrogen
- Liquefaction and separation of air
- Recovery of volatile organic compounds

**Refrigerators/Cryocoolers**

- Cooling of water traps and cryo vacuum panels in the manufacture of semiconductors, hard disks, LCD displays

- Cooling of telescopes, electronic devices, computers, CCD cameras
- Cooling of infrared, gamma-ray, and X-ray detectors used in a variety of applications
- Cryosurgical devices used in gynecology, cardiac, prostrate and dental surgeries
- Cryofreezers, biofreezers, etc. used in the preservation of cells, tissues and cultures

The main aim of this monograph is to teach the different mixed refrigerant processes and the methods to optimize the composition of refrigerants used in these processes.

It is necessary to understand the fundamental cryogenic processes that operate with pure fluids thoroughly to be able to design mixed refrigerant processes that overcome the deficiencies of conventional systems. The concept of exergy efficiency/exergy loss and the working of fundamental cryogenic refrigeration and liquefaction processes operating with pure fluids are discussed in this chapter.

## 1.2 Sign convention

The following sign convention is followed in this monograph. The heat transfer to a system (from the surroundings) is considered positive, and heat transfer from the system to the surroundings is considered negative. Similarly, the work delivered by a system is considered positive, and the work done on the system is considered negative. The sign conventions are illustrated in Fig. 1.1 with reference to a heat engine and a refrigerator. Note that $\dot{Q}_o$ and $\dot{W}_c$ are negative, whereas $\dot{Q}_h$, $\dot{Q}_l$, and $\dot{W}$ are positive.



$$\text{Efficiency} = \frac{\text{work output}}{\text{heat input}} = \frac{\dot{W}}{\dot{Q}_h} = \frac{\dot{W}}{\dot{Q}_h + \dot{Q}_o}$$

(a) Heat engine

$$\text{COP} = \frac{\text{heat absorbed}}{\text{work input}} = \frac{\dot{Q}_l}{-\dot{W}_c} = \frac{\dot{Q}_l}{\dot{Q}_l + \dot{Q}_o}$$
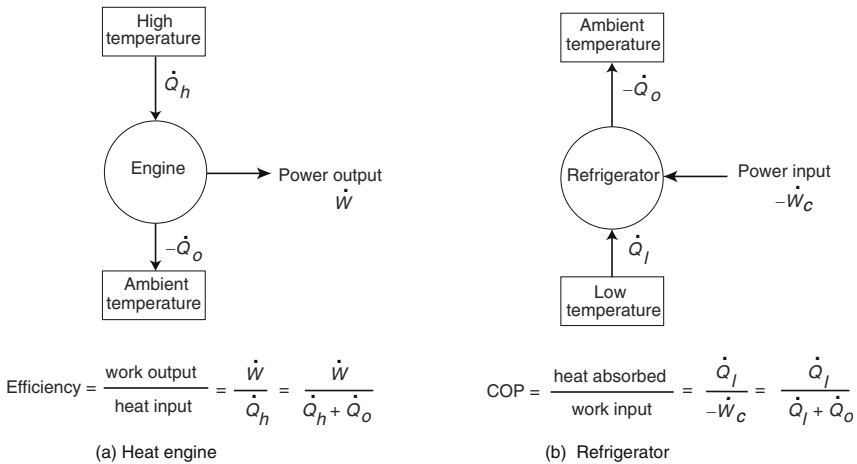
(b) Refrigerator

**Fig. 1.1.** Sign convention used in this monograph.

## 1.3  Ideal refrigeration and liquefaction processes

Refrigeration systems can be largely divided into two groups based on the refrigeration temperature as follows:

- refrigerators that provide refrigeration over a constant temperature such as Carnot, Stirling, Erricson (Fig. 1.2), and
- refrigerators that provide refrigeration over a range of temperatures such as those required for cooling a gas from room temperature to a low temperature, viz., the reverse Brayton refrigerator (Fig. 1.3).

### 1.3.1  Ideal constant-temperature refrigeration process

Consider a refrigerator that provides refrigeration over a constant temperature and operates on reversible thermodynamic processes. Such a refrigerator will henceforth
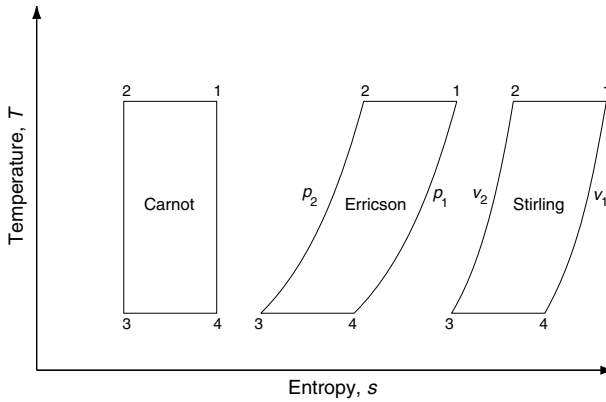


**Fig. 1.2.** Ideal refrigerator cycles that provide constant-temperature refrigeration (process 3–4).
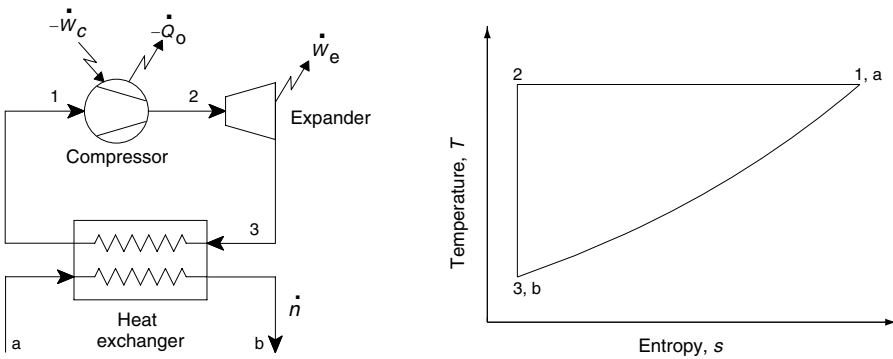


**Fig. 1.3.** Ideal reverse Brayton cycle for cooling a gas from state point a to state point b.
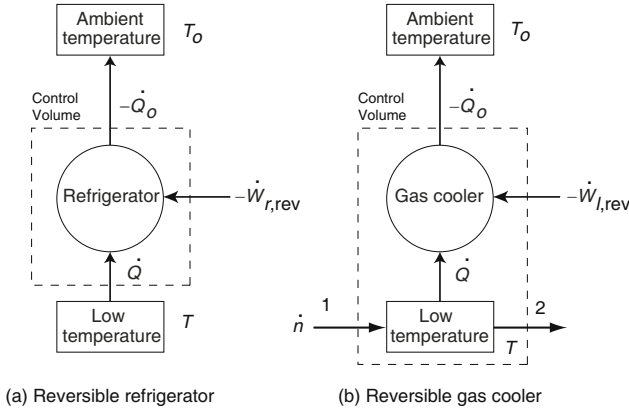
**Fig. 1.4.** Schematic of (a) a reversible refrigerator and (b) reversible gas cooler for cooling/liquefying a gas from state 1 to state 2.

be called a reversible refrigerator [Fig. 1.4(a)]. Heat is rejected to the surroundings at a temperature $T_o$ and absorbed at a temperature $T$ ($T < T_o$). The heat transfer between the refrigerator and source/sink is assumed to occur at a zero temperature difference in all reversible refrigerators. The temperature of the refrigerant is therefore the same as that of the ambient ($T_o$) during the heat rejection process and that of the load ($T$) during the heat absorption process. The first and second laws of thermodynamics can be written for a reversible refrigerator as follows:

$$\text{first law: } \dot{W}_{r,\,\text{rev}} = \dot{Q} + \dot{Q}_o, \tag{1.1}$$

$$\text{second law: } \frac{\dot{Q}}{T} + \frac{\dot{Q}_o}{T_o} = 0. \tag{1.2}$$

Substituting Eq. (1.2) into Eq. (1.1) gives the expression for the power required by a reversible refrigerator as follows:

$$\boxed{-\dot{W}_{r,\,\text{rev}} = \dot{Q}\left(\frac{T_o}{T} - 1\right)}, \tag{1.3}$$

where $T$ and $T_o$ refer to the refrigeration and ambient temperatures, respectively. $\dot{Q}$ and $-\dot{Q}_o$ are the heat absorbed and heat rejected, respectively.[1]

The coefficient of performance (COP) of any refrigerator is defined as follows:

$$COP = \frac{\text{heat absorbed at low temperature}}{\text{compressor work input}} = \frac{Q}{-W_c} = \frac{\dot{Q}}{-\dot{W}_c}, \tag{1.4}$$

where $Q$ and $-W_c$ refer to the heat absorbed and compressor work input in joules, and $\dot{Q}$ and $-\dot{W}_c$ refer to the heat transfer rate from the low-temperature source and the power supplied to the compressor in watts.

---

[1] $\dot{Q} > 0$, $\dot{Q}_o < 0$, $\dot{W}_{r,\,\text{rev}} < 0$.

The coefficient of performance (COP) of an ideal reversible refrigerator providing refrigeration at constant temperature can be expressed in terms of the temperatures for the heat source and heat sink using Eq. (1.3) as follows:

$$COP_{r,\,\text{rev}} = \frac{\dot{Q}}{-\dot{W}_{r,\,\text{rev}}} = \frac{T}{T_o - T}. \tag{1.5}$$

### 1.3.2 Ideal gas-cooling/liquefaction process

Figure 1.4(b) shows the schematic of a gas cooler in which the process fluid is cooled from a temperature $T_1$ to a temperature $T_2$. The first and second laws of thermodynamics can be written for the control volume of an ideal gas cooler [Fig. 1.4(b)] operating on reversible processes and providing refrigeration over a range of temperatures as follows:

$$\text{first law:} \quad \dot{W}_{l,rev} = \dot{Q} + \dot{Q}_o = \dot{n}(h_1 - h_2) + \dot{Q}_o, \tag{1.6}$$

$$\text{second law:} \quad \dot{n}(s_1 - s_2) + \frac{\dot{Q}_o}{T_o} = 0, \tag{1.7}$$

where $-\dot{W}_{l,\,\text{rev}}$ refers to the power input to the reversible gas cooler and $\dot{n}$ is the mole flow rate of the process fluid.[2]

Substituting Eq. (1.7) into Eq. (1.6) gives the expression for the minimum power required for cooling a gas from state 1 to state 2 as follows:

$$\boxed{-\dot{W}_{l,\,\text{rev}} = \dot{n}[(h_2 - h_1) - T_o(s_2 - s_1)] = \dot{n}(\text{ex}_2 - \text{ex}_1)}. \tag{1.8}$$

In the above expression, ex refers to the exergy of the fluid being cooled [ex $=$ $(h - h_o) - T_o(s - s_o)$], and $T_o$ is the ambient temperature [see Eq. (1.16)]. It is evident from Eq. (1.8) that the minimum work required to cool a unit mole of a gas using an ideal gas cooler operating on reversible processes is the same as the exergy change of the fluid being cooled and is independent of the process used for cooling.

Consider the gas-cooling process shown in Fig. 1.5. The gas to be liquefied is compressed in an isothermal compressor (process 1–2) and expanded in an isentropic expander (process 2–3) to the required pressure and temperature (state point 3). The net power input to the process is given by the expression

$$- \dot{W}_{\text{net},\,l} = -\dot{W}_c - \dot{W}_e = \dot{n}[(h_2 - T_o\, s_2) - (h_1 - T_o\, s_1)] - \dot{n}(h_2 - h_3). \tag{1.9}$$

Since the entropy at state points 2 and 3 is the same ($s_2 = s_3$), the above expression for the net power required to cool the gas from temperature $T_1$ to $T_3$ can be expressed as

$$- \dot{W}_{\text{net},\,l} = \dot{n}[(h_3 - T_o\, s_3) - (h_1 - T_o\, s_1)] = \dot{n}(\text{ex}_3 - \text{ex}_1). \tag{1.10}$$

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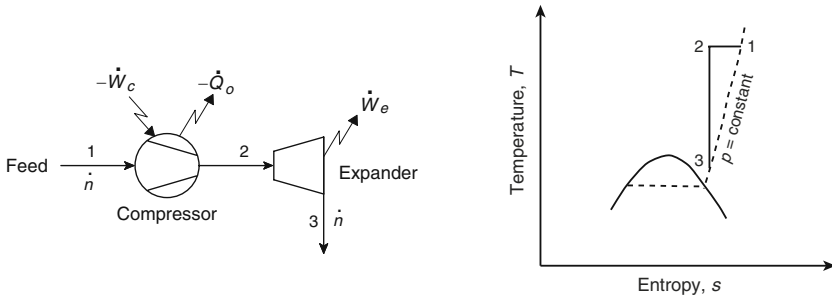[2] $\dot{Q} > 0$, $\dot{Q}_o < 0$, and $\dot{W}_{l,\,\text{rev}} < 0$.
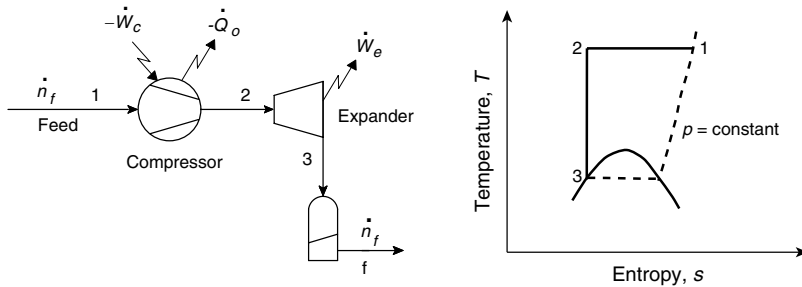
**Fig. 1.5.** Ideal gas cooling process.



**Fig. 1.6.** Ideal process for gas liquefaction.

It can be seen that the net power required in the process shown in Fig. 1.5 is the same as that required by a reversible gas cooler for cooling a gas from state 1 to 3 [Eq. (1.8)].

The process shown in Fig. 1.5 is thus a reversible gas cooler. In order to differentiate the process shown in Fig. 1.5 from the generic ideal gas cooler shown in Fig. 1.4(b), the process shown in Fig. 1.5 is termed the ideal gas-cooling process.

Equation (1.8) is also valid when a gas is cooled from ambient temperature to the point where it is a saturated liquid. An ideal process for the liquefaction of a gas is shown in Fig. 1.6. The ideal gas liquefaction process shown in Fig. 1.6, however, has certain limitations:

- The operating pressure required for the reversible process is very high.
- Most expansion machines can tolerate only a very small fraction of liquid, making it difficult to use practical expanders for liquefaction.

Figure 1.7 shows an ideal liquefaction process operating at pressures of 10,000 bar and 1 bar with nitrogen. It can be observed that complete liquefaction of nitrogen is not possible with the ideal liquefaction process, even at an operating pressure of 10,000 bar. The concept of minimum power required for liquefaction using an ideal process, however, is useful to compare the performance of different processes.
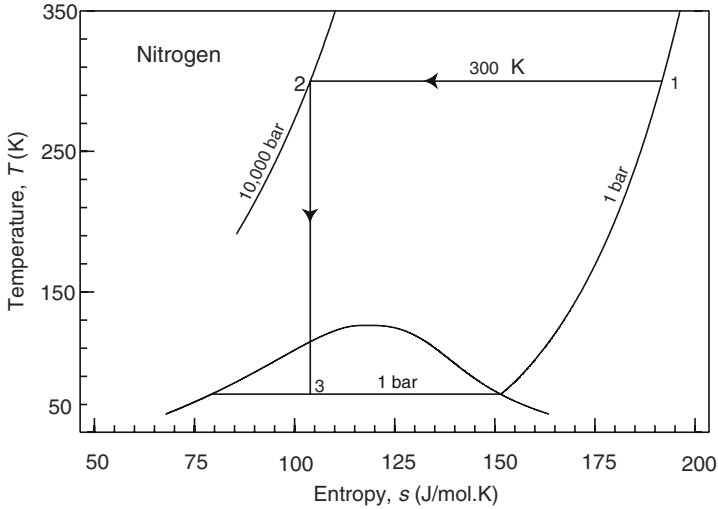
**Fig. 1.7.** Ideal nitrogen liquefaction process operating between pressures of 10,000 bar and 1 bar.

## 1.4 Exergy

The performance of a number of refrigeration and liquefaction processes is studied in this monograph. The performance of different systems can be compared on a common-denominator basis using the concept of exergy efficiency. Exergy efficiency is also used as the objective function in the optimization of low-temperature processes discussed in this monograph. A good understanding of the basic concepts of exergy, exergy efficiency, and exergy loss is essential to design efficient mixed refrigerant processes.

Exergy has several definitions [28, 82]. In this section, the concepts of exergy are introduced in relation to refrigerators and liquefiers. The reader may refer to advanced textbooks on exergy for more generalized approaches. The performance of systems that transfer heat to and from the ambient is strongly related to the ambient temperature and pressure. Consider a refrigerator that absorbs a certain quantity of heat $Q$ at a temperature $T$. The heat absorbed along with the work supplied is rejected to the ambient. The work required by the refrigerator for providing the required refrigeration is therefore related to the ambient temperature. The work required will be minimized when a refrigerator operates on a reversible thermodynamic process, for example, Carnot, Stirling, etc. in which heat transfer between the refrigerant and the surroundings occurs at a zero temperature approach. This minimum work $(-W_{rev})$ required to provide a refrigeration $Q$ at temperature $T$ while rejecting the heat to ambient at temperature $T_o$ is called exergy.

The coefficient of performance (COP) of a refrigerator operating on reversible processes is related to the temperature at which heat is absorbed ($T$) and the temperature of the ambient ($T_o$) as follows (Fig. 1.1):

$$COP_{r,\text{rev}} = \frac{Q}{-W_{\text{rev}}} = \frac{T}{T_o - T}. \tag{1.11}$$

The exergy or minimum work $(-W_{rev})$ required to transfer heat $Q$ at temperature $T$ using a reversible refrigerator is given by the expression

$$-W_{\text{rev}} = Q\left(\frac{T_o - T}{T}\right). \tag{1.12}$$

In the case of heat engines, exergy is the maximum work that can be obtained from a reversible heat engine while absorbing heat $Q$ at a temperature $T$ and rejecting part of this heat to ambient at a temperature $T_o$. It can easily be shown that the above expression relating exergy and the operating temperatures is also applicable for a heat engine (see Fig. 1.8).

The concept of exergy can be extended to other systems as well. Consider a reversible heat engine in which the heat is supplied by a fluid stream as shown in Fig. 1.9. The fluid stream enters at state 1 and leaves at state 2. The first and second laws of thermodynamics can be expressed for a reversible heat engine as follows:

$$\text{first law:} \quad W_{\text{rev}} = Q + Q_o = n(h_1 - h_2) + Q_o, \tag{1.13}$$

$$\text{second law:} \quad n(s_1 - s_2) + \frac{Q_o}{T_o} = 0, \tag{1.14}$$

where $W_{\text{rev}}$ refers to the work output from the heat engine and $n$ is the number of moles of the fluid stream.

Substituting Eq. (1.14) into Eq. (1.13) gives the expression for the work that can be obtained from a fluid stream as

$$W_{\text{rev}} = n[(h_1 - h_2) - T_o(s_1 - s_2)]. \tag{1.15}$$
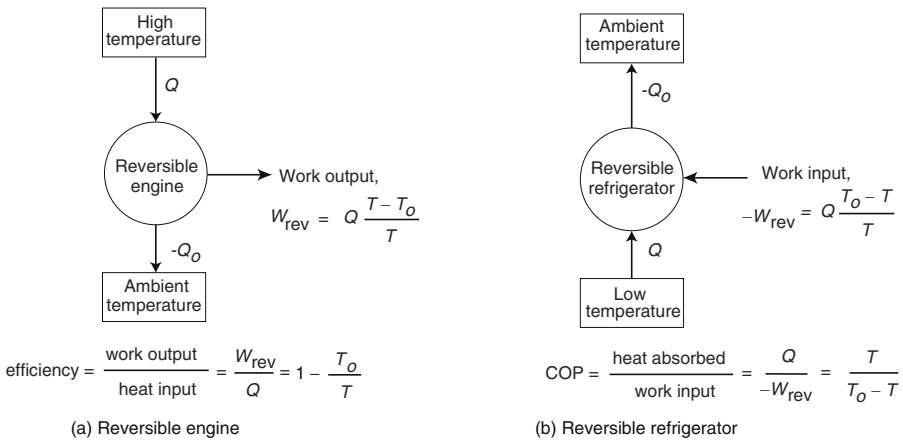


Fig. 1.8. Relationship between (a) work obtained from a reversible engine and (b) work supplied to a reversible refrigerator.
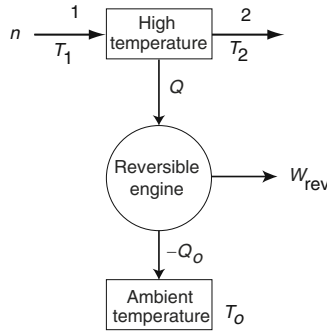
**Fig. 1.9.** Heat engine receiving heat from a fluid stream.

The above expression gives the relationship between the reversible work that can be extracted from a fluid between state points 1 and 2, the ambient temperature, and the thermodynamic properties of the fluid at the two states. The maximum work is obtained from the fluid stream when it is cooled from state 1 to the ambient temperature and pressure (state 0). The specific exergy of a fluid stream can be defined as the maximum work that can be obtained from the fluid when it follows reversible processes to reach equilibrium with the surroundings and can be expressed as follows:

$$\text{ex} = \frac{W_{\text{rev}}}{n} = (h - h_o) - T_o(s - s_o), \tag{1.16}$$

where ex refers to the specific exergy of the fluid stream at an enthalpy $h$ and entropy $s$. $h_o$ and $s_o$ are the enthalpy and entropy of the stream at ambient temperature and pressure, respectively.

## 1.5 Exergy loss and exergy efficiency

Consider the system shown in Fig. 1.10. The first law of thermodynamics (energy balance) can be written as follows:

$$\dot{n}_1 \, h_1 - \dot{n}_2 \, h_2 + \dot{Q}_1 + \dot{Q}_2 - \dot{W}_1 - \dot{W}_2 = 0. \tag{1.17}$$

The second law of thermodynamics (Clausius inequality) can be written as follows:

$$\dot{n}_1 \, s_1 - \dot{n}_2 \, s_2 + \frac{\dot{Q}_1}{T_1} + \frac{\dot{Q}_2}{T_2} \leq 0. \tag{1.18}$$

Equations (1.17) and (1.18) can be combined after multiplying Eq. (1.18) with the surroundings (ambient) temperature $T_o$ as follows:

$$\dot{n}_1 \{(h_1 - T_o \, s_1)\} - \dot{n}_2 \{(h_2 - T_o \, s_2)\} + \dot{Q}_1 \left(1 - \frac{T_o}{T_1}\right) + \dot{Q}_2 \left(1 - \frac{T_o}{T_2}\right) - \dot{W}_1 - \dot{W}_2 \geq 0. \tag{1.19}$$
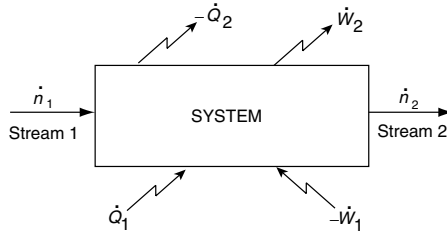
**Fig. 1.10.** General thermal system.

The above expression can also be expressed in terms of the exergy of the streams as follows:

$$\dot{n}_1 \, ex_1 - \dot{n}_2 \, ex_2 + \dot{Q}_1 \left( 1 - \frac{T_o}{T_1} \right) + \dot{Q}_2 \left( 1 - \frac{T_o}{T_2} \right) - \dot{W}_1 - \dot{W}_2 \geq 0, \quad (1.20)$$

which can be generalized as follows:

$$\sum \dot{n}_{in} \, ex_{in} - \sum \dot{n}_{out} \, ex_{out} + \sum_i \dot{Q}_i \left( 1 - \frac{T_o}{T_i} \right) + \sum_j -\dot{W}_j \geq 0, \quad (1.21)$$

where first two terms represent the exergy of the streams entering and leaving the system, respectively. The third term in the above equation is the net power that can be obtained from the heat transfer rate to the system ($\dot{Q}_i$) using a reversible heat engine (see Fig. 1.8). The fourth term is the net power supplied to the system.[3] Equation (1.21) can be considered as the exergy balance equation for any system.
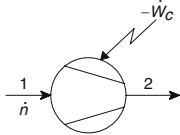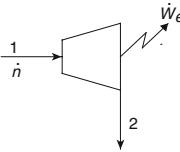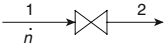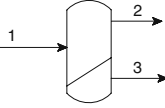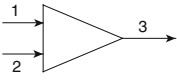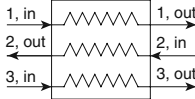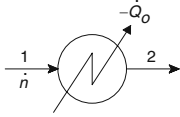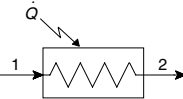
The left-hand side of Eq. (1.21) represents the difference between the input and output exergy, which is known as exergy loss, and can also be expressed as

$$\sum \text{exergy loss in each component} \geq 0. \quad (1.22)$$

The sum of all exergy losses is zero if the system operates on reversible thermodynamic processes and is greater than zero if the system operates on irreversible thermodynamic processes. The exergy loss in different components of a cryogenic refrigeration or liquefaction system has been summarized in Table 1.1.

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[3] $-\dot{W} > 0.$

**Table 1.1.** Exergy loss in different components

| Equipment | Symbol | Exergy loss (kW) |
|---|---|---|
| Compressor | | $\Delta\mathrm{ex}_{\mathrm{loss}} = \dot{n}(\mathrm{ex}_1 - \mathrm{ex}_2) - \dot{W}_c$ |
| Expander | | $\Delta\mathrm{ex}_{\mathrm{loss}} = \dot{n}(\mathrm{ex}_1 - \mathrm{ex}_2) - \dot{W}_e$ |
| Throttle valve | | $\Delta\mathrm{ex}_{\mathrm{loss}} = \dot{n}(\mathrm{ex}_1 - \mathrm{ex}_2)$ |
| Phase separator or stream splitter | | $\Delta\mathrm{ex}_{\mathrm{loss}} = \dot{n}_1\mathrm{ex}_1 - \dot{n}_2\mathrm{ex}_2 - \dot{n}_3\mathrm{ex}_3$ |
| Stream mixer | | $\Delta\mathrm{ex}_{\mathrm{loss}} = \dot{n}_1\mathrm{ex}_1 + \dot{n}_2\mathrm{ex}_2 - \dot{n}_3\mathrm{ex}_3$ |
| Heat exchanger | | $\Delta\mathrm{ex}_{\mathrm{loss}} = \sum_{i=1}^{n} \dot{n}_i (\mathrm{ex}_{i,\,\mathrm{in}} - \mathrm{ex}_{i,\,\mathrm{out}})$ |
| Condenser or aftercooler exchanging heat with ambient | | $\Delta\mathrm{ex}_{\mathrm{loss}} = \dot{n}(\mathrm{ex}_1 - \mathrm{ex}_2)$ |
| Evaporator operating at low temperature | | $\Delta\mathrm{ex}_{\mathrm{loss}} = \dot{n}(\mathrm{ex}_1 - \mathrm{ex}_2) + \dot{Q}(1 - T_o/T)$ |

$\dot{W}_c < 0, \dot{W}_e > 0, \dot{Q} > 0, \dot{Q}_o < 0.$

The exergy efficiency of any refrigeration or liquefaction system is defined as follows:

$$\eta_{\text{ex}} = \frac{\text{minimum power required by a reversible system}}{\text{actual power supplied}}. \qquad (1.23)$$

or
$$\eta_{\text{ex}} = 1 - \frac{\sum \text{exergy loss in each component}}{\text{actual power supplied}}. \qquad (1.24)$$

The concept of exergy efficiency can also be used in processes where there is no work transfer, for example, an open-cycle Linde–Hampson refrigerator. Similarly, the exergy efficiency can also be determined for part of a process (control volume). In all such cases, the actual power supplied is replaced by exergy expenditure as follows:

$$\eta_{\text{ex}} = 1 - \frac{\sum \text{exergy loss in each component}}{\text{exergy expenditure}}, \qquad (1.25)$$

or
$$\eta_{ex} = 1 - \frac{\sum \dot{n}_{\text{in}}\, \text{ex}_{\text{in}} - \sum \dot{n}_{\text{out}}\, \text{ex}_{\text{out}} + \sum_i \dot{Q}_i \left(1 - \frac{T_o}{T_i}\right) + \sum_j -\dot{W}_j}{\text{exergy expenditure}}. \qquad (1.26)$$

The exergy expenditure depends on the type of system. When a system receives heat and produces work as in a heat engine, the exergy expenditure of the system is $\dot{Q}(1 - T_o/T)$. On the other hand, when a system receives work and absorbs heat as in a refrigerator, the exergy expenditure of the system is $(-\dot{W})$. The expressions for input exergy, exergy loss, and exergy efficiency of different commonly used systems (Fig. 1.11) are summarized in Table 1.2.

**Table 1.2.** Expressions for input exergy, exergy loss, and exergy efficiency of some commonly used cryogenic process equipment [see Eq. (1.26)]

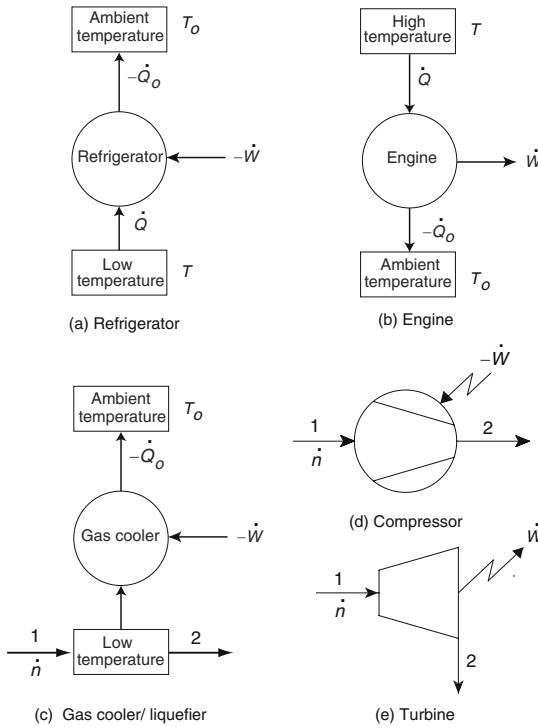| System | Figure | Input exergy (W) | Exergy loss (W) | Exergy efficiency |
|---|---|---|---|---|
| Refrigerator | Fig. 1.11(a) | $-\dot{W}$ | $\dot{Q}(1 - T_o/T) - \dot{W}$ | $\frac{\dot{Q}(T_o/T - 1)}{-\dot{W}}$ |
| Heat engine | Fig. 1.11(b) | $\dot{Q}(1 - T_o/T)$ | $\dot{Q}(1 - T_o/T) - \dot{W}$ | $\frac{\dot{W}}{\dot{Q}(1 - T_o/T)}$ |
| Gas cooler/ liquefier | Fig. 1.11(c) | $-\dot{W}$ | $\dot{n}(\text{ex}_1 - \text{ex}_2) - \dot{W}$ | $\frac{\dot{n}(\text{ex}_2 - \text{ex}_1)}{-\dot{W}}$ |
| Compressor | Fig. 1.11(d) | $-\dot{W}$ | $\dot{n}(\text{ex}_1 - \text{ex}_2) - \dot{W}$ | $\frac{\dot{n}(\text{ex}_2 - \text{ex}_1)}{-\dot{W}}$ |
| Turbine | Fig. 1.11(e) | $\dot{n}(\text{ex}_2 - \text{ex}_1)$ | $\dot{n}(\text{ex}_1 - \text{ex}_2) - \dot{W}$ | $\frac{\dot{W}}{\dot{n}(\text{ex}_1 - \text{ex}_2)}$ |

**Fig. 1.11.** Some commonly used systems.

## 1.6 Exergy efficiency of processes without any work interaction

The exergy efficiency was defined in the previous section with reference to the work interaction between a system and the surroundings when operating on irreversible and reversible processes.

Consider an open-cycle Linde–Hampson liquefier used in the cooling of infrared detectors on missiles (Fig. 1.12). High-pressure nitrogen is supplied from a gas bottle to the system (stream 1). There is no compressor or turbine in the process. The mole flow rate of the refrigerant through the system is $\dot{n}$.
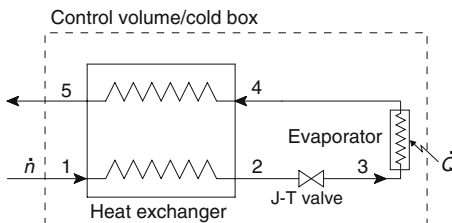


**Fig. 1.12.** open-cycle Linde–Hampson liquefier.

The work necessary for providing the required refrigeration is provided by the refrigerant stream. Therefore, the expenditure in this system is the difference between the exergy of the refrigerant entering and leaving the system $\dot{n}(\text{ex}_1 - \text{ex}_5)$. The exergy efficiency of the open-cycle Linde–Hampson liquefier can be obtained from Eq. (1.26) and Table 1.2 as follows:

$$\eta_{\text{ex}} = 1 - \frac{\sum \text{exergy loss}}{\text{exergy expenditure}} = 1 - \frac{\dot{n}\,\text{ex}_1 - \dot{n}\,\text{ex}_5 + \dot{Q}\left(1 - \frac{T_o}{T}\right)}{\dot{n}\,\text{ex}_1 - \dot{n}\,\text{ex}_5} \qquad (1.27)$$

or
$$\eta_{\text{ex}} = \frac{\dot{Q}\left(\frac{T_o}{T} - 1\right)}{\dot{n}\,(\text{ex}_1 - \text{ex}_5)}. \qquad (1.28)$$

Consider the Linde gas-cooling process shown in Fig. 1.13 for cooling or liquefying a gas. The compressor power input $(-\dot{W}_c)$ is the exergy expenditure when the entire process is considered. If only the cold box is considered, the exergy expenditure is the difference between the exergy of the refrigerant entering and leaving the cold box.

The overall exergy efficiency of the entire process can be expressed using Eq. (1.26) and Table 1.2 as follows:

$$\eta_{\text{ex, o}} = 1 - \frac{\sum \text{exergy loss}}{\text{exergy expenditure}} = 1 - \frac{\dot{n}_7\,\text{ex}_7 - \dot{n}_8\,\text{ex}_8 - \dot{W}_c}{-\dot{W}_c} \qquad (1.29)$$

or
$$\eta_{\text{ex, o}} = \frac{\dot{n}_7(\text{ex}_8 - \text{ex}_7)}{-\dot{W}_c}. \qquad (1.30)$$

Similarly, the exergy efficiency of the cold box of the process can be expressed using Eq. (1.26) and Table 1.2 as follows:

$$\eta_{\text{ex, cb}} = 1 - \frac{\dot{n}_7\,\text{ex}_7 - \dot{n}_8\,\text{ex}_8 + \dot{n}_3\,\text{ex}_3 - \dot{n}_6\,\text{ex}_6}{\dot{n}_3\,\text{ex}_3 - \dot{n}_6\,\text{ex}_6} \qquad (1.31)$$

or
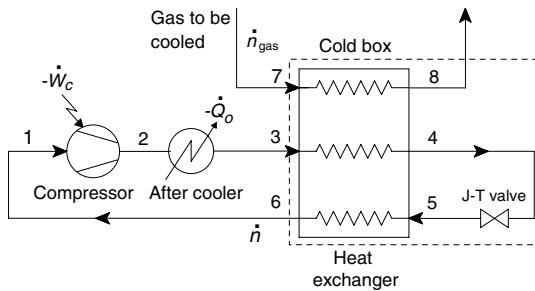$$\eta_{\text{ex, cb}} = \frac{\dot{n}_7(\text{ex}_8 - \text{ex}_7)}{\dot{n}_3(\text{ex}_3 - \text{ex}_6)}. \qquad (1.32)$$



**Fig. 1.13.** Linde gas-cooling process.