superconductor-derived magnetic fields to create a fast, high-intensity *electromagnetic pulse* (EMP) to disable an enemy's electronic equipment.

1.4.2 Emerging Superconductive Devices

Among emerging technologies is a stabilising momentum wheel (gyroscope) for earth-orbiting satellites that employs the *flux-pinning* properties of imperfect superconductors to reduce friction to near zero. Superconducting X-ray detectors and ultra-fast superconducting light detectors are being developed due to their inherent ability to detect extremely weak amounts of energy. Superconductors may even play a role in the Internet communications. Since the Internet traffic is increasing exponentially, superconductor technology is being called upon to meet this super speed.

Another impetus to the wider use of superconductors is political in nature. The reduction of emissions of green house gases (GHG) has become a dominant issue due to the Kyoto Protocol, which requires the European Union (EU) to reduce its emissions by 8% from 1990 levels by 2012. Physicists in Finland have calculated that the EU could reduce carbon dioxide emissions by up to 53 million tonnes if superconductors were used in power plants.

The future of superconductors primarily depends on the advancements in the field of cryo-cooling and materials. The advent of the high-efficiency compounds such as gadolinium-silicon-germanium would result in compact refrigeration units to facilitate additional HTS applications.

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2

Thermodynamic Analysis of Low Temperature Processes

2.0 INTRODUCTION

The design of any cooling process below the ambient temperature requires thermodynamic analysis of the minimum work needed for the desired cooling duty. The actual work requirement will be much higher than this minimum work due to process constraints, irreversibilities and mechanical inefficiencies encountered in real processes. However, the process and the process conditions for the specific requirement of production of low temperatures are selected based on the highest achievable thermodynamic efficiency as well as on the optimum process performance in terms of ease of operation, reliability, safety and costs. The present chapter discusses the salient points for minimization of energy requirements and describes the different processes and refrigeration systems available for the production of low temperatures from ambient to near absolute zero.

2.1 REFRIGERATION

Refrigeration is a process of extracting heat from a system or a substance to achieve cooling or condensation at a temperature level lower than the ambient temperature. The extracted heat is absorbed by a heat exchanger, for evaporation of the refrigerant undergoing the refrigeration cycle. William Cullen at the University of Glasgow demonstrated the first refrigeration cycle in 1748. Jacob Perkins built the first practical refrigerating machine in 1834. German engineer Carl von Linde, patented not only a refrigerator but also the process of liquefying a gas, as a part of the basic refrigeration technology as early as in 1876.

In addition to cooling, refrigeration is widely used for air conditioning. Air conditioning is a process by which air is cooled and dehumidified. An air conditioner essentially operates on

refrigeration at near ambient temperatures. There are many physical principles that relate to air conditioning. Basically, most air conditioning systems operate on the principle of evaporation and condensation of a refrigerant. In the past, a chloro-fluorocarbon (CFC), R-12, used to be employed as a refrigerant for air conditioning in cars. As CFC is detrimental to the earth's ozone layer, a more environmental-friendly refrigerant, R-134A, has been mostly in use since 1996.

The most commonly used refrigeration cycle is based on the principle of vapour compression, as schematically described in Figure 2.1 along with the corresponding T–s diagram of the refrigerant. The cycle comprises four process steps, namely:
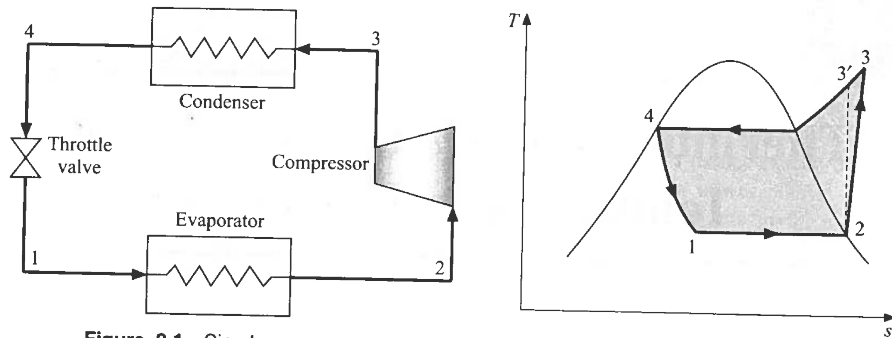

Figure 2.1 Simple vapour compression refrigeration cycle with T–s diagram.

(i) 1–2: the partially vaporized refrigerant liquid is rapidly vaporized by absorbing heat from the system to be cooled.

(ii) 2–3: the refrigerant vapour is compressed.

(iii) 3–4: the vapour gets cooled by losing energy to the surroundings and becomes liquid.

(iv) 4–1: the liquid refrigerant is throttled. The quickly expanding vapour requires kinetic energy and draws the energy needed from the immediate area, which loses energy or becomes cooler and partially condensed.

The cooling duty, Q_2 is represented by the step (1–2) and the rate of refrigerant circulation is obtained by the ratio of the cooling duty to the enthalpy difference $(h_2 - h_1)$ after and before evaporation. The power consumption or the rate of work done for compression $(-\dot{W}_c)$ is calculated from the enthalpy difference $(h_3 - h_2)$ across the compressor multiplied by the refrigerant circulation rate. The pressure in the condenser is selected such that the refrigerant has the dew point temperature more than the ambient temperature to facilitate transfer of heat of condensation of the refrigerant vapour to the sink at the ambient temperature.

The vapour compression refrigeration cycle can be operated with a single refrigerant on a *single cycle mode* as shown in Figure 2.1 or with multiple refrigerants on a *cascade mode* as shown in Figure 2.2. In the cascade mode the heat required for evaporation of one refrigerant is obtained from the heat to be removed from the condenser of another refrigerant. This is known as *condenser–evaporator* system and by proper selection of the refrigerants and pressure conditions it is possible to provide cooling at low to very low temperatures.
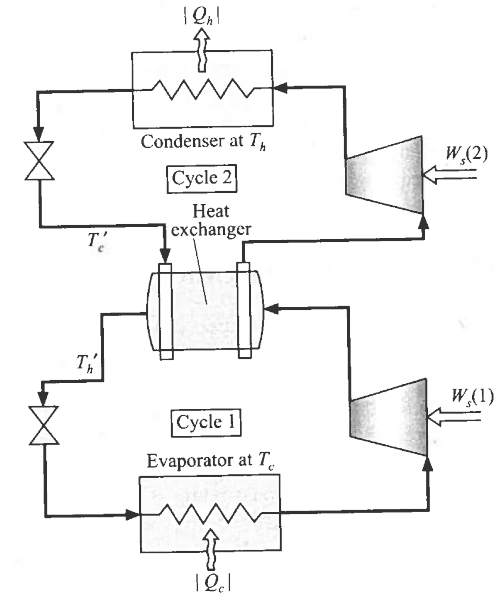

Figure 2.2 Vapour compression refrigeration cycle in cascade mode.

The refrigeration may also be operated on the vapour–absorption cycle as shown in Figure 2.3. The only difference in this cycle from that in the vapour compression cycle is that
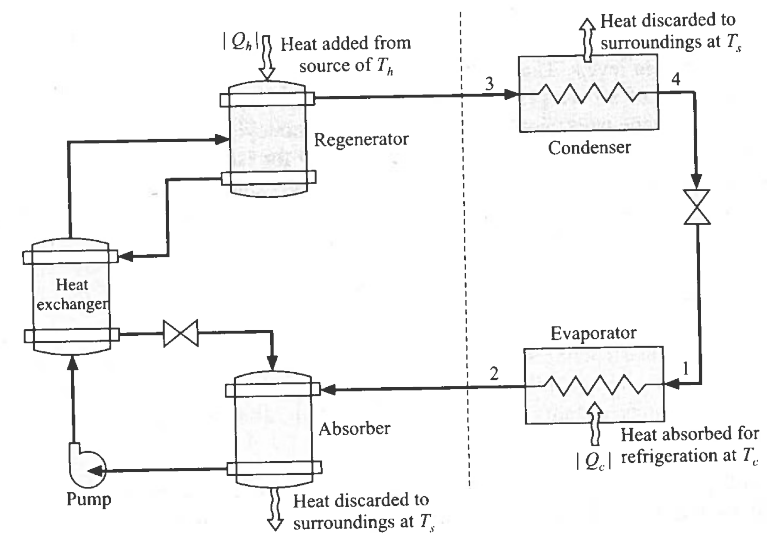

Figure 2.3 Absorption refrigeration cycle.

the saturated vapour from the evaporator is absorbed in a solvent, say water, and subsequently the solution is pumped to a higher pressure. This reduces the energy requirement for raising the pressure by a compressor, as the work requirement for a pump is much lower than that for the compressor. Consequently, this system also has a lower capital cost. The vapour-absorption refrigeration cycle is applicable for a refrigerant like NH_3, which has high solubility at low temperature and low solubility at ambient temperature in a solvent, e.g. water. However, some amount of heat is needed for stripping the refrigerant NH_3 from the (NH_3–water) solution at the higher pressure for its regeneration as NH_3 vapour, prior to its condensation.

2.2 THERMODYNAMIC MINIMUM WORK

Thermodynamically, any heat absorbed from a source can be converted to useful work, with a part of it being rejected to a heat sink at the ambient temperature provided that the temperature level of heat absorption is higher than that of heat rejection. However, some work input is required if heat is to be absorbed from a source at a temperature level lower than the sink (or ambient) temperature for heat rejection. A refrigerator is such a device that provides cooling by absorption of heat from a system at a lower temperature level, while rejecting heat to the sink at a higher temperature level, whereas a heat pump is a device that provides heating by heat rejection to a system at a higher temperature level, while absorbing heat from a source at a lower temperature level. The two devices have one thing in common, that is, heat is absorbed from a source at a lower temperature level than that of the ambient and accordingly some work input is needed for running the device.

For absorption of heat from the low temperature source at T_2 and rejection of heat to the sink at the ambient temperature T_0 the extent of work required is governed by the Second Law of Thermodynamics. The thermodynamic minimum work is depicted by the work required for a Carnot cycle operated in a reversed manner, called a Carnot refrigerator, utilising the same amounts of heat to be absorbed and rejected respectively in a reversible manner between the same two temperature levels. The thermodynamic minimum work for isothermal cooling, that is, for condensation of a pure gas, at a temperature level lower than the sink temperature T_0, is thus equivalent to the work required by a reversed Carnot cycle operating between these two temperature levels. The thermodynamic minimum work for isobaric cooling, that is, for removal of sensible heat of a gas from T_1 to T_2 without any phase change, is calculated from the work required by a Carnot refrigerator, first for a differential change in temperature, and then integrating over the entire range of temperature of the cooling process.

2.2.1 Cooling Duty and Coefficient of Performance

The amount of latent heat or sensible heat required to be removed from a substance for cooling at steady state is called cooling duty. If the cooling duty is Q_2 and the heat rejected to sink is Q_0, then according to the First Law of Thermodynamics, the thermodynamic minimum work, $-W_{min}$ (a positive quantity) required by the system, is expressed as

$$-W_{min} = Q_0 - Q_2 \qquad (2.1)$$

The cooling duty at a constant temperature T_2 (e.g. for condensation of a pure substance) is depicted on the T–s diagram (Figure 2.4) for the reversed Carnot cycle. The area of the

rectangle between T_0 and T_2 represents the thermodynamic minimum work, $-W_{min}$, whereas the area of the rectangle between T_2 and absolute zero represents the cooling duty, Q_2. Therefore the work requirement is higher, if T_2 is lower and vice versa. The *coefficient of performance* (COP) of the refrigeration cycle, designated ω, is defined as the ratio of the cooling duty to the work required, namely, $Q_2/-W_{min}$, and is given by
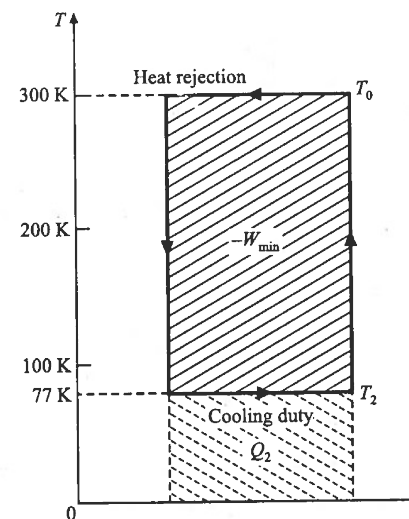
$$\omega = \frac{Q_2}{Q_0 - Q_2} \qquad (2.2)$$

Figure 2.4   Thermodynamic minimum work from reversed Carnot cycle for cooling at constant temperature.

The maximum value of COP, i.e. ω_{max} corresponds to the thermodynamic minimum work for a Carnot refrigerator and is expressed in terms of the temperatures of the isothermal operations of heat absorption at T_2 and heat rejection at T_o respectively as

$$\omega_{max} = \frac{T_2}{T_0 - T_2} \qquad (2.3)$$

Equation (2.3) clearly indicates that the cooling duty per unit of amount of work input required, decreases with the lowering of its temperature, T_2. For example, for liquefaction of nitrogen at atmospheric pressure, the reversible heat absorption from nitrogen gas takes place at 77 K and so the temperature of heat source, T_2 is 77 K (i.e. –196°C). If the reversible heat rejection to cooling water is at 300 K (i.e. 27°C), then T_0 is 300 K. The value of ω_{max} for an isothermal cooling duty at 77 K (i.e. to condense nitrogen gas at atmospheric pressure), is 77/(300 – 77) or 0.345. Similarly, the values of ω_{max} for liquefaction of different cryogens by using a Carnot refrigerator at atmospheric pressure with heat rejection at 300 K are given in

Table 2.1. From these values, it is apparent that the work requirement for liquefaction at atmospheric pressure increases as the normal boiling temperature of the cryogen decreases.

Table 2.1 Normal boiling points and maximum COP for liquefaction of different gases

Gas	Normal boiling point (K)	ω_{max} for liquefaction
Ethylene	169.0	1.290
Methane	112.0	0.597
Oxygen	90.4	0.431
Argon	83.1	0.383
Nitrogen	77.0	0.345
Hydrogen	20.4	0.073
Helium	4.2	0.014

Expressing quantitatively, one joule of cooling duty at the refrigeration temperature of 263 K (or −10°C), requires 0.14 joules of work, whereas the same cooling duty of one joule at the cryogenic temperature of 173 K (or −100°C), requires 0.73 joules of work, and at the extremely low cryogenic temperature of 4.2 K, requires 70.48 joules of work. Further, the actual process becomes increasingly more inefficient as the temperature level goes down or if the temperature gap between heat rejection and heat absorption widens. Accordingly, the ratio of the actual work to the thermodynamic minimum work steeply increases with lowering of the liquefaction temperature.

2.2.2 Minimum Work for Isobaric Cooling

If the cooling duty is intended for removal of sensible heat of a gas from T_1 to T_2 without any phase change, then the Carnot refrigerator or the reversed Carnot cycle is considered over a differential change in temperature during the cooling process. As shown on the T–s diagram in Figure 2.5, the cooling duty Q_2 or Δh is represented by the area under the isobaric cooling curve whereas the area between the line $T = T_0$ and the isobaric cooling curve depicts $-W_{min}$, as

$$Q_2 = \int_{T_1}^{T_2} T \, ds = \Delta h \tag{2.4}$$

$$W_{min} = \int_{T_1}^{T_2} (T_0 - T) \, ds = T_0 \, \Delta s - \Delta h \tag{2.5}$$

$$\omega_{max} = \frac{\Delta h}{T_0 \, \Delta s - \Delta h} \tag{2.6}$$

This analysis can be applied to any isobaric process irrespective of the nature of the working substance.
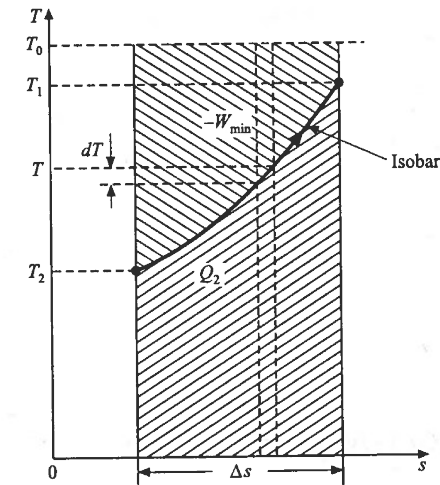
Figure 2.5 Thermodynamic minimum work from reversed Carnot cycle for cooling at constant pressure.

2.2.3 Minimum Work for Isobaric Liquefaction

For a gas, say nitrogen, initially at 293 K (or 20°C) and atmospheric pressure, and ambient temperature at 303 K (or 30°C), a simple liquefaction process would involve (i) isobaric cooling of the gas to its condensation temperature and (ii) isothermal condensation of the gas till it is completely liquefied. This cooling duty has two parts, namely sensible heat and latent heat. The thermodynamic minimum work of liquefaction for each part is given by the general expression

$$-W_{min} = \Delta h - T_0 \Delta s \tag{2.7}$$

The relative magnitudes of sensible heat and latent heat of the cooling duty from $T_1 = 293$ K (with $T_0 = 303$ K) and also the minimum work for liquefaction [1] of different cryogens at 1 atmospheric pressure, are compared in Table 2.2. However, this method of simple isobaric liquefaction in a single-step is not practical for a cryogen as it requires an external refrigerant as a coolant for removal of the heat of condensation from the gas undergoing liquefaction.

For heat absorption by the refrigerant at a lower temperature level and heat rejection at a higher temperature T_0, it cannot be assumed that there is no irreversibility due to the temperature difference between the condensing temperature of the gas and the evaporation temperature of the refrigerant. However, in order to simplify the concepts in the present thermodynamic analysis, it is assumed that the thermodynamic availability of the heat rejected by the liquefying gas is the same as that of the heat absorbed by the refrigerant. So the thermodynamic minimum work and the coefficient of performance for the liquefaction process, are given by the reversed Carnot cycle even though liquefaction is essentially an open-system process and not a cycle.

Table 2.2 Cooling duties and thermodynamic minimum work for liquefaction at 1 atm

Gas	Normal boiling point (K)	Δh (kJ/kg)		Min. work (kJ/kg)		
		Sensible heat	Latent heat	Sensible heat	Latent heat	Total
Ethylene	169.4	163	485	75	396	471
Methane	111.8	397	512	277	870	1147
Oxygen	90.2	197	213	133	498	631
Nitrogen	77.3	224	199	197	580	777
Neon	27.3	275	86	482	859	1341
Hydrogen	20.4	3413	434	6100	6090	12190
Helium	4.2	1509	21	6901	1488	8389

2.3 PRODUCTION OF LOW TEMPERATURES

There are essentially three methods of continuous production of cold or low temperatures, namely, (i) throttling process or *Joule–Thomson* (J–T) *expansion*, (ii) *adiabatic turbine expansion* and (iii) *isobaric cooling by an external refrigerant*. The first two methods are direct, as the substance to be cooled undergoes the process, whereas the third method is indirect, as the substance to be cooled, transfers heat to the refrigerant by means of a heat exchanger. The refrigerant, which undergoes the phase change, is cooled by the first method. The direct methods are undoubtedly more efficient than the indirect one while the indirect method is employed for cooling because of the ease of operation and/or for a part of the net cooling required. There are also other methods of producing extremely low temperatures by bringing about discontinuous changes in the thermo-physical properties of the working substance for providing specific cooling requirements.

2.3.1 Joule–Thomson Expansion

The *Joule–Thomson* (J–T) expansion is the name given to the *throttling* process after the scientists who originally developed the use of this process. The flow of fluids through a restriction, such as an orifice or a partly closed valve or a porous plug, is called the throttling process. The throttling device is used to lower the pressure of a flowing fluid without significantly accelerating it and without producing any shaft work. If the line is insulated making the process adiabatic, and the potential and kinetic energy changes are negligible, then the process becomes isenthalpic, as no shaft work is achievable. Since for an ideal gas, enthalpy is simply dependent on temperature, an isenthalpic expansion of an ideal gas results in no temperature change or cooling. It is due to the non-ideality of a substance that makes its temperature change because of isenthalpic expansion. The throttling process does not produce any useful work and is inherently irreversible. As a result, the net entropy increases during the expansion process.

For most real gases the J–T expansion results in a decrease in temperature only within a certain domain of pressure and temperature, even if it is non-condensable. If a saturated liquid is throttled to a lower pressure, a flash evaporation takes place producing a partly vaporised mixture at the lowered saturation temperature, corresponding to the lower pressure.

The throttling process does not necessarily entail cooling or phase change. It depends on the initial condition and whether its enthalpy is in a certain thermodynamic domain. Beyond this domain, the process may even result in a rise in temperature. The higher the pressure and/or lower the temperature, the higher the non-ideality to produce sufficient cooling by the process. The throttling process is characterised by a parameter called the J–T coefficient μ_{JT}, defined as

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h \tag{2.8}$$

When μ_{JT} is positive, a decrease in temperature occurs by throttling, and when it is negative, throttling increases the temperature. The temperature at which μ_{JT} is zero, is called *inversion temperature* and the locus of all pressure–temperature combinations at which μ_{JT} is zero is called *inversion curve* as shown in Figure 2.6.
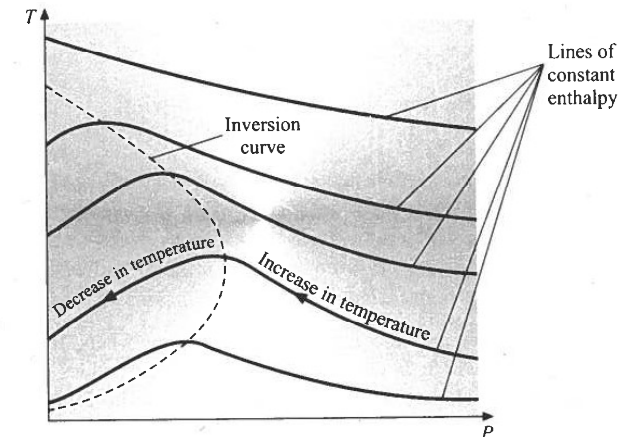

Figure 2.6 *P-T* behaviour of isenthalps and inversion curve for real gases.

The J-T coefficient, μ_{JT} can be estimated from the *P–V–T* properties or an equation of state (EOS), such as the Virial EOS. Since $h = f(T, P)$,

$$dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP \tag{2.9}$$

Also,

$$dh = T\,ds + V\,dP \tag{2.10}$$

So

$$dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \left[T\left(\frac{\partial s}{\partial P}\right)_T + V\right]dP \tag{2.11}$$

Using the Maxwell's relation, $\left(\dfrac{\partial s}{\partial P}\right)_T = -\left(\dfrac{\partial V}{\partial T}\right)_P$ $\qquad$ (2.12)

the J–T coefficient μ_{JT} can be obtained as

$$\mu_{JT} = \frac{T\left(\dfrac{\partial V}{\partial T}\right)_P - V}{C_p} \qquad (2.13)$$

From Equation (2.13), it is apparent that for an ideal gas (i.e. $PV = RT$), $\mu_{JT} = 0$ and μ_{JT} can be positive or negative depending on the magnitude of the term, $T\left(\dfrac{\partial V}{\partial T}\right)_P$, i.e. whether it is greater or less than V, where V is the molar volume of the gas. In terms of the compressibility factor Z, where

$$Z = \left(\frac{PV}{RT}\right) \qquad (2.14)$$

$$\mu_{JT} = \frac{RT^2}{C_p P}\left(\frac{\partial Z}{\partial T}\right)_P \qquad (2.15)$$

Using the virial equation of state (truncated after the second term)

$$V = \frac{RT}{P} + B(T) \qquad (2.16)$$

where B, the second virial coefficient may be obtained from the van der Waal's constants, a and b as

$$B = b - \frac{a}{RT} \qquad (2.17)$$

It can be seen that the low-pressure inversion temperature, where μ_{JT} changes sign, is twice the Boyle temperature where B changes its sign [2]. The values of van der Waal's constants and inversion temperatures of different gases are listed in Table 2.3.

The temperature drop in a throttling process without undergoing a phase change may be calculated using an iterative process by a simple Equation (2.18) given as:

$$\Delta T = \int_{T_1}^{T_2} \left(\frac{\partial T}{\partial P}\right)_h dP \qquad (2.18)$$

where, the right-hand side (RHS) term is also dependent on temperature.

Alternatively, considering enthalpy as a point function (meaning the change in the value of the parameter depends on the initial and the final conditions, and not on the path followed), the enthalpy change in the throttling process may be simplified as a sum of two terms. The first term is for an isothermal expansion from the initial pressure to the final pressure and then the second term is for isobaric cooling/heating from the initial temperature to the final temperature,

Table 2.3 van der Waals constants* and inversion temperatures of cryogens

Gas	T_c (K)	P_c (atm)	a (atm-m^6/mol^2 $\times 10^6$)	b (m^3/mol $\times 10^6$)	Maximum inversion temperaure (K)
Carbon Dioxide	304.1	72.8	3.6085	42.86	1500
Methane	190.7	45.8	2.2556	42.70	939
Oxygen	154.8	50.1	1.3587	31.68	761
Argon	150.7	48.0	1.3440	32.20	794
Carbon Monoxide	132.9	34.5	1.4543	39.51	652
Air	133.0	39.0	1.2884	34.97	603
Nitrogen	126.3	33.5	1.3526	38.67	621
Neon	44.4	26.2	0.2137	17.39	250
Hydrogen	33.2	12.8	0.2446	26.60	205
Helium 4	5.2	2.26	0.0340	23.60	45

*$a = (27\ R^2 T_c^2)/(64 P_c)$; $b = RT_c/(8P_c)$; $R = 8.20575 \times 10^{-5}$ atm-m^3/mol-K.

such that the net change in the enthalpy is nil. From Equations (2.9) and (2.11), we can get the final temperature T_2 by solving Equation (2.19) given as:

$$\int_{T_1}^{T_2} [C_p\, dT]_{P_2} = \int_{P_1}^{P_2} \left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]_{T_1} dP \qquad (2.19)$$

The RHS of Equation (2.19) can be calculated from an EOS and C_p values are easily available at low pressure, as a function of temperature.

If there is a two-phase region after the throttling process, then the final temperature corresponds to the boiling point at the final pressure, which is the saturated vapour pressure of the substance. In that case, the fraction of condensation can be obtained by equating the initial and final enthalpies. It will be seen later that the higher the non-ideality (i.e. the higher the pressure or the lower the temperature), the larger is the fraction of liquefaction. The throttling constitutes the final step in most continuous large-scale liquefaction processes.

Sample Problem 2.1: Find the maximum inversion temperatures for helium, hydrogen, nitrogen, argon and methane.

Solution: The inversion temperature is defined as the temperature at which the J-T coefficient, μ_{JT} is zero. It is known that

$$\mu_{JT} = \frac{T\left(\dfrac{\partial V}{\partial T}\right)_P - V}{C_p}$$

For $\mu_{JT} = 0$, we get

$$T\left(\frac{\partial V}{\partial T}\right)_P = V \qquad \text{(i)}$$

6. An ideal Phillips cryo-refrigerator using helium operates between 1 atm and 7 atm to provide refrigeration at 110 K operating from an ambient temperature of 300 K. Find the cooling duty and COP, assuming that all the steps are ideal and helium is a perfect gas. Repeat the calculations for 95% effectiveness of the regenerator.

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3

Cryogenic Liquefaction Processes

3.0 INTRODUCTION

Liquefaction of cryogenic gases is accomplished by cooling and condensation with proper energy integration between the streams at different conditions of the process without and with an external refrigerant. The present chapter describes chronological development of various processes for liquefaction of cryogens along with their relevant thermodynamic analysis and process design considerations. Each of these processes has been studied in terms of the energy requirement and performance efficiency with respect to the ideal liquefaction process. These processes have been evaluated to illustrate how a few critical process parameters can improve the process performance so that the most appropriate process and its conditions can be selected for liquefaction of a specific cryogen. Illustrations for the liquefaction processes covered are for production of liquid nitrogen, liquefied natural gas, liquid hydrogen, and liquid helium.

3.1 THERMODYNAMICALLY IDEAL SYSTEM FOR LIQUEFACTION

Liquefaction is best described by a sequence of a few continuous processes in an open system rather than by a cycle in a closed system. A thermodynamically ideal system for direct liquefaction, considers only the first two processes of the Carnot cycle, namely, a reversible isothermal compression followed by a reversible isentropic expansion. According to this thermodynamically ideal process, the feed gas would be isothermally and reversibly compressed to a supercritical pressure to attain an entropy value that equals the entropy of the saturated liquid. Subsequently, the compressed fluid would be expanded adiabatically and reversibly through an ideal expander to attain the saturated liquid state. A schematic flow sheet and the T–s diagram of such an ideal hypothetical liquefaction process is shown in Figure 3.1. However, this ideal thermodynamic method of direct liquefaction is not practical as the pressure ratio required for an isothermal

compressor and an isentropic expander is too high. This ideal liquefaction process merely serves as the basis for improving the performance of an actual liquefaction process, as the actual work required is much higher than the ideal work due to the thermodynamic limitations and irreversibilities encountered in the continuous flow process, as will be seen later.
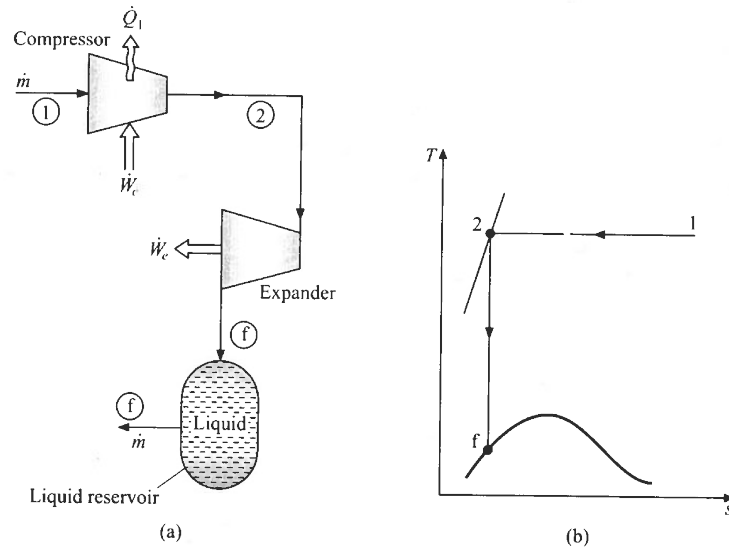

Figure 3.1   (a) Schematic flow sheet and (b) T–s diagram of an ideal liquefaction process.

3.1.1   Theoretical Minimum Work for Liquefaction

The thermodynamically ideal liquefaction system is analysed for 100% liquefaction of the incoming gas as described in Figure 3.1(a). From the T–s diagram it can be noted that the work requirement is much reduced for such an ideal process compared to the isobaric liquefaction process at ambient pressure discussed earlier (Table 2.2). The process of removal of latent heat and sensible heat, and the consequent requirement of an external refrigerant for the ambient pressure process are obviated in this high pressure process.

According to the schematics of the ideal liquefaction process as shown in Figure 3.1(b), the heat transfer process is reversible and isothermal, and the expansion process is isentropic, as in the Carnot cycle. The gas to be liquefied is initially at point 1. It is compressed reversibly and isothermally from point 1 to a high supercritical pressure (point 2) such that the gas has the same entropy as that of the saturated liquid at the initial pressure. Combining the First and the Second Laws of Thermodynamics for the open system for continuous steady flow of gas, neglecting kinetic and potential energy changes, we can write

$$\dot{Q} - \dot{W}_i = \sum \dot{m}_o h_o - \sum \dot{m}_i h_i \tag{3.1}$$

$$\dot{m} T_1(s_2 - s_1) - \dot{W}_i = \dot{m}(h_f - h_1) \tag{3.2}$$

or

$$-\frac{\dot{W}_i}{\dot{m}} = T_1(s_1 - s_f) - (h_1 - h_f) \tag{3.3}$$

since $s_2 = s_f$, where $\dot{Q}$ is the net rate of heat transfer to the system and $\dot{W}_i$ is the net rate of work done by the system, $\dot{m}_o$ is the outgoing mass flow rate and $\dot{m}_i$ is the incoming mass flow rate.

In the thermodynamically ideal liquefaction process, the gas compressed is completely liquefied, i.e. $\dot{m}_i = \dot{m}_f = \dot{m}$, so that the fraction of liquefaction, $y[=(\dot{m}_f/\dot{m})]$ is one. For a practical liquefier, y is always less than unity. For liquefaction, work is done on the system and so $(-\dot{W}/\dot{m})$ is positive. Any practical liquefier needs to be designed such that the net rate of work required for liquefaction, $-\dot{W}_l$ or $(-\dot{W}_i/\dot{m}_f)$ approaches this value. Here $-\dot{W}_l$ is the net rate of work required for a practical liquefier, $\dot{m}_f$ is the mass flow rate of liquid and is the mass flow rate of gas compressed in the isothermal compressor.

As an illustration, for the liquefaction of nitrogen initially at 1 atm and 300 K, computation of the thermodynamic ideal work requires the following thermodynamic properties of nitrogen the numerical values [1] of which are:

$$h_1 = 462 \text{ kJ/kg at 1 atm, 300 K}$$
$$h_f = 29 \text{ kJ/kg at 1 atm, saturated liquid}$$
$$s_1 = 4.42 \text{ kJ/kg-K at 1 atm and 300 K}$$
$$s_f = 0.42 \text{ kJ/kg-K at 1 atm and saturated liquid}$$

Using Equation (3.3),

$$-W_i = 300(4.42 - 0.42) - (462 - 29) = 767 \text{ kJ/kg}$$

Table 3.1 lists the data on ideal work of liquefaction required per unit mass of different cryogenic gases by the thermodynamically ideal liquefaction process.

Table 3.1   Thermodynamic ideal work for liquefaction of cryogens initially at 1 atm, 300 K

Cryogen	Normal boiling point (K)	Min. work required for kJ/kg of liquid
Helium-3	3.19	8178
Helium-4	4.21	6819
Hydrogen	20.27	12,019
Neon	27.09	1335
Nitrogen	77.36	767
Air	78.8	739
Argon	87.28	479
Oxygen	90.18	636
Methane	111.7	1091
Ethane	184.5	353

3.1.2   Figure of Merit for the Actual Liquefaction Process

The thermodynamic efficiency of the liquefaction process is compared with respect to the Carnot refrigeration cycle, whereas the figure of merit (FOM) characterises the performance of the liquefaction process with respect to the ideal liquefaction process. The figure of merit (FOM) for a liquefaction process is thus defined as the ratio of the ideal work, $-W_i$ for a thermodynamically ideal liquefaction process to the actual work $-W_l$ required for the actual liquefaction process. Thus,

$$FOM = \frac{-W_i}{-W_l} \tag{3.4}$$

If the initial temperature of the gas and the temperature of the sink are considered different, the ideal work required for complete liquefaction, W_i, is given as

$$-W_i = T_0(s_1 - s_f) - (h_1 - h_f) \tag{3.5}$$

where the subscripts 1 and f refer to the respective values at the initial and the final (saturated liquid) conditions respectively and T_0 is the sink (ambient) temperature.

3.2   LIQUEFACTION PROCESSES FOR NITROGEN, OXYGEN, AND ARGON

The common feature of most liquefaction processes is that the Joule–Thomson (J–T) expansion is utilised after attaining a certain level of nonideality in the cryogenic gas, by way of high pressure or low temperature or a combination of both. For starting the process of liquefaction, it is first necessary to lower the temperature of the high pressure feed gas by the counter-current heat exchange with the low-pressure return gas after the J–T expansion to the atmospheric pressure. Prior to attaining the steady state for continuous liquefaction, it is this low-pressure return gas which facilitates significant lowering of temperature, in order that the liquid–vapour phase separation occurs after the J–T expansion of the high-pressure feed gas. The liquefaction processes are classified according to the maximum inversion temperature of the gas to be liquefied, in order to facilitate lowering of temperature by the J–T expansion process for initiating the process. Cooling takes place on throttling, only if the maximum inversion temperature of the gas is higher than the ambient temperature. As can be seen from Table 2.3, all gases except neon, hydrogen and helium have maximum inversion temperature above the ambient temperature and the liquefaction processes of these gases, namely, nitrogen, oxygen, argon, methane and natural gas will be discussed in this section. In general, any fluid having a triple point temperature below that of the maximum inversion temperature of neon, hydrogen and helium can be used as a precoolant for lowering their temperature prior to their cooling by the J–T expansion. So the liquefaction of these gases, namely neon, hydrogen and helium are classified separately due to their requirement of precooling.

3.2.1   The Simple Linde–Hampson Process

Historically, the first cryogenic liquefaction was performed based on the cascade refrigeration cycles. However, due to the inherent irreversibilities and other limitations in this process, in

1895, Linde and Hampson independently developed the next continuously operating process for liquefaction of air, nitrogen, oxygen, argon, and methane. The Simple Linde–Hampson Process is solely based on the throttling expansion for lowering temperature, as shown schematically in Figure 3.2(a) and the corresponding T–s diagram in Figure 3.2(b). The high pressure of the
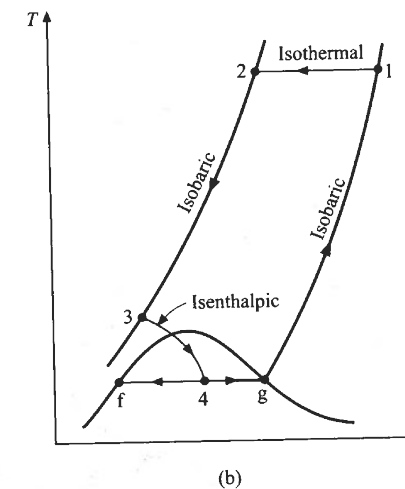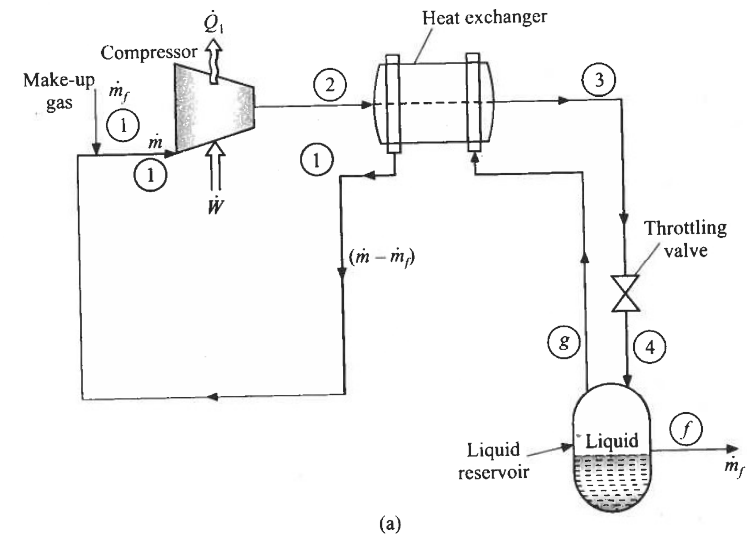

(a)

(b)

Figure 3.2   (a) Schematic representation of Simple Linde–Hampson Process and (b) the corresponding T–s diagram.

feed gas may be generated by isothermal or polytropic compression. In case of the polytropic compression, the gas is cooled to ambient temperature either in the same compressor or by inter-stage coolers and after-coolers. The compressed gas is then cooled in the main heat exchanger by the outgoing saturated vapour stream from the separator and then throttled to atmospheric pressure. A fraction of the gas is liquefied and the liquid is then separated from the saturated vapour in the separator. The return gas at atmospheric pressure and near-ambient temperature is recycled with the make-up gas. The fraction of liquefaction depends on the pressure and temperature prior to throttling. The heat integration by utilising the cold of its own return stream facilitates to bring down the temperature of the incoming gas from the ambient to the normal boiling point of the cryogen without having to use an external refrigerant. By compressing the gas to a supercritical pressure, the requirement of an external refrigerant as a coolant is avoided for removal of the latent heat. The steps of the Simple Linde–Hampson Liquefaction Process are as follows:

1–2:   Isothermal compression
2–3:   Precooling by outgoing stream
3–4:   Throttling expansion
4–5:   Separation of saturated vapour
4–f: Separation of saturated liquid
g–1:   Return of the saturated vapour for recycling at the ambient temperature

Applying the first law for steady state enthalpy exchange for feed mass flow rate of $\dot{m}$ and amount of liquid formed, $\dot{m}_f$, and assuming an ideal heat exchanger (100% effective), no temperature of approach at the warm end of the heat exchanger and no pressure drops, and no heat in-leaks, one can write

$$\dot{m}h_2 = (\dot{m} - \dot{m}_f)h_1 + \dot{m}_f h_f \tag{3.6}$$

The fraction of liquefaction, y, is defined as $(\dot{m}_f/\dot{m})$ and is given by

$$y = \frac{h_1 - h_2}{h_1 - h_f} \tag{3.7}$$

The fraction of the incoming gas liquefied (y) thus depends on the pressure and temperature of the gas at ambient condition (point 1), which fix the values of the enthalpies, pressure after isothermal compression. That is, 1 and f cannot be changed.

However, if the heat exchanger is considered to have a minimum temperature of approach at the warm end, then the return gas is at point 7, i.e. at slightly below point 1, then the enthalpy balance between the entry and exit of the heat exchanger gives

$$\dot{m}h_2 = (\dot{m} - \dot{m}_f)h_7 + \dot{m}_f h_f \tag{3.8}$$

and the fraction of liquefaction, y^+ is given as

$$y^+ = \frac{h_7 - h_2}{h_7 - h_f} \tag{3.9}$$

It may be noted that the enthalpy (h_7) at the exit of the heat exchanger has to be higher than that (h_2) at the entry of the heat exchanger for liquefaction to occur, which is opposite, with respect to temperature, i.e. the temperature at point 7 is lower than that at point 2. It is thus clear that the liquefaction is dictated by the nonideality of the gas attained before entering the heat exchanger (i.e. at point 2). So for a maximum fraction of liquefaction, the pressure of the feed gas has to be such that the enthalpy is minimum after isothermal compression at ambient temperature. For example, for nitrogen at the ambient temperature of 300 K, such a pressure required would be 350 atm [2] in order to give the maximum fraction of liquefaction. However, such a high compression ratio is not practical in a single compressor and so multi-stage compression would be required with inter-stage and after-cooling. Also the energy requirement for liquefaction per unit mass liquefied is also increased. For optimum power consumption for liquefaction, the pressure required is much lower—not more than 200 bar. The lower the feed gas temperature, the higher is the fraction liquefied. Considering compression to be reversible isothermal, the energy requirement is:

$$-\frac{\dot{W}}{\dot{m}} = T_1(s_1 - s_2) - (h_1 - h_2) \tag{3.10}$$

The energy per unit mass liquefied, W_l, is given as

$$-W_l = -\frac{\dot{W}}{\dot{m}_f} = -\frac{\dot{W}}{\dot{m}y} \tag{3.11}$$

The FOM is given by Equation (3.4). The performance of the Simple Linde–Hampson Process has been compared in Table 3.2 for different cryogenic fluids which involve isothermal compression from 1 atm to 200 atm at 300 K with 100% thermodynamic efficiency and the main heat exchanger with 100% effectiveness and negligible temperature of approach at the warm end [1].

Table 3.2   Work of liquefaction and FOM of the Simple Linde–Hampson Process*
for different cryogens

Cryogen	Normal boiling point (K)	% liquefied	Work of liquefaction, (kJ/kg)	FOM
N_2	77.4	7.08	6673	0.115
Air	78.8	8.08	5621	0.131
Ar	87.3	11.83	2750	0.174
O_2	90.2	10.65	3804	0.167
CH_4	111.7	19.77	3957	0.276
C_2H_6	184.5	52.57	611	0.588

*$P_1 = 1$ atm, $P_2 = 200$ atm, $T_1 = T_2 = 300$ K, 100% thermodynamic efficiency of isothermal compressor and 100% effectiveness of the main heat exchanger with no temperature difference between the incoming and outgoing streams at the inlet.

Sample Problem 3.2: In a reversible Linde–Hampson Liquefaction System for nitrogen, the gaseous nitrogen enters the isothermal compressor at 300 K and 1 atm and is compressed to a high pressure, passed through a heat exchanger, and finally expanded through an expansion valve to 1 atm. Determine the high pressure so that the system will have a liquid yield of 0.10 mass liquefied/mass compressed. Could the liquid yield be increased to 0.12? If the yield can be increased to this value, determine the high pressure required.

Solution: Consider the exit temperature of recycled gas from the heat exchanger 1 is 5 K less than the entrance temperature of compressed gas.

$h_7 = 102.86$ cal/g at 1 atm and 295 K

$h_f = 0$ cal/mole at 1 atm and saturated liquid

$h_2 = ?$ at 300 K and $P_2 = ?$

$y = 0.10$

Liquid yield, y, for Linde–Hampson Liquefaction System is given as

$$y = \frac{h_7 - h_2}{h_7 - h_f}$$

Therefore,
$$h_2 = (1 - y)h_7 \quad (\because h_f = 0)$$
$$= (1 - 0.1)102.86$$
$$= 92.574 \text{ cal/mole}$$

From the enthalpy–temperature diagram for nitrogen at temperature 300 K and enthalpy 92.57 cal/mole, pressure (P_2) is found to be 240 atm.

The liquid yield could not be increased to 0.12. Liquid yield, $y > 0.10$ gives the value of $h_2 < 92.57$ cal/mole. At temperature 300 K (or above) no pressure is there for which $h_2 < 92.57$ cal/mole. So, to get $y > 0.10$, the inlet temperature must be decreased.

3.2.2 The Precooled Linde–Hampson Process

As seen earlier, the fraction of liquefaction in the Simple Linde–Hampson process can be improved by lowering the enthalpy value of the high pressure gas at the warm-end of the heat exchanger, namely h_2 in Equation (3.9). This can be achieved either by increasing the pressure or by lowering the temperature. As the pressure cannot be economically increased to a very high value, it is the temperature which is lowered. As the temperature at the warm-end of the heat exchanger is very close to that of the ambient; it can be lowered by precooling it before the incoming high-pressure stream enters the main heat exchanger. In other words, an additional auxiliary heat exchanger is added prior to the main heat exchanger, as schematically shown in Figure 3.3(a) and the corresponding T–s diagram in Figure 3.3(b). The return gas at atmospheric pressure and near-ambient temperature is recycled with the make-up gas. The steps of the Precooled Linde–Hampson Liquefaction process are as follows:
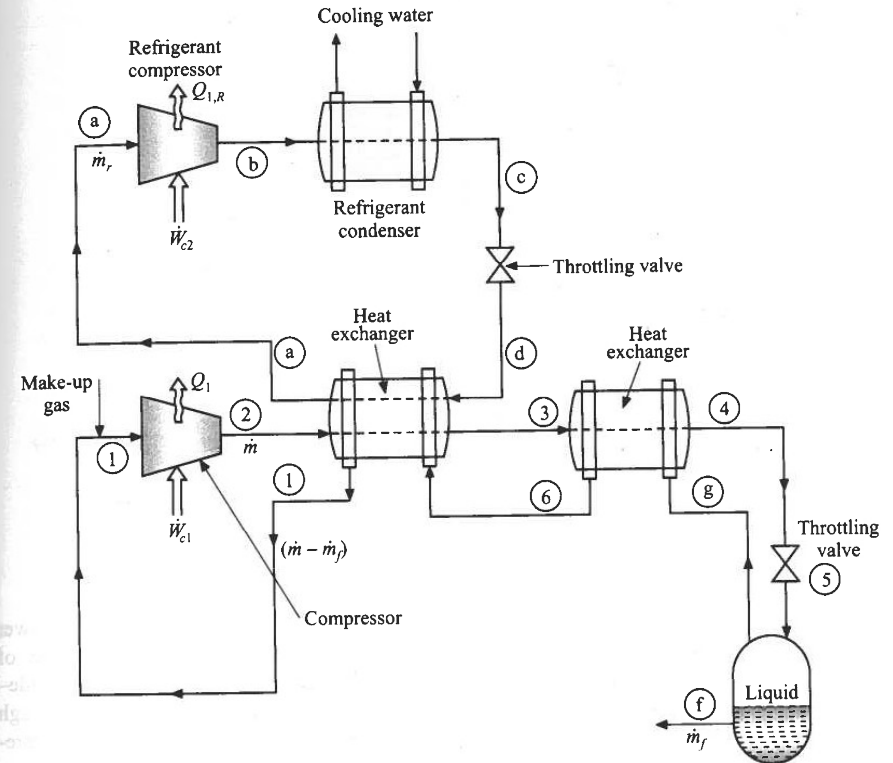
Figure 3.3(a) Schematic representation of Precooled Linde–Hampson Process.

1–2:　Isothermal compression

2–3:　Precooling by a refrigerant and outgoing stream

3–4:　Cooling by the outgoing saturated vapour stream

4–5:　Throttling expansion

5–g:　Separation of saturated vapour

5–f:　Separation of saturated liquid

g–6:　Return of the saturated vapour for providing cooling in 3–4

6–1:　Return of the outgoing stream for providing cooling in 2–3

d–a:　Evaporation of the refrigerant to provide precooling in 2–3

a–b:　Compression of saturated vapour of the refrigerant

b–c:　Cooling and condensation of high pressure refrigerant
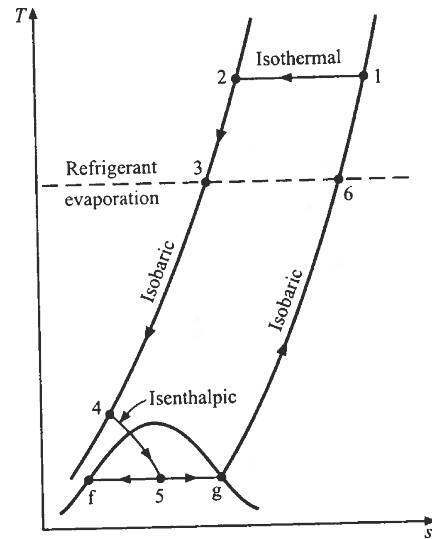
c–d:　J–T expansion of saturated liquid refrigerant

Figure 3.3(b) *T-s* diagram of Pre-cooled Linde–Hampson Process.

This precooling not only enhances the fraction of liquefaction, but also requires a lower pressure ratio of the compressor [1], as explained in Figure 3.4, depicting the fraction of liquefaction y vs. T_2 at various pressures, P_2. The performance of the Precooled Linde–Hampson Process is thus better than that of the Simple Linde–Hampson Process, though additional work is required for the additional compressor for the refrigeration cycle for pre-cooling. The work requirement of the two compressors is given as

$$\frac{\dot{W}}{\dot{m}} = T_1(s_1 - s_2) - (h_1 - h_2) + r(h_b - h_c) \tag{3.12}$$

and the fraction of liquefaction is obtained from Equation (3.13) as

$$y = \frac{h_1 - h_2}{h_1 - h_f} + \frac{r(h_a - h_a)}{h_1 - h_f} \tag{3.13}$$

where r is the refrigerant mass flow ratio defined by

$$r = \frac{\dot{m}_f}{\dot{m}} \tag{3.14}$$

The first term on the RHS of Equation (3.13) gives the same liquid fraction as in the Simple Linde–Hampson Process and the second term gives the improvement in the liquid fraction obtained due to precooling. The maximum fraction of liquid formed is given by
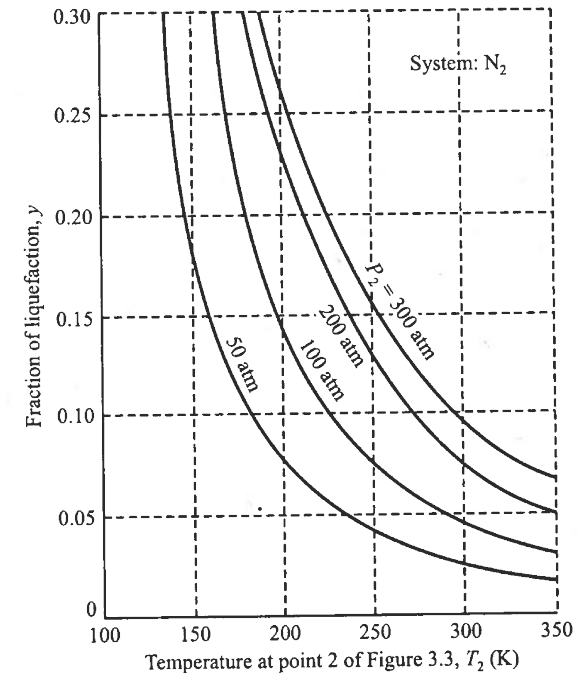
Figure 3.4 Effect of pressure and temperature on the fraction of liquefaction in the Pre-cooled Linde–Hampson Process.

$$y_{max} = \frac{h_6 - h_3}{h_6 - h_f} \tag{3.15}$$

where h_6 and h_3 represent the enthalpies of the outgoing low pressure stream and incoming high pressure stream respectively at the inlet of the main heat exchanger. These enthalpies are selected at the saturation temperature of the refrigerant at the lower pressure of the refrigeration cycle, assuming no temperature difference across the two streams exchanging heat. If the value of r is too high, the refrigerant liquid would not be completely vaporised in the auxilliary heat exchanger, and a liquid fraction of refrigerant would enter the refrigerant compressor, which is not desirable. Figure 3.5 compares the liquid fraction formed from the incoming high pressure nitrogen gas vs. refrigerant mass flow ratio at different upstream pressures P_2, to which the gas is compressed [1]. It is to be noted that the maximum liquid fraction y_{max}, increases with the increasing values of P_2, and with the increasing values of r, for freon 12 as the refrigerant (operating between 1 atm and 5.77 atm).
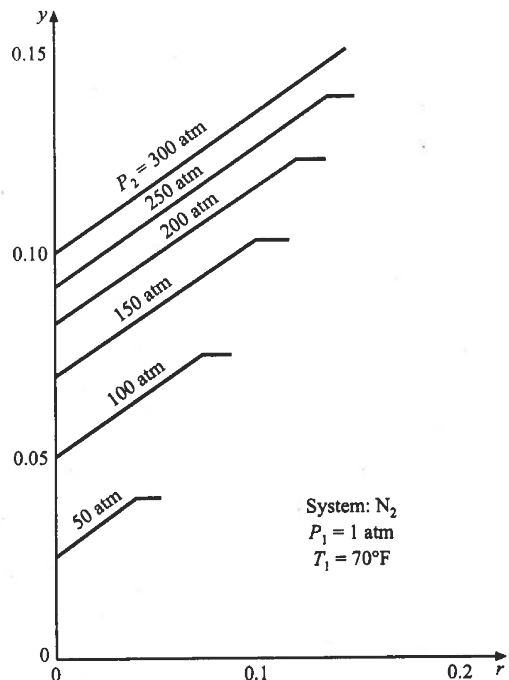
Figure 3.5   Effect of pre-coolant flow rate ratio on the fraction of liquefaction in the Pre-cooled Linde–Hampson Process.

Assuming that the compressor is reversible and isothermal, and the compressor for the refrigeration cycle is adiabatic and reversible, the work requirement per unit mass of gas compressed is given as

$$-\frac{\dot{W}}{\dot{m}} = T_1(s_1 - s_2) - (h_1 - h_2) + r(h_b - h_a) \tag{3.16}$$

So the work requirement in the Precooled Linde–Hampson process is higher than that without precooling, at least by 10%. However, the increase in the liquid fraction achieved more than compensates the additional work requirement compared to the Simple Linde-Hampson process [1] as shown in Figure 3.6. As an illustration for liquefaction without and with the addition of precooling to the Simple Linde–Hampson process, the following data are available for computing the liquid fraction:

(i)   Simple Linde–Hampson Process:

$h_1 = 462$ kJ/kg at 1 atm and 300 K

$h_2 = 432$ kJ/kg at 200 atm and 300 K

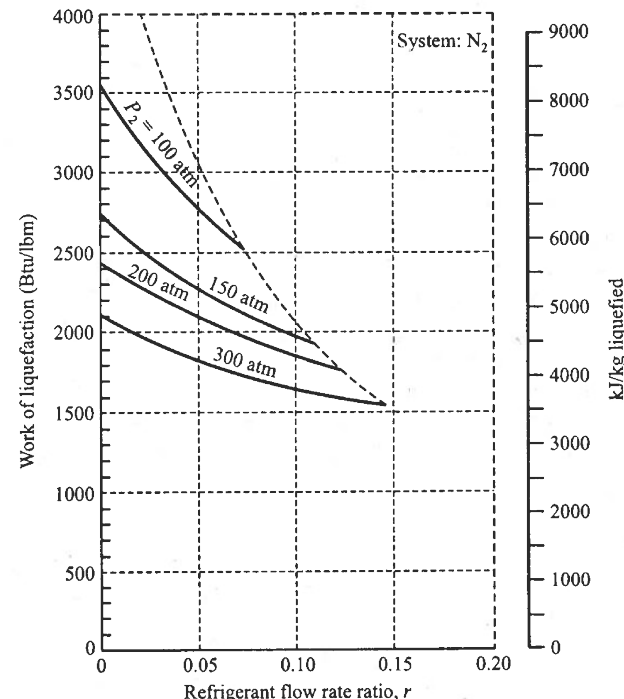$h_f = 29$ kJ/kg at 1 atm and saturated liquid

Figure 3.6   Effect of pre-coolant flow rate ratio on the work of liquefaction in the Pre-cooled Linde–Hampson Process.

The liquid fraction y, by Equation (3.7), $\dfrac{h_1 - h_2}{h_1 - h_f} = \dfrac{462 - 432}{462 - 29} = 0.0693$

The work of compression by Equation (3.10) is 474 kJ/kg
The work of liquefaction by Equation (3.11) is 6840 kJ/kg
FOM by Equation (3.4) is 0.1121

(ii)   Precooled Linde–Hampson Process (for $r = 0.1$) with freon 12 as refrigerant

$h_a = 207.94$ kJ/kg at 1 atm and 300 K

$h_b = 250.20$ kJ/kg at 6.8 atm and 372.9 K

$h_c = 61.23$ kJ/kg at 300 K, saturated liquid

$h_d = 61.23$ kJ/kg ($= h_c$) at 243.4 K and 1 atm (2-phase region)

The liquid fraction y, by Equation (3.13) is 470 kJ/kg, work of liquefaction by Equations (3.16) and (3.11) is 4554 kJ/kg and FOM by Equation (3.4) is 0.1684.

So it can be seen that the performance of the Simple Linde–Hampson Process using a single compressor can be improved by 50% by addition of a freon-cooled Refrigeration Cycle.

In the above calculation, it is assumed that $T_1 = T_2 = 300$ K, $T_3 = T_6 = T_d = 243.4$ K, 100% thermodynamic efficiency of isothermal compressor and 100% effectiveness of the main heat exchanger with no temperature difference between the incoming and outgoing streams at the inlet. However, in an actual liquefaction process, considering that the compressor may have 70% isothermal efficiency and the minimum temperature of approach is 5 K at the warm end of the heat exchanger, it can be seen that FOM is much lower.

Sample Problem 3.3: Find the fraction of liquefaction (y), the work of liquefaction (W_l) and the Figure of Merit (FOM) for different pressures (P_2) delivered by the compressor in a Pre-cooled Linde–Hampson cycle operating with nitrogen for values of $P_2 = 200, 100, 50$ atm. The inlet stream is at 1 atm and 300 K. Liquid nitrogen is removed at 1 atm. Freon-12 is used as the refrigerant for pre-cooling. The ratio of mass of refrigerant used to the total mass of gas compressed, $r = 0.1$. Assume a 5 K temperature difference at approach for the heat exchanger. Enthalpy data for the refrigerant: $h_a = 207.94$ J/g, $h_b = 250.2$ J/g, $h_c = 61.23$ J/g.

Solution: Applying the enthalpy balance, we get

$$y = \frac{h_9 - h_2}{h_9 - h_6} + \frac{r(h_a - h_c)}{h_9 - h_6} = \frac{457 - 430}{457 - 35} + \frac{0.1(207.94 - 61.23)}{457 - 35} = 0.09874 \qquad \text{(i)}$$

Work done per unit mass of liquid obtained is written as

$$\dot{W}_l = \frac{[T_1(s_1 - s_2) - (h_1 - h_2) + r(h_b - h_a)]}{y} = \frac{\begin{array}{c}300(4.42 - 2.75) - (462 - 430) \\ + 0.1(250.2 - 207.94)\end{array}}{0.09874} = 4792.38 \qquad \text{(ii)}$$

$$\text{FOM} = \frac{749}{W_l} = 0.1563 \qquad \text{(iii)}$$

749 J/g is the ideal work of liquefaction (W_i), this is the same as in *Sample Problem 3.2*.

We now mention the enthalpy and the entropy data needed to solve for the various pressures developed by the compressor. The results of the calculations have been tabulated later on.

(1) $P_2 = 200$ atm

Required entropy and enthalpy data (from T–s diagram for nitrogen) are as follows:

Stream	Pressure (atm)	Temperature (K)	Enthalpy (J/g)	Entropy (J/g-K)
1	1	300	462	4.42
2	200	300	430	2.75
6	1	77	35	0.5
9	1	295	457	

Note that stream 9 is at 295 K due to the assumed temperature difference at approach.

With the above data, we calculate y, $\dot{W}_l$ and FoM using Equations (i) to (iii). The results have been reported after part (iii).

(2) $P_2 = 100$ atm

Streams 1, 6 and 9 are again at the same conditions. Due to a different P_2, stream 2 changes. We have

$$h_2 = 444 \text{ J/g and } s_2 = 3 \text{ J/g-K}$$

$$y = \frac{h_9 - h_2}{h_9 - h_6} + \frac{r(h_a - h_c)}{h_9 - h_6} = \frac{457 - 444}{457 - 35} + \frac{0.1 \times (207.94 - 61.23)}{457 - 35} = 0.06556$$

$$W_l = \frac{[T_1(s_1 - s_2) - (h_1 - h_2) + r(h_b - h_a)]}{y}$$

$$= \frac{300(4.42 - 3) - (462 - 444) + 0.1 \times (250.2 - 207.94)}{0.6556} = 6287.25$$

$$\text{FOM} = \frac{744}{W_l} = \frac{749}{6287.25} = 0.1191$$

(3) $P_2 = 50$ atm

Streams 1, 6 and 9 remaining the same, we have

$$h_2 = 452 \text{ J/g and } s_2 = 3.22 \text{ J/g-K}$$

$$y = \frac{457 - 452}{457 - 35} + \frac{0.1 \times (207.94 - 61.23)}{457 - 35} = 0.04662$$

$$W_l = \frac{300(4.42 - 3.22) - (462 - 452) + 0.1(250.2 - 207.94)}{0.04662} = 7598.15$$

$$\text{FOM} = \frac{749}{W_l} = \frac{749}{7598} = 0.09885$$

Results:

P_2 (atm)	y	W_l (J/g)	FOM
200	0.09874	4792.38	0.1563
100	0.06556	6287.25	0.1191
50	0.04662	7598.15	0.09885

3.2.3 The Dual-Pressure Linde–Hampson Process

For achieving a higher fraction of liquefaction after the final step of the J–T expansion, it is necessary to increase the non-ideality of the feed gas. This is facilitated by either increasing the pressure (as in the Simple Linde–Hampson Process), or lowering the inlet temperature of the high pressure gas to the main heat exchanger or both (as in the Precooled Linde–Hampson

Process). Yet there is another method which not only lowers the temperature but also lowers the work of liquefaction, by dual pressure compression, that is, by using one low-pressure and another high-pressure compressor. The compressed gas from the high pressure compressor is partially expanded to an intermediate pressure by the J–T expansion as schematically described in Figure 3.7(a) and the T–s diagram in Figure 3.7(b). This stream at the intermediate pressure after the first J–T expansion valve is separated into vapour and liquid fractions in the first stage separator. The saturated vapour stream is then returned to the high pressure compressor after it is used as a coolant, to lower the temperature of the incoming high pressure gas in a 3-channel heat exchanger. The saturated vapour thus replaces an external refrigerant for precooling. This way the high nonideality due to high pressure may be utilised in the first stage J–T expansion. Also the saturated liquid from the first-stage separator (at its bubble point) may be directly throttled to atmospheric pressure, or alternatively, it may be cooled further by exchanging cold with the saturated vapour from the second stage separator prior to the second stage J–T expansion. The saturated vapour from the second stage separator is then passed through the 3-channel main heat exchanger for precooling the incoming high pressure gas. In other words, the incoming high pressure gas is cooled by exchanging cold with the streams
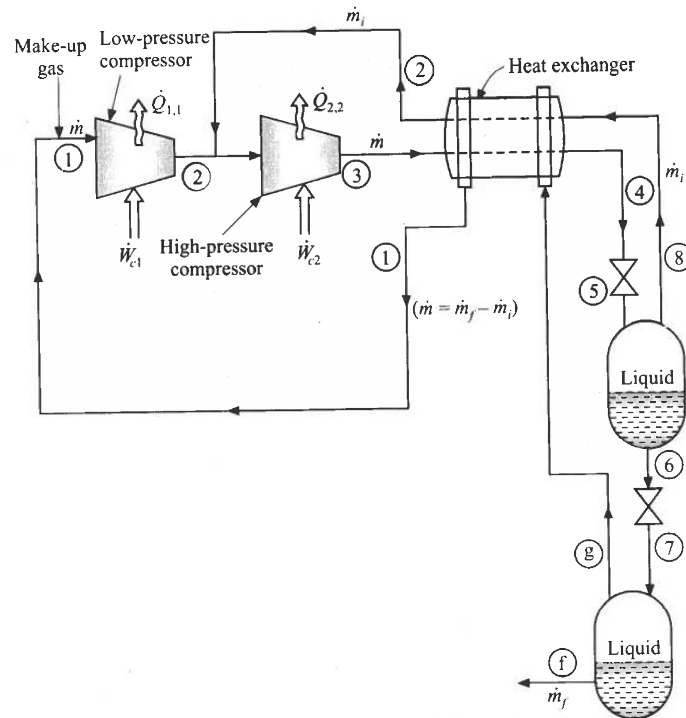

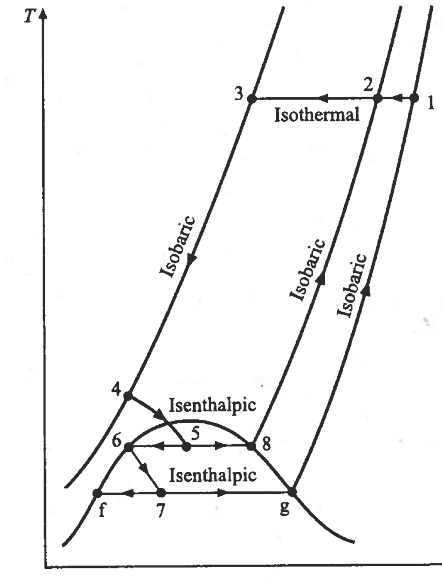**Figure 3.7(a)** Schematic representation of Dual-Pressure Linde–Hampson Process.

Figure 3.7(b) T–s diagram of Dual-Pressure Linde–Hampson Process.

of saturated vapour from the first stage separator at the intermediate pressure and from the second stage separator at atmospheric pressure in succession. The work of compression is reduced due to a reduced mass flow rate in the first compressor. The return gas at atmospheric pressure and near-ambient temperature is recycled with the make-up gas. The steps of the Dual Pressure Linde-Hampson Liquefaction Process are as follows:

1–2: First stage isothermal compression in low-pressure compressor

2–3: Second stage isothermal compression in high-pressure compressor

3–4: Precooling by outgoing streams of saturated vapour from two separators

4–5: First stage Throttling Expansion to intermediate pressure

6–7: Second stage Throttling Expansion to ambient pressure

5–8: Separation of saturated vapour from first stage separator

7–g: Separation of saturated vapour from second stage separator

5–6: Separation of saturated liquid from first stage separator

7–f: Separation of saturated liquid from second stage separator

g–1: Return of saturated vapour to the low-pressure compressor after providing cooling in 3–4 at the ambient pressure

8–2: Return of saturated vapour to the high-pressure compressor after providing cooling in 3–4 at the intermediate pressure

Applying the heat balance between the inlet of the 3-channel heat exchanger, and the outlet of the second separator, one can write the fraction of liquid formed as

$$y = \frac{h_1 - h_3}{h_1 - h_f} - i\frac{h_1 - h_2}{h_1 - h_f} \qquad (3.17)$$

where i is the intermediate pressure stream flow ratio and is in the range of 0.7–0.8.

$$i = \frac{\dot{m}_i}{\dot{m}} \qquad (3.18)$$

where $\dot{m}_i$ is the mass flow rate of the saturated vapour from the first separator at the intermediate pressure and $\dot{m}$ is the total mass flow rate through the high pressure compressor. The second term on the R.H.S. of Equation (3.17) represents the reduction in the liquid fraction in the dual-pressure process due to the first J–T expansion to the intermediate pressure and returning the separated saturated vapour to the high-pressure compressor, instead of the J–T expansion directly to atmospheric pressure. The reduction in the work of compression process is represented by the second term in Equation (3.19)

$$-\frac{\dot{W}}{\dot{m}} = T_1[(s_1 - s_3) - (h_1 - h_3)] - i[T(s_1 - s_2) - (h_1 - h_2)] \qquad (3.19)$$

The reduction in work requirement more than offsets the reduction in fraction of liquid formed and is minimum at an optimum intermediate pressure for different values of the flow rate ratio, i, [1] as shown in Figure 3.8. As an illustration for liquefaction of nitrogen, operating between 1 atm and 200 atm with an intermediate pressure of 50 atm and an intermediate pressure flow ratio (i) of 0.8, the following set of data on nitrogen is used for comparing the performance of the Dual-pressure Linde–Hampson Process.

$$h_1 = 462 \text{ kJ/kg at 1 atm and 300 K}$$
$$h_2 = 452 \text{ kJ/kg at 50 atm and 300 K}$$
$$h_3 = 432 \text{ kJ/kg at 200 atm and 300 K}$$
$$h_f = 29 \text{ kJ/kg at 1 atm and saturated liquid}$$
$$s_1 = 4.42 \text{ kJ/kg-K at 1 atm and 300 K}$$
$$s_2 = 3.23 \text{ kJ/kg-K at 50 atm and 300 K}$$
$$s_3 = 2.74 \text{ kJ/kg-K at 200 atm and 300 K}$$

Equation (3.17) can be used to find y as 0.0508, Equation (3.19) for work of compression as 196.4 kJ/kg and work of liquefaction as 3866 kJ/kg and FoM as 0.1984.

In another example, if the intermediate pressure P_2 is 20 atm and x is 0.9, considering 70% isothermal efficiency for the compressors and minimum temperature drop of 5 K in the warm-end of the heat exchangers, and neglecting the frictional pressure drops and heat in-leaks, y is increased to 0.0635, the work of liquefaction is increased to 5250 kJ/kg and FOM is reduced to 0.148.
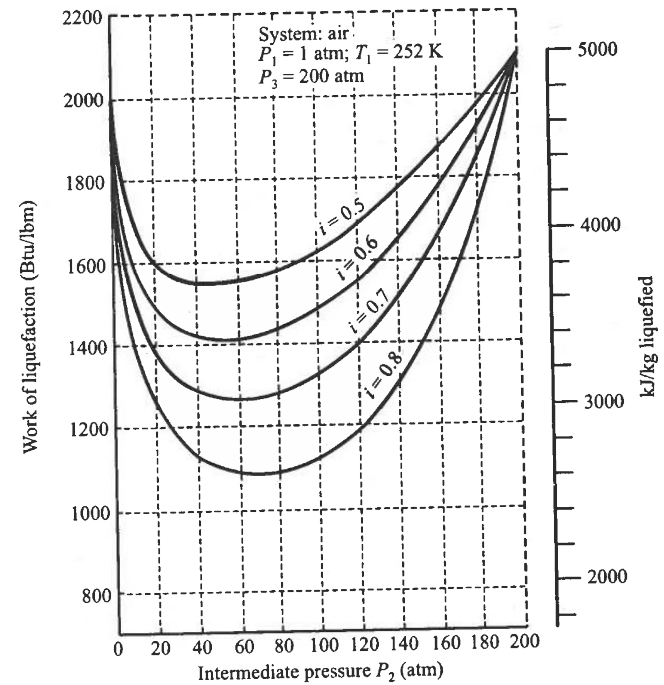
Figure 3.8   Effect of intermediate pressure on the work of liquefaction in the Dual-Pressure Linde–Hampson Process.

Sample Problem 3.4: Find the fraction of liquefaction (y), the work of liquefaction (W_l) and the Figure of Merit (FOM) for different pressures (P_2) delivered by the first compressor in a Linde Dual-Pressure System operating with nitrogen. The inlet stream is at 1 atm, 300 K. The pressure delivered by the second compressor is $P_3 = 200$ atm. Liquid nitrogen is removed at 1 atm. The intermediate-pressure-stream flow-rate ratio, $i = 0.8$. Calculate for $P_2 = 50, 100$ atm. Assume a 5 K temperature difference of approach for the heat exchanger.

Solution: Applying the first law of thermodynamics to the heat exchanger and the two separators,

$$y = \frac{h_{10} - h_3}{h_{10} - h_f} - \frac{i(h_{10} - h_9)}{h_{10} - h_f} \qquad (i)$$

where

$$i = \frac{m_i}{m} = 0.8$$

Work done per unit mass of liquid removed is given by

$$\dot{W}_l = \frac{\{[T_1(s_1 - s_3) - (h_1 - h_3)] - i[T_1(s_1 - s_2) - (h_1 - h_2)]\}}{y} \qquad (ii)$$

Determination of the enthalpy and the entropy at e:

Let h_e^* and s_e^* be the enthalpy and the entropy at e for isentropic expansion to 5 atm. Therefore, $s_e^* = s_3 = 2.75$ J/g-K and $h_e^* = 245$ J/g. For an efficiency of the expander = 0.75, $h_3 - h_e = 0.75(h_3 - h_e^*) = 139.5$

So
$$h_e = 291.5 \text{ J/g}$$

Using Equation (i),
$$y = 0.0616 + 0.3282x$$

From Equations (ii) and (iii),
$$W_l = \frac{470 - 280.5x}{y}$$

For $x = 0.5$,
$$y = 0.2257, \ W_l = 1461 \text{ and FOM} = 0.5126 \quad \text{[from Equation (iv)]}$$

Similarly one may calculate for $x = 0.7$ as well. However, the temperature and pressure conditions will not change anywhere.

(2) $P_2 = 50$ atm

The conditions at streams 2, 10 and e will be different now.

$$P_2 = 50 \text{ atm}, \ T_2 = 300 \text{ K, so } h_2 = 453 \text{ J/g and } s_2 = 3.23 \text{ J/g-K}$$

$$P_{10} = 50 \text{ atm}, \ T_{10} = 275 \text{ K, so } h_{10} = 424 \text{ J/g and } s_{10} = 3.14 \text{ J/g-K}$$

Determination of the enthalpy and the entropy at e:

Let h_e^* and s_e^* be the enthalpy and the entropy at e for isentropic expansion to 50 atm. Therefore, $s_e^* = s_3 = 2.75$ J/g-K and $h_e^* = 335$ J/g. For an efficiency of the expander = 0.75, $h_3 - h_e = 0.75(h_3 - h_e^*) = 72$

So
$$h_e = 359 \text{ J/g}$$

Using Equation (i),
$$y = 0.0616 + 0.0924x$$

From Equations (ii) and (iii),
$$\dot{W}_l = \frac{470 - 420x}{y}$$

For $x = 0.5$
$$y = 0.1078, \ W_l = 2411.87 \text{ and FOM} = 0.3105 \quad \text{[from Equation (iv)]}$$

Similarly, one may calculate for $x = 0.7$ as well. However, the temperature and pressure conditions will not change anywhere.

P_2 (atm)	P_3 (atm)	x	y	W_l (J/g)	FOM
5	200	0.5	0.2257	1461	0.5126
5	200	0.7	0.2913	939.4	0.7973
50	200	0.5	0.1078	2411.87	0.3105
50	200	0.7	0.1263	1393.5	0.5375

3.3 LIQUEFACTION OF METHANE OR NATURAL GAS

The natural gas is primarily methane (greater than 90% v/v), the hydrocarbon having the highest calorific value, the rest being ethane and propane and so it is used as a clean fuel either in the form of compressed natural gas (CNG) or liquefied natural gas (LNG). The advantage of natural gas as a fuel is that it burns cleanly with least exhaust emissions of CO and other hydrocarbons. It is also used as the building block for production of fertiliser, chemicals and petrochemicals. The major disadvantage of natural gas is that it is a very light gas and accordingly it needs to be compressed up to 250 atm to be used as CNG, whereas LNG can be stored and transported at a much lower pressure (60–80 atm) than CNG, and has been proved to be practicable, though LNG requires proper insulation. The natural gas has a normal boiling point of –162°C (or 111 K), and so cryogenic liquefaction is needed with special design consideration to minimize the boil-off and safety during storage. However, according to a rough estimate, the liquefaction of natural gas is economically viable only for long distance transportation and the minimum distance covered should be more than 2500 km. LNG is transported across the countries and even across the continents through pipelines on land or via barge-mounted ships across the sea or ocean.

3.3.1 Pure Component Refrigeration (PCR) Cascade Process

The first large-scale commercial plant for liquefied natural gas (LNG) was built in 1939, which was based on conventional cascade refrigeration with ammonia (normal boiling point of 240 K) and ethylene (normal boiling point of 170 K) as the refrigerants in succession. A similar plant was designed and built in 1948 using ammonia, ethylene and methane as the refrigerants in cascades; the drawbacks of these methods being highly inefficient and requiring huge compressors. However, in 1954 Morrison developed a novel expansion turbine liquefaction process in which methane or natural gas was compressed to about 70 bar, pre-cooled to about –60°C and then expanded down to 1 atm pressure in the turbine. The turbine was designed to tolerate 10–20% condensation, which was separated and the rest was returned through the heat exchanger for providing the cooling of the incoming gas. The process was very simple, though it had inherent thermodynamic inefficiencies and physical limitations in separating the liquid fraction from the fog. Accordingly the large liquefier that was built in 1963 was again switched over to the PCR cascade refrigeration process due to the relative simplicity of operation 4[2]. This process was based on propane (normal boiling point 231 K), ethylene and methane as the refrigerants in succession, as illustrated in Figure 3.14.

3.3.2 Multicomponent Refrigerant (MCR) Process

The concept of using multicomponent mixture as a refrigerant in the vapour compression refrigeration cycle was first introduced by Ruhemann in 1947, though it was extended to liquefaction of natural gas simultaneously in the US and the then USSR in 1959 and in France in 1967. Natural gas contains several hydrocarbon components that condense at different temperature levels. The multicomponent refrigerant (MCR) comprises some of these components suitably extracted from the natural gas in a separate unit and optimally diluted with nitrogen, commensurate with the composition of the feed natural gas. The composition of these components is carefully optimised in order that MCR may be used for progressive condensation, phase
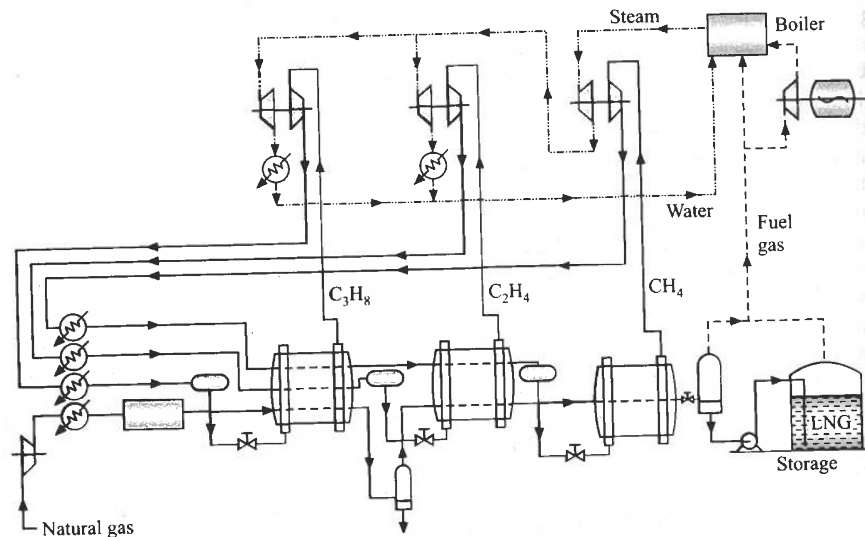
Figure 3.14   Schematic representation of LNG by PCR Cascade Process.

separation of vapour and liquid fractions to provide cooling to the feed natural gas separately, and progressive evaporation of different liquid fractions of MCR in successive stages. In this way temperature is progressively lowered in each stage to cater to the cooling requirements of the next stage until the MCR vapour is completely condensed. This provides the controlled coordinated co-current cooling of the feed natural gas over a temperature range spanning from the dew point to the bubble point of MCR. This obviates the need for multiple compressors for separate pure component refrigerants in succession as in the case of the PCR cascade refrigeration process.

The MCR process employs four heat exchangers and three phase separators in addition to an after-cooler and a centrifugal compressor. The feed natural gas is successively cooled in these four heat exchangers at a pressure in the range of 39–53 atm using different vapour and liquid fractions of MCR in successive stages of phase separation [2]. The gaseous MCR is first compressed in a single-stage centrifugal compressor and partially (about 25%) condensed in an after-cooler by means of cold water as described in Figure 3.15. MCR is then separated into vapour and liquid fractions in the first phase separator [S1] and both fractions pass through the first heat exchanger (HE1) separately. The liquid fraction of MCR is then expanded by a throttling valve, mixed with the return fraction at the same pressure from the second heat exchanger (HE2), and enters the shell side of HE1 to provide cooling to the incoming feed natural gas. The vapour fraction of MCR from S1 is also partially condensed in HE1 and is then fed to the second phase separator (S2). Again, the liquid fraction of MCR from (S2) passes through HE2, and is throttled and mixed with the return fraction at the same pressure from the third heat exchanger (HE3). This then enters the shell side to provide cooling in HE2. The vapour
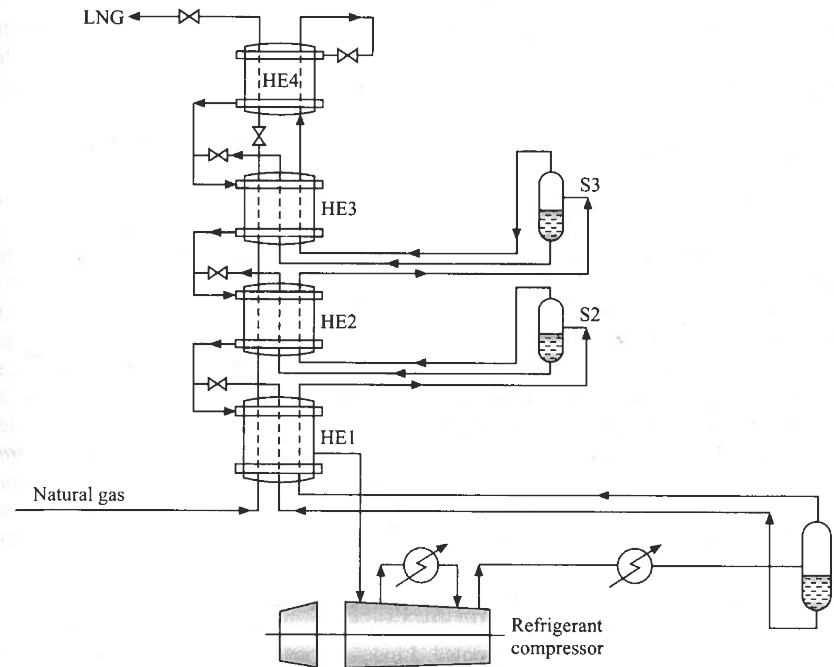

Figure 3.15   Schematic representation of LNG by MCR Process.

fraction of MCR from S2 is also cooled in HE2 and then separated in the third phase separator (S3). Again the liquid fraction of MCR from S3 passes through HE3, and is throttled and mixed with the return fraction at the same pressure from HE3. This enters the shell side to provide cooling in HE4. The vapour fraction of MCR from S3 is also cooled in HE3 and then completely condensed in HE4. This is then throttled and returned to the shell side of the same HE4 to provide cooling to the incoming natural gas. Thus the feed natural gas is completely liquefied after HE4 and LNG is produced, which is then stored in the reservoir at the desired pressure.

The temperature of MCR gradually goes down over a range as the liquid stream containing heavier component propane is removed and gets enriched in the lighter component methane. The feed natural gas contains ethane, propane and a little nitrogen in addition to more than 90% methane v/v. These components condense over a wide temperature range and accordingly a relatively uniform temperature difference needs to be maintained between the heat exchanging streams through a proper selection of the composition of MCR. The performance of practical LNG plant however depends to a great extent on the design of the heat exchangers in coordination with the phase separator, in view of progressively varying flow rates and uneven distribution of the phases. The calculation of phase equilibrium compositions of the MCR

mixture is important for minimizing the chances of the temperature pinches during operation. For very small capacities of LNG plant, however, a large Stirling refrigerator is likely to have economic advantage over the MCR process.

3.4   LIQUEFACTION PROCESSES FOR NEON AND HYDROGEN

It may be recalled that the maximum inversion temperature of helium, hydrogen and neon is lower than the ambient temperature (e.g. hydrogen has inversion temperature of 204 K) and so it is not possible to liquefy these gases by throttling alone. Accordingly pre-cooling is a must for these gases. Another problem arises particularly in the case of liquefaction of hydrogen due to occurrence of two isotopes, namely ortho and para hydrogen in equilibrium with each other at low temperatures. At room temperature diatomic hydrogen contains 25% para hydrogen at equilibrium, which increases to 100% para hydrogen at 20 K. This ortho-para conversion is exothermic and is a very slow process unless it is treated with metallic catalysts, such as chromium oxide on alumina support or granular iron hydroxide gel. If liquid hydrogen needs to be stored, then hydrogen needs to be catalytically converted to para hydrogen, prior to cooling and liquefaction owing to liberation of exothermic heat of reaction. For liquefaction of hydrogen and neon, the less volatile trace impurities like nitrogen, oxygen and methane need to be removed from the feed gas by silica gel or active charcoal adsorbers at liquid nitrogen temperature.

3.4.1   The Pre-cooled Linde–Hampson Process

For laboratory-scale liquefiers, the pre-cooled. Linde–Hampson Process is a good choice for liquefaction of neon and hydrogen. The first large hydrogen liquefier at NBS cryogenic laboratory at Boulder, Colorado was based on this process and so hydrogen liquefier based on this process of liquefaction is also known as Boulder liquefier. The Simple Linde–Hampson process is not adequate to initiate the process of cooling of the gases from ambient temperature by throttling. For economic and safety considerations, nitrogen is mostly chosen as the refrigerant for pre-cooling neon and hydrogen for liquefaction by Linde–Hampson process. A schematic representation of the Pre-cooled Linde–Hampson Process is shown in Figure 3.16. For a small Lab-scale liquefier, liquid nitrogen may be taken from a small storage vessel and can be used in a pre-cooling bath. The vapor emanated from the bath may be utilised in the first heat exchanger and discarded later to 1 atm pressure. For a large-scale liquefier, however, separate nitrogen liquefaction plant is needed for economic considerations. The feed gas is compressed to 100 bar and pre-cooled by the outgoing nitrogen and then hydrogen vapour streams. This is then further cooled in a liquid nitrogen bath at 66 K (at about 0.2 bar) and is then cooled by the return hydrogen vapour stream before the final throttling expansion.

Following the nomenclature given in Figure 3.16, the fraction of liquefaction is given by

$$y = \frac{h_7 - h_4}{h_7 - h_f} \qquad (3.24)$$

Applying the heat balance over the two heat exchangers, liquid nitrogen bath, separator, one can get
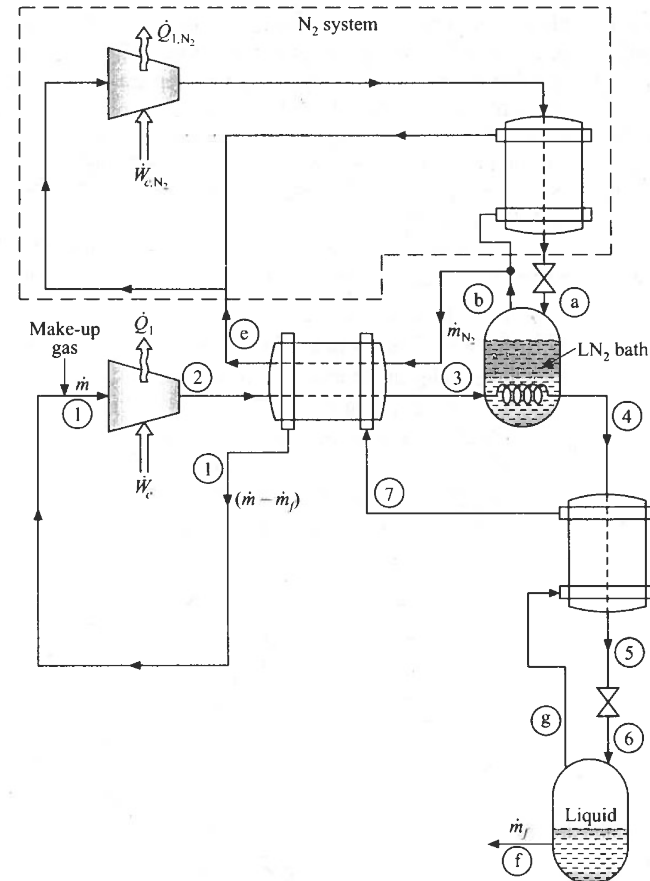

Figure 3.16   Schematic representation of pre-cooled Linde-Hampson Process for hydrogen.

$$\dot{m}_{N_2} h_c + (\dot{m} - \dot{m}_f) h_1 + \dot{m}_f h_f = \dot{m}_{N_2} h_a + \dot{m} h_2 \qquad (3.25)$$

where $\dot{m}_{N_2}$ is the mass flow rate of liquid nitrogen boiled away for pre-cooling, $\dot{m}$ is mass flow rate of hydrogen or neon entering the compressor and $\dot{m}_f$ is mass flow rate of liquid formed. Thus the nitrogen boil-off rate per unit mass of hydrogen or neon entering the compressor is z.

$$z = \frac{\dot{m}_{N_2}}{\dot{m}} \qquad (3.26)$$

$$z = \frac{h_2 - h_1}{h_c - h_a} + y \left[\frac{h_2 - h_f}{h_c - h_a} \right] \qquad (3.27)$$