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Cryogenics

Course for students of Master Academic

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Preface

Cryogenics is the set of techniques for producing cold, liquefying substances and separating mixtures. It has many applications, particularly in the food, medical and industrial sectors. This handout is intended for students in the master's degree in mechanical engineering with an energy option. It provides them with the various basic principles for obtaining low temperatures as well as the various gas liquefaction processes. To facilitate the understanding of the various cryogenic processes, the course is reinforced by application examples. This document is accompanied by appendices containing tables of thermodynamic properties and diagrams that allow the values of the various thermodynamic variables used in the numerical of the exercises to be determined. I would be grateful to anyone who makes comments or suggestions for developing this work.

Abstract:

Cryogenics is the scientific module that focuses on the production, study, and application of extremely low temperatures, typically below -150°C . At such temperatures, the physical behavior of materials changes dramatically, allowing scientists and engineers to explore unique properties of gases, liquids, and solid materials. One of the most important outcomes of cryogenics is the liquefaction of gases such as nitrogen, oxygen, and helium, which enables their storage and use in compact and stable forms. Cryogenic systems rely on specialized equipment including cryocoolers, liquefiers, insulated, and vacuum-jacketed piping designed to minimize heat transfer. These systems allow precise temperature control and are essential in many scientific and industrial applications. In medicine, cryogenics enables the operation of machines through superconducting magnets cooled with liquid helium. It is also used in cryosurgery, cryopreservation of biological samples, and long-term storage of genetic materials. In space and aviation, cryogenic fuels such as liquid hydrogen play a crucial role in high-efficiency propulsion. Cryogenics is also vital in particle physics, where accelerators require ultra-low temperatures to maintain superconductivity. Despite its benefits, the field faces challenges such as material brittleness, safety risks, and the need for advanced insulation. Overall, cryogenics remains a key technology enabling innovation in research, medicine, and aerospace.

Keywords: Gas Liquefaction Cycle; Joule–Thomson Effect; Turbo-expander; Phase Transition; Critical Temperature

Résumé:

Cryogénie est une modèle scientifique qui étudie la production, le comportement et les applications des très basses températures, généralement inférieures à -150°C . À ces températures extrêmes, les matériaux adoptent des propriétés physiques particulières, permettant la liquéfaction de gaz tels que l'azote, l'oxygène et l'hélium. Cette capacité est essentielle pour le stockage, le transport et l'utilisation de ces gaz dans un état stable et compact. Les systèmes cryogéniques utilisent des équipements spécialisés comme les cryoréfrigérateurs, les liquéfacteurs, les cuves isolées et les conduites sous vide, conçus pour réduire les pertes thermiques. Grâce à ces technologies, la cryogénie joue un rôle central dans de nombreux domaines modernes. En médecine, elle permet le fonctionnement des appareils grâce aux aimants supraconducteurs refroidis à l'hélium liquide. Elle est également utilisée pour la cryochirurgie et la conservation de cellules, tissus et échantillons biologiques. Dans l'aérospatial, des carburants cryogéniques comme l'hydrogène liquide sont indispensables aux moteurs de fusées haute performance. En physique des particules, la cryogénie garantit la supraconductivité dans les accélérateurs. Malgré ses avantages, elle présente des défis, notamment la fragilité des matériaux, les risques liés à la manipulation et la nécessité d'une isolation très performante. La cryogénie demeure ainsi une technologie clé pour la recherche, la médecine et l'aérospatial.

Mots-clés: Cycle de liquéfaction des gaz; Effet Joule–Thomson; Turbo-détendeur; Changement de phase; Température critique

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Nomenclature

$\dot{m}$	Flow rate , kg/s
z	Compressibility factor
y	Fraction of liquefied gas
T	Temperture,K
μ	Joule Thomson coefficient
u	Internal energy , J/kg
Q	Heat , J/kg
h	Enthalpy, J/g
s	Entropy , J/g.K
p	Pressure , Pa
C_p	Heat capacity , J/kg.K
η	Efficiency

Abbreviations

JT	Joule Thomson
NG	Natural Gas
NRU	Nitrogen Recovery Unit
PSA	Pressure Swing Adsorption
PRICO	Pritchard Corporation
LIN	Liquid Nitrogen
APCI	Air Products Company Inc
EQHHP	Euro-Quebec Hydro-Hydrogen Pilot Project

v	Molar volume, m ³ /mol
t	Time, s
ε	Effectiveness
x	Fraction of gas enters the expander
i	Fraction of gas flow at intermediary pressure
r	Fraction of refrigerant gas
$\dot{W}$	Power , W
$\dot{Q}$	Heat rate , W
Subscripts	
g	Gas
$L; f$	Liquid
e	Expander
t	ton

Chapter 1:

Review on the Main Processes for Obtaining Low Temperatures

1.1 Introduction

To try to define cryogenics, let us first examine the thermodynamic temperature scale (Figure 1.1). Paradoxically, if we know the ultimate, and inaccessible, limit of the field of cryogenics – absolute zero, the other border, between cryogenics and refrigeration, has always been essentially fluctuating in time and space[1, 2].

What is the meaning of word “**cryogenics**” ?

Cryo (Kryos): Cold

Genics (Genes): To produce or Produced

Cryogenics is the science and technology associated with the generation (production) of low temperatures less than 123 K.

Born around 1877 when oxygen was liquefied for the first time by Pictet and Cailletet ($T \approx 90$ K), the notion of cryogenics is not appreciated in the same way in a research center currently working at a few millikelvins and in an industrial installation testing the engine of the third stage of Ariane V. The recent discovery of superconductors at high critical temperatures (125 K in 1992) has even caused temperatures previously described as hot by cryogenics to be “re-annexed”: in fact, the Condensed matter physicists are still seeking to understand the deep mechanisms of this new manifestation of a property discovered in 1911 by Kamerlingh Onnes shortly after the first liquefaction of helium around 4 K [3].

The undoubtedly main characteristic of low temperature developments is in fact the constant and very fertile confrontation between technological advances and understanding fundamental of nature.

Temperature characterizes the kinetic energy of the constituents of a body. Also, lowering the temperature opens up the possibility of distinguishing often very tenuous properties, but essential for testing the validity of scientific theories, and usually masked by thermal agitation at ordinary temperature: superconductivity and superfluidity are macroscopic manifestations of quantum theory. Developments in cooling tools now make it possible to highlight fascinating phenomena: non-ohmic resistivity of submicron systems, magnetic order of copper or silver, quantum Hall effect, detection of new particles, temperature of the Universe. These unexpected manifestations often lead to the development of new means of investigation, which in turn are sources of original questions. This wealth is well characterized by the dozen Nobel Prizes awarded in this field. Figure 1.2 presents the main steps in obtaining low temperatures and some associated discoveries[4].

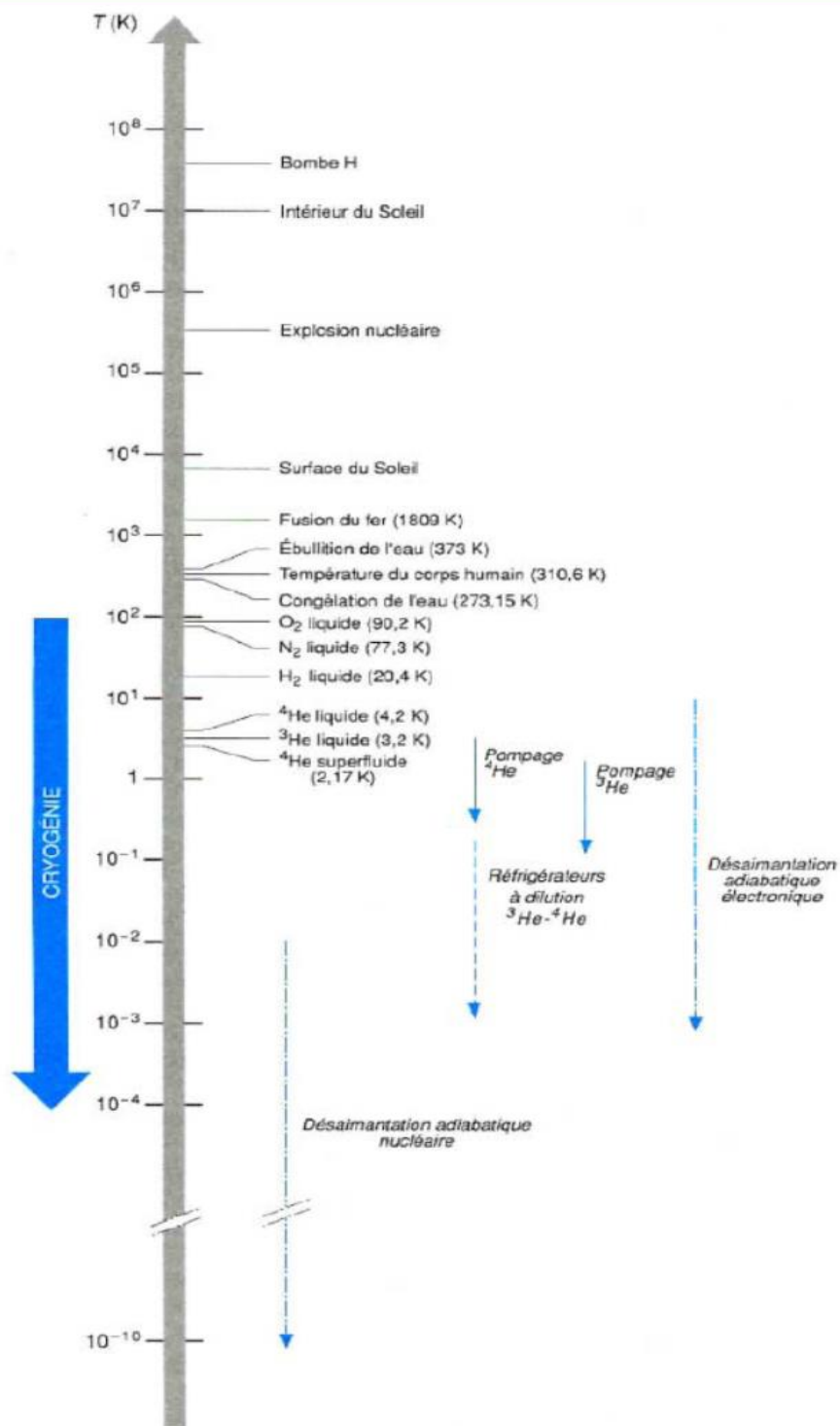


Figure 1.1 Thermodynamic temperature scale

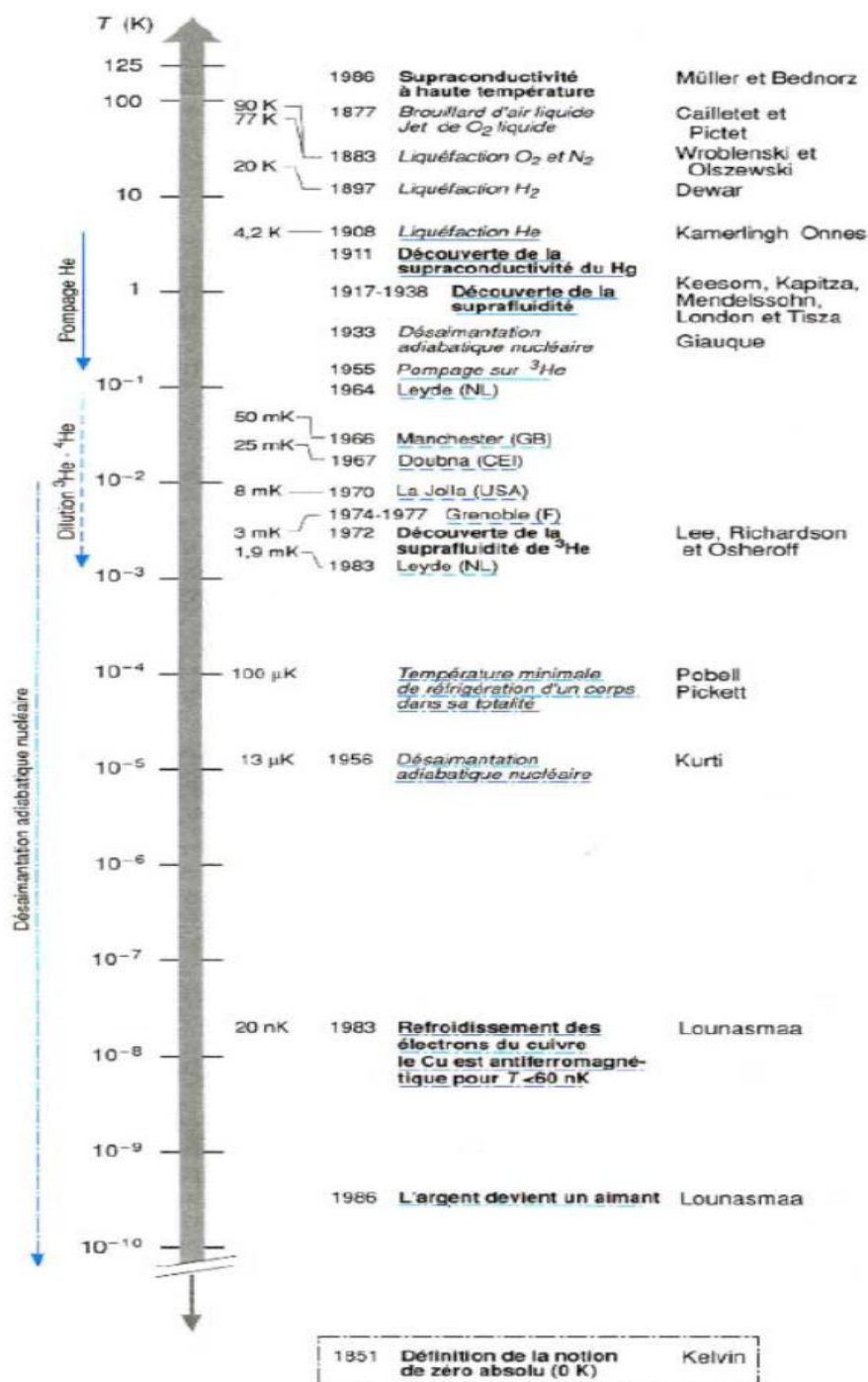


Figure 1.2 Different steps towards low temperatures

These advances in knowledge are only possible through experimental advances of high technological significance. But cryogenics has also widely spread towards applications. We can cite the field of liquefied gas storage: the founding of L'Air Liquide by Georges Claude in the very first years of the century and its development clearly show that cryogenics is not only about Knowledge! The slowing down of chemical reactions associated with lowering temperature is also a long-known example for food preservation; cryogenics has opened up new perspectives in the medical field by allowing the long-term preservation of numerous biological systems[5].

1.1.1 Temperature scales:

Degree Celsius, symbol °C, is the unit of the Celsius temperature scale, which is a unit derived from the International System.

Degree Kelvin (named after William Thomson, known as Lord Kelvin), with symbol K, is the SI base unit of thermodynamic temperature.

Degree Fahrenheit (symbol: °F) is a unit of measurement of temperature, proposed by the German physicist Daniel Gabriel Fahrenheit in 1724.

Degree Rankine (symbol: °R) is a temperature scale named in honor of the Scottish engineer and physicist William John Macquorn Rankine, who proposed it in 1859 [5].

$$[^{\circ}\text{R}] = [^{\circ}\text{F}] + 459,67$$

$$[^{\circ}\text{F}] = [^{\circ}\text{C}] \times 1.8 + 32$$

$$[^{\circ}\text{R}] = [\text{K}] \times 1,8$$

$$[\text{K}] = [^{\circ}\text{C}] + 273.15$$

1.1.2 Applications of cryogenics[2, 6]

- Space Applications

- Cooling of infrared (IR) sensors spatial simulation
- Cryogenic engines are powered by cryogenic thrusters.

-Mechanical Applications

- Magnetic separation technique is used in various applications such as improving the quality of ultra-high purity quartz
- Cryogenic recycling – transforms scrap metal into raw material by subjecting it to cryogenic temperatures.

-Medical Applications

- Cryotherapy is a new technique in which harmful tissue is destroyed by freezing it at a cryogenic temperature.
- Nuclear Magnetic Resonance (NMR) is used by the pharmaceutical industry to study molecular structure.

- Magnetic Resonance Imaging (MRI) are used for body scanning.
- The magnets of the NMR and MRI scanner are cooled by liquid helium.

-Gas industry applications

- Liquefaction
- Separation
- Storage
- The transport of gas around the world takes place in the liquid state. This is done by storing the liquid at cryogenic temperature.

1.2 Review of thermodynamics

Thermodynamics is based on four major postulates (hypotheses), which are called the four principles of thermodynamics [4, 7, 8].

Zeroth law of thermodynamics just says that the idea of temperature means something.

First principle of thermodynamics is simply the principle of conservation of energy. Inelegantly stated, the first principle announces that everything that enters a system must either exit or accumulate.

Heat added to the system + Work done on the system = change in internal energy

Second principle is also a conservation equation, stating that in the ideal engine, entropy (S) is conserved. All real engines change entropy. We postulate a property in thermodynamics to describe these observations that meets the following qualitative requirements:

1. Adding Q causes a property change of the system.
2. The way (the path) in which Q is added fixes the magnitude of the property change.
3. Adding Q at a lower temperature causes a greater change than adding the same amount of Q at a higher temperature. Thus, we invent a property of the system to adapt these three criteria, namely entropy,

Third principle just says that there is a temperature so low that it can never be reached.

These familiar expressions of the four main principles of thermodynamics have a calming effect. It will not be able to quantitatively evaluate its analyze unless we employ much more precise definitions and, expressly, mathematical statements of these principles. This is the task to which we must now turn. Therefore, we begin our discussion of fundamental thermodynamic concepts with some definitions.

Thermodynamics: Thermodynamics is concerned with the interaction between a system and its environment, the effect of this interaction on the properties of the system and the heat and work between the system and its environment.

System: Any part of the entire material universe set apart by arbitrarily chosen but specific boundaries. It is essential that the system must be clearly defined in any thermodynamic analysis.

Environment: All parts of the material universe not included in the system. The definitions of system and environment are related. The system is any quantity or region in question mentally set apart from the rest of the universe, which then becomes the environment. The imaginary envelope which distinguishes the system of the environment is called the system boundary

System property, or state variable: Any observable characteristic of the system, such as temperature, pressure, specific volume, entropy, or other distinct characteristic.

Energy: A very general term used to represent heat, work, or the capacity of a system to make heat or work.

Heat: The energy in transition between a system and its environment that is caused by a temperature difference.

Work: Work is always defined as the product of a force external to the system and a displacement of the system. If there is no system movement, there is no work. If there is no energy in the transition, there is no work.

Processes: The method or path by which the properties of a system change from one set of values in an initial state to another set of values in a final state. For example, a process may take place at a constant temperature, at a constant volume, or by some other specified method. A process for which $Q = 0$ is called a process adiabatic.

1.3 Cryogenic Fluids

The relationship of specific or molar volume with temperature and pressure for a pure substance in an equilibrium state can be represented by a surface in three dimensions, as shown in Figure 3. The hatched surfaces marked S, L and G in Figure 1.3 represent, respectively, the solid, liquid and gas regions in the diagram. The unhatched surfaces are the coexistence regions of two phases in equilibrium, and there are three such regions: solid-gas (S-G), solid-liquid (S-L), and liquid-gas (L-G)[9, 10].

Bold lines separate the various regions and form the boundaries of the surfaces representing the individual phases. Because of the difficulty of visualizing and drawing these surfaces, it is customary to depict the data on projections such as PT and PV plans.

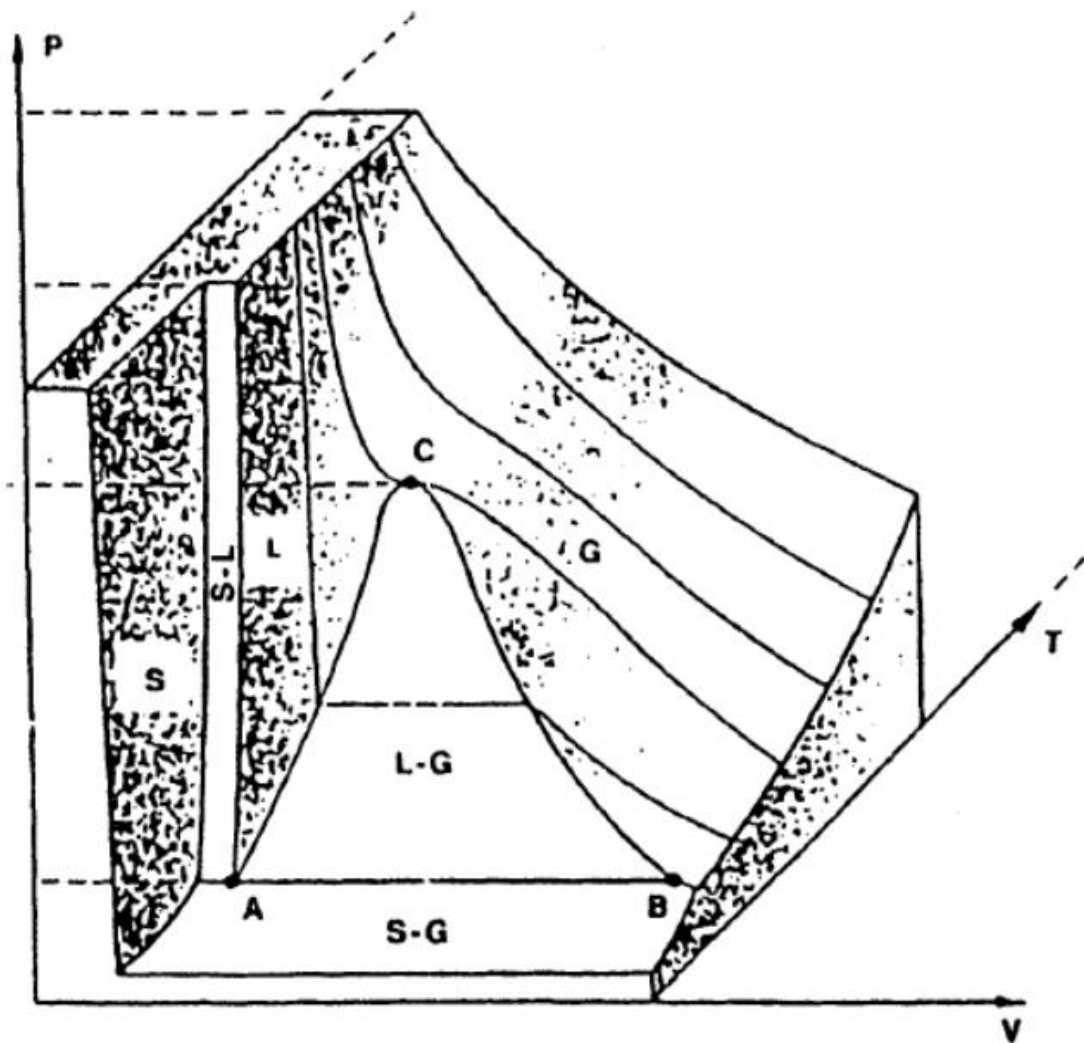


Figure 1.3 P-V-T surface for a pure substance.

The bold line through A and B marks the intersections of the two-phase regions and is the three-phase line, along which solid, liquid, and gas phases exist in the three-phase equilibrium. According to the phase rule, such as these three phases, single-component systems have zero degrees of freedom; they exist for a given pure substance for only one temperature and pressure. For this reason, the projection of this line on the PT plane of Figure 1.4 is a point. This is known as the triple point. **The triple point** is simply the point of intersection of vaporization and sublimation curves. It should be understood that only on a P-T diagram is the triple point represented by a point. (On a P-V diagram it is a line.) The phase rule also requires that systems composed of two phases in equilibrium have just one degree of freedom, and therefore two-phase regions must project as lines on the plane PT, forming a P-T diagram of three lines- fusion, sublimation and vaporization which meets at the triple point[5, 7, 11].

The solid lines in Figure 4 clearly represent phase boundaries. The melting curve (line 2-3) normally has a positive slope, but for some substances (water is the best known) it has a negative slope. This line is believed to continue upward indefinitely. The two curves 1-2 and 2-C represent the vapor pressures of solid and liquid, respectively. Terminal point C is the critical point, which represents the highest pressure and highest temperature at which liquid and gas can coexist in equilibrium. The termination of the vapor pressure curve at point C means that at higher temperatures and pressures there is no clear distinction between what is called liquid and what is called gas. At the critical point, there is no distinction between vapor and liquid phases.

Homogeneous fluids are normally divided into two classes, liquids and gases. However, the distinction cannot always be precisely drawn, because the two phases become indistinguishable at the critical point.

Thus, there is a region extending indefinitely upward and indefinitely to the left of the critical point which is simply called the liquid region. The fluid region, existing at higher temperatures and pressures, is marked by dashed lines which do not represent phase changes, but depend on arbitrary definitions of what constitute liquid and gas phases.

The region designated as liquid in Figure 1.5 lies above the vaporization curve. Thus, a liquid can always be vaporized by a sufficient reduction in pressure at the constant temperature. The gas region in Figure 5 is to the left of the sublimation and vaporization curves.

Thus, a gas can always be condensed by a sufficient reduction in temperature at constant pressure. Because the fluid region does not fit either of these definitions, it cannot be called either a gas or a liquid [9, 12, 13].

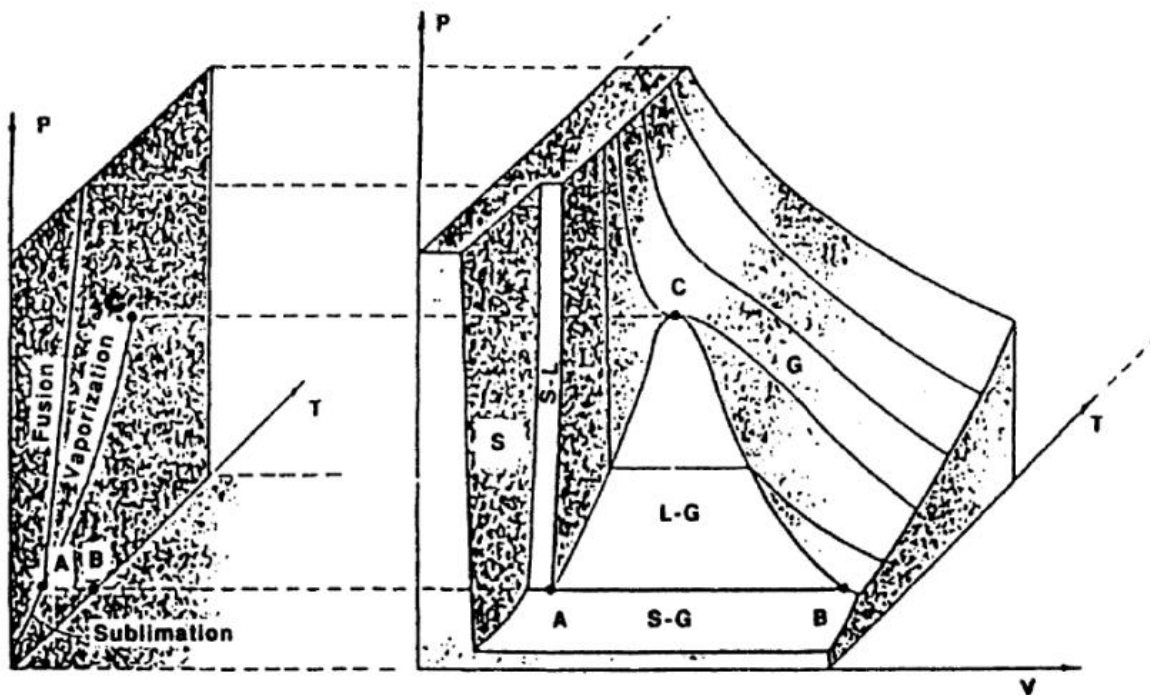


Figure 1.4 PT projection of the P-V-T surface for a pure fluid.

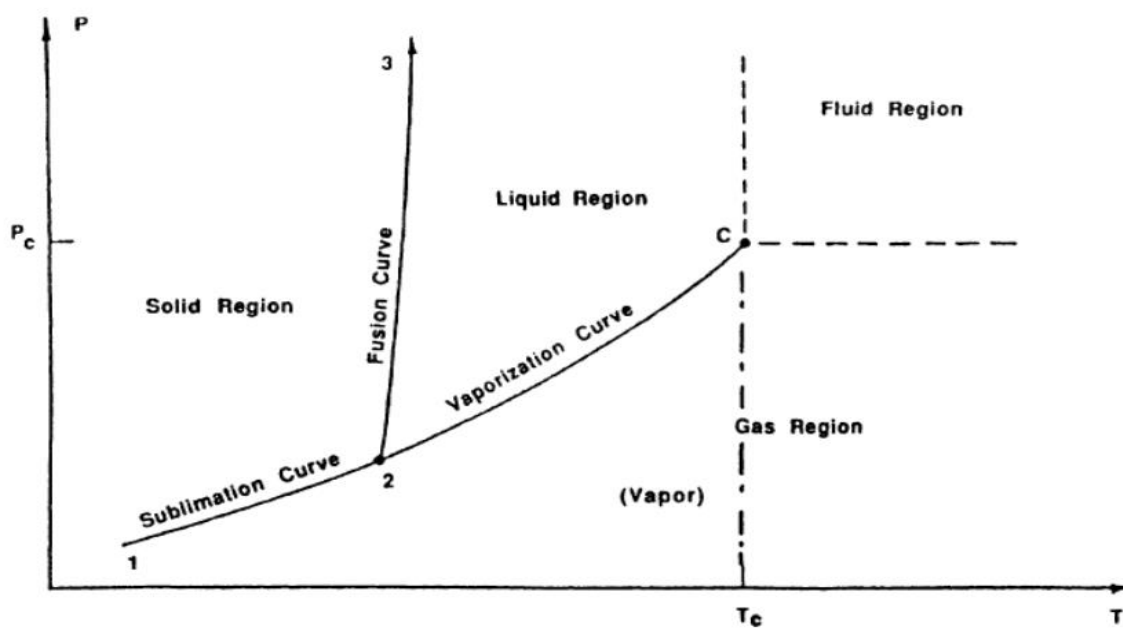


Figure 1.5 P-T diagram for a pure substance.

1.4 Joule-Thomson expansion (Isenthalpic process)

The effect of the temperature change for an isenthalpic change in pressure is represented by the Joule-Thomson coefficient defined by:

$$\mu_{JT} = \left. \frac{\partial T}{\partial p} \right|_h \quad (1)$$

The Joule-Thomson coefficient represents the laying of enthalpy lines. It will be able to plot a series of exit condition points for given input conditions and obtain constant enthalpy lines. If the gases were ideal, in the T-p diagram, the isenthalpic lines are horizontal straight lines due to the unique dependence of the enthalpy of the temperature, consequently, when the enthalpy variation is zero, the temperature must remain constant. For real gases, as shown in Figure 1.6, the lines isenthalpic curves are curves, which present a maximum. We acknowledge the appearance of two regions, in the first, a decrease in pressure causes an increase in temperature, while in the second region, and relaxation causes a decrease in temperature. The curve that separates the two regions is called the gas inversion curve. Along this curve the Joule-Thomson coefficient is zero. In the region of temperature decrease (positive effect). In the region of temperature increase (negative effect)[14, 15].

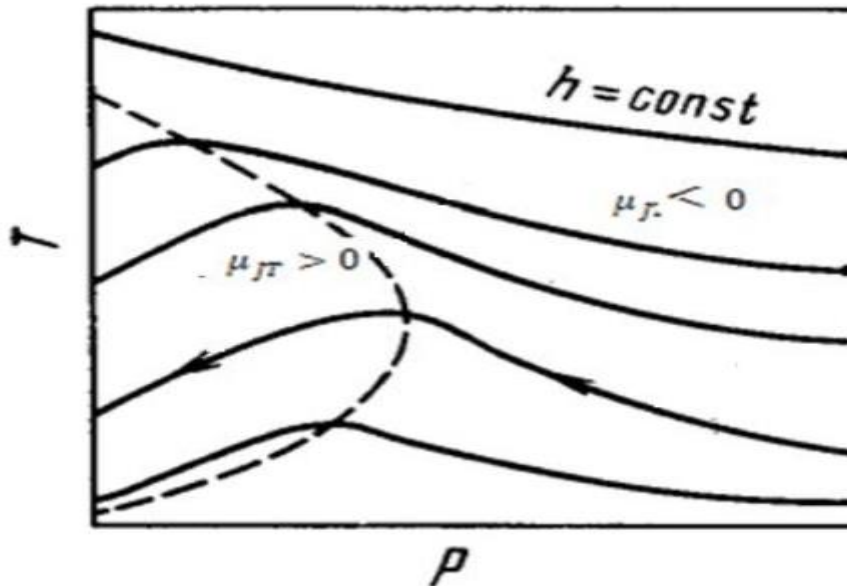


Figure 1.6 Joule-Thomson inversion curve

"curve the Joule-Thomson coefficient is zero" ($\mu_{JT} = 0$).

"In the region temperature decrease" $\mu_{JT} > 0$ (*positive effect*).

"In the region of increasing temperature" $\mu_{JT} < 0$ (*negative effect*).

We can write:

$$\begin{aligned}\mu_{JT} &= \left(\frac{\partial T}{\partial P} \right)_h = - \left(\frac{\partial T}{\partial h} \right)_P \left(\frac{\partial h}{\partial P} \right)_T \\ dh &= \left(\frac{\partial h}{\partial T} \right)_P dT + \left(\frac{\partial h}{\partial P} \right)_T dP\end{aligned}\tag{2}$$

$$\begin{aligned}&= C_p dT + \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right] dP \\ \mu_{JT} &= \frac{1}{C_p} \left[T \left(\frac{\partial v}{\partial T} \right)_P - v \right]\end{aligned}\tag{3}$$

An ideal gas would not undergo a change in temperature when it expands through the Joule-Thomson valve. An equation of state for gases that illustrates the behavior of real gases is the Van der Waals equation [11, 16]

$$\left(P + \frac{a}{v^2} \right) (v - b) = RT\tag{4}$$

a:measures intermolecular forces

b:measures the dimensions of molecules.

$$\mu_{JT} = \frac{(2a/RT)(1-b/v)^2 - b}{C_p \left[1 - (2a/vRT)(1-b/v)^2 \right]}\tag{5}$$

$$\mu_{JT} = \frac{1}{C_p} \left[\frac{2a}{RT} - b \right]\tag{6}$$

$$\begin{aligned}
v &= \frac{RT}{P} \\
\left(\frac{\partial v}{\partial T} \right)_P &= \frac{R}{P} = \frac{v}{T} \\
\mu_{JT} &= \frac{1}{C_p} \left[T \frac{v}{T} - v \right] = 0
\end{aligned} \tag{7}$$

Table1.1 The maximum inversion temperature of some gases [1, 2, 7]

Gas	K	°R
Oxygen	761	1370
Argon	722	1300
Azote	622	1120
Air	603	1085
Neon	250	450
Hydrogen	202	364
Helium	40	72

It can be observed that all gases can be classified into two families, the first includes those which have a maximum inversion temperature above ambient temperature (the majority of gases) and the second brings together gases whose maximum inversion temperature is lower than the room temperature which includes neon, hydrogen and helium. This classification allows us to determine the process of obtaining low temperature, the Joule–Thomson process or other process. Thus, for a gas to be liquefied by throttling, it is necessary, above all, bring its temperature below its maximum inversion temperature. If this condition is satisfied, we ask ourselves at what pressure we must compress the gas to have a maximum Joule-Thomson effect at a given initial temperature[1, 2, 7].

1.5 Isentropic process:

To produce an isentropic expansion of a real gas, the gas would have to relax adiabatically and in the absence of any friction. It would therefore be necessary that all the energy of the gas is transformed into work transferred to the external environment. He it is obvious that at this point, the drop in the internal energy of the gas will be at its maximum comparable to other expansion processes at the same initial conditions and at same degree of relaxation. Thus, such a process is accompanied by a maximum decrease in temperature. The work produced by the expansion of the gas in this process must be transmitted to a gas-separated device[11, 17].

The temperature variation in the isentropic process can be determined from the equation:

$$ds = \frac{\delta Q}{T} \tag{8}$$

$$ds = \frac{cp}{T} dT - \left(\frac{\partial v}{\partial T} \right)_p dP = 0 \quad (9)$$

$$\left(\frac{\partial T}{\partial P} \right)_s = \mu_s = \frac{T}{Cp} \left(\frac{\partial v}{\partial T} \right)_p = \frac{\beta v T}{Cp} \quad (10)$$

μ_s is the isentropic expansion coefficient for gases obeying the law

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p \quad (11)$$

With Z is the compressibility factor

$$Pv = ZRT \quad (12)$$

$$\mu_s = \frac{RT}{PCp} \left[Z + T \left(\frac{\partial Z}{\partial T} \right)_p \right] \quad (13)$$

If it compares between μ_T and μ_s we obtain the relation: From the previous equations, we can notice that:

- The value of μ_s " is practically positive in the entire region of state of the" fluid.
- An increase in temperature is accompanied by an increase in the isentropic expansion coefficient μ_s and therefore in the expansion work.

$$\mu_s = \mu_T + \frac{v}{Cp} \quad (14)$$

1.6 Constant U process:

If we expand a gas under the same conditions as during expansion isenthalpic, that is to say without exchange of heat or work with the environment outside. The expansion occurs in a rigid wall system, the total energy of the system during such a process will remain constant. The device diagram used to carry out this process is shown in Figure1.7 . It consists of two rigid-walled chambers connected by a pipe, the flow rate of the fluid is controlled by a valve. The whole thing is thermally insulated.

Initially, chamber A is filled with a gas at pressure P_1 and at temperature T_1 while chamber B is empty. It opens the valve to allow the gas to diffuse into chamber B. After a certain time, the system is in equilibrium with a final temperature T_2 and final pressure P_2

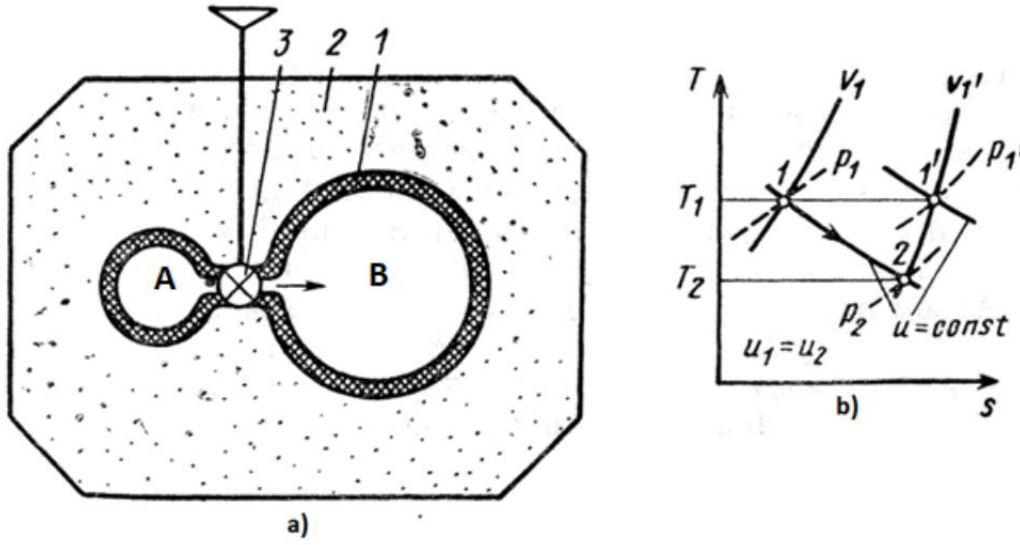


Figure 1.7 Schematic of the device used to carry out the $U=Cst$ process and the representation of the process on a T-S diagram

$$T_2 < T_1 \text{ et } P_2 < P_1$$

The temperature variation during the expansion process at $U=cst$ will be given by the expression:

$$\left(\frac{\partial T}{\partial v} \right)_U = -\frac{1}{C_v} \left(\frac{\partial U}{\partial v} \right)_T \quad (15)$$

$$\mu_U = \left(\frac{\partial T}{\partial P} \right)_U = - \left(\frac{\partial U}{\partial P} \right)_T / \left(\frac{\partial U}{\partial T} \right)_P \quad (16)$$

$$\left(\frac{\partial U}{\partial T} \right)_P = T \left(\frac{\partial s}{\partial T} \right)_P - P \left(\frac{\partial v}{\partial T} \right)_P = C_p - \beta v P \quad (17)$$

$$\mu_U = \left(\frac{\partial T}{\partial P} \right)_U = - \left(\frac{\partial U}{\partial P} \right)_T / (C_p - \beta v P) \quad (18)$$

For an ideal gas: $\left(\frac{\partial U}{\partial v} \right)_T = \left(\frac{\partial U}{\partial P} \right)_T = 0$ consequently $dT=0$ However for a real gas μ_U is always positive, that is to say that there is always cooling of the gas during an expansion at $U=cst$.

Chapter 2: Gas Liquefaction Processes

2.1 Importance and use of liquefied gases:

It can note three points of importance of liquefied gases:

- a- Obtaining pure gases from a mixture by the phenomenon of boiling or condensation at constant temperature and pressure
- b- Ease and economy of transport: the liquid occupies less space than that occupied by the gas which makes it easier to transport and save their means
- c- Uses of low temperatures: some gases have condensation temperatures lower than the ambient temperature

2.2 Brief History of Low Temperature Production[2, 4, 18]:

1789	Martin Van Marum liquefies ammonia by simple compression, wanting to verify Boyle Mariotte's law $PV/T = \text{cst}$
1823	Michael Faraday liquefies chlorine in the same way but he failed with air gases, which he therefore considered as permanent gases.
1845	Mr. Faraday was able to liquefy the most known gases at the time. Six of them, however, still resisted (O_2 , H_2 , N_2 , CO , CH_4 , NO)
1863	T. Andrews showed that $T_{\text{liq}} = f(P) < T_{\text{critical}}$ gases
1877	Louis Paul Cailletet was able to liquefy O_2 and N_2 .
1884	Wroblewski and Olszewski completed the liquefaction of Nitrogen and Oxygen at the laboratory of the University of Cracow (Poland.)
1892	Dewar invented a vacuum insulated tank for the storage of cryogenic fluids
1902	Claude developed a system for liquefying air using an expansion engine
1908	Onnes liquefied Helium
1934	Kapitza designed and built the first expansion engine for helium
1948	The first oxygen production plant in the USA with a capacity of 140 tons/day
1949	Production reaches 300 tons/day of oxygen
1959	Large liquid hydrogen plant installed in Torrance, California for NASA
1963	Production of 60 tons/day of liquid hydrogen by Linde

2.3 Ideal thermodynamic system:

Among the processes used in cryogenics, we find some elementary processes including in particular the maintenance of cryogenic temperatures, cooling, liquefaction of pure substances or mixtures and separation of gaseous mixtures. All these operations require an expenditure of energy even from a theoretical point of view, when all the transformations are reversible. This demand for energy increases with the lowering of temperature. Indeed the total energy expressed in the form of the work expended during a cryogenic process which can be written in the form[2, 8, 16]:

$$W = W_i + \Delta W \quad (19)$$

W_i the work required to accomplish an ideal process

ΔW the extra work required to compensate for losses in actual transformations.

2.4 Liquefaction cycle

2.4.1 Ideal liquefaction cycle

The ideal cycle from a thermodynamic point of view is the Carnot cycle (Figure 2.1). There Liquefaction is a process in an open system. It choose both first transformations in the Carnot cycle; isothermal compression reversible from the initial state to a relatively high pressure followed by an expansion reversible adiabatic through an expansion motor until the saturated state of the substance to liquefy[1, 2].

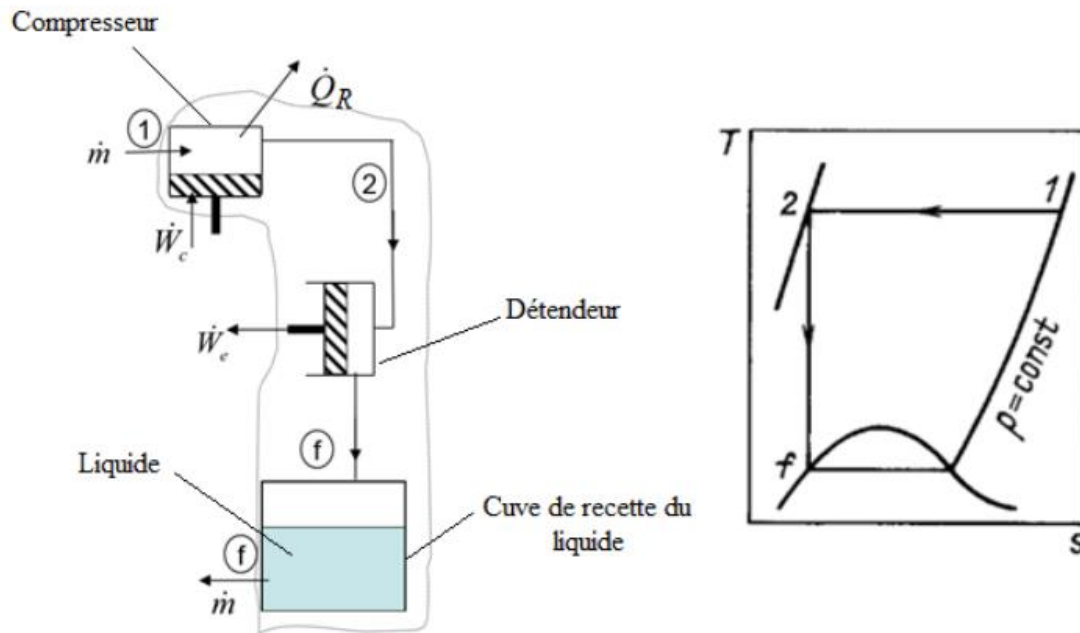


Figure 2.1 Schematic of the installation and the ideal liquefaction cycle

The first law of thermodynamics for open systems is written:

$$\dot{Q}_{net} + \dot{W}_{net} = \sum_{sortie} \dot{m}h - \sum_{entree} \dot{m}h \quad (20)$$

Its application on the compressor, regulator and recipe tank assembly gives:

$$\dot{Q} + \dot{W}_i = \dot{m} (h_L - h_1) \quad (21)$$

The second law of thermodynamics allows us to write:

$$\dot{Q} = \dot{m} T (s_1 - s_L) \quad (22)$$

So :

$$\frac{\dot{W}_i}{\dot{m}} = T_1 (s_1 - s_L) - (h_1 - h_L) \quad (23)$$

2.4.2 FOM (Figure of Merit)

For a liquefaction cycle the thermodynamic efficiency is written [1, 2]

$$FOM_{liquefaction} = \frac{\dot{W}_i / \dot{m}_L}{\dot{W} / \dot{m}_L} \quad (24)$$

2.4.3 Simple Linde-Hampson Cycle:

The Linde-Hampson system is the second system used for liquefaction of gases after the system using cascade cooling, the diagram of the installation and the transformation cycle are presented on the Figure 2.2 ; The gas enters the compressor in state 1 ($P_1=1$ atm, $T_1=T_{ambiant}$); he undergoes an isothermal compression which brings it back to state 2 ($P_2, T_2= T_1$). So it is cooled at constant pressure ($P_3=P_2$) in the exchanger, before being expanded up to atmospheric pressure ($P_4=P_g= P_L=P_1$) in a regulator (pressure valve Joule–Thomson) The fluid leaving the regulator is a mixture of gas and liquid. The liquid is extracted from the tank while the saturated vapor (state g) is returned to the heat exchanger (g - 1) to cool the incoming gas (2 – 3)[5, 10, 19, 20].

To analyze the performance of the system, we assume that:

- ☐ All transformations are reversible except relaxation isenthalpic in the Joule-Thomson valve
- ☐ No heat exchange with the surrounding environment.
- ☐ 100% efficient heat exchanger.

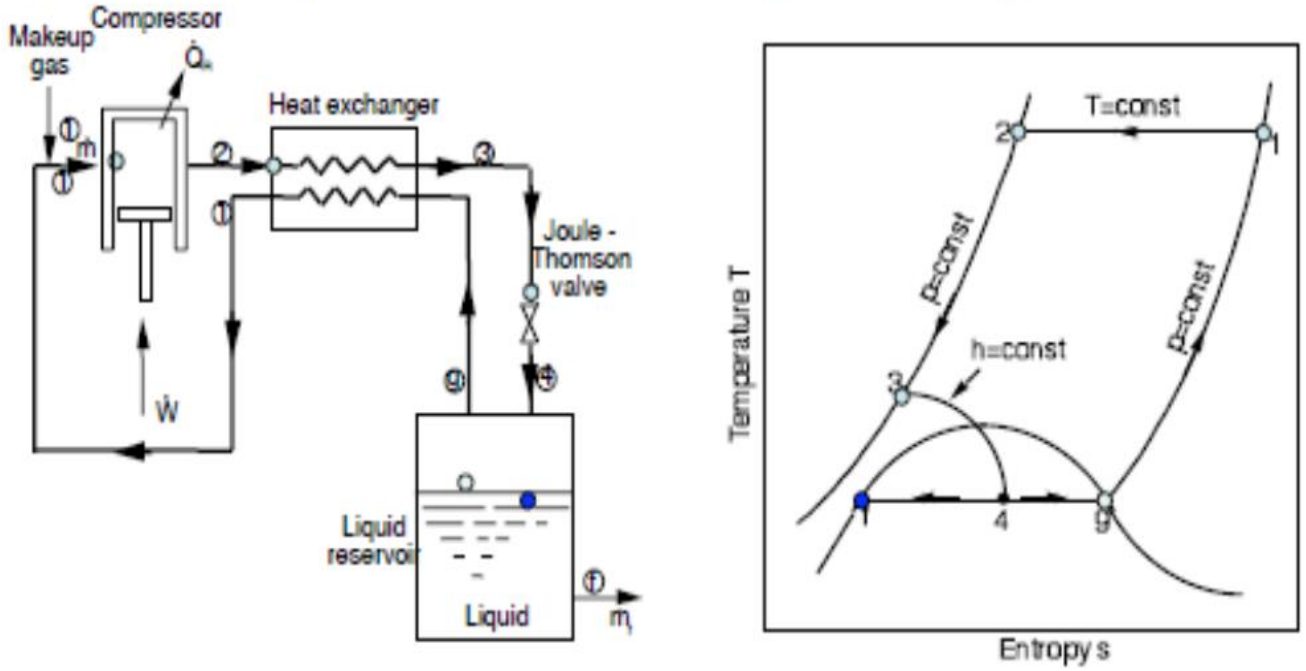


Figure 2.2 Schematic of the simple Linde liquefaction system and the transformation cycle

In steady state, the first law of thermodynamics around the exchanger, valve and liquid reservoir assembly gives[2]:

$$0 = (\dot{m} - \dot{m}_f) h_1 + \dot{m}_L h_L - \dot{m} h_2 \quad (25)$$

$$\frac{\dot{m}_L}{\dot{m}} = y = \frac{h_1 - h_2}{h_1 - h_L} \quad (26)$$

The liquefied fraction depends on the initial state 1 (P_1, T_1), and states 2 (P_2). The state 1 is practically prescribed, so to maximize the liquefied fraction we must optimize the pressure P_2 in order to minimize the enthalpy at point 2 h_2 . The work necessary for liquefaction is determined by the application of the first principle of thermodynamics on the compressor which gives:

$$\dot{W} + \dot{Q} = \dot{m} (h_2 - h_1) \quad (27)$$

$$\dot{Q} = \dot{m} T_1 (s_2 - s_1) \quad (28)$$

$$\frac{\dot{W}}{\dot{m}} = T_1(s_1 - s_2) - (h_1 - h_2) \quad (29)$$

$$\frac{\dot{W}}{\dot{m}_L} = \frac{\dot{W}}{\dot{m} \times y} = \frac{(h_1 - h_L)}{(h_1 - h_2)} [T_1(s_1 - s_2) - (h_1 - h_2)] \quad (30)$$

The thermodynamic efficiency of the simple Linde process is written:

$$FOM = \frac{\dot{W}_i / \dot{m}_L}{\dot{W} / \dot{m}_L} = \frac{[T_1(s_1 - s_L) - (h_1 - h_L)] (h_1 - h_2)}{[T_1(s_1 - s_2) - (h_1 - h_2)] (h_1 - h_L)} \quad (31)$$

2.4.4 Pre-cooled Linde-Hampson process:

The study of the variation of the liquefied fraction y as a function of the temperature at the inlet of the exchanger showed that the performance of the Linde Hampson process (Figure 2.3) could be improved if the temperature at the inlet of the exchanger is below room temperature. For 100% efficiency of the heat exchanger, temperatures T_3 and T_6 are the same and cannot be lower than the boiling temperature refrigerant. The application of the first law of thermodynamics applies to all heat exchangers, valve and liquid tank give[2, 17]:

$$0 = (\dot{m} - \dot{m}_L)h_1 + \dot{m}_L h_L + \dot{m}_r h_a - \dot{m} h_2 - \dot{m}_r h_d \quad (32)$$

Setting $r = \frac{\dot{m}_r}{\dot{m}}$ it obtain:

$$y = \frac{h_1 - h_2}{h_1 - h_L} + r \frac{h_a - h_c}{h_1 - h_L} \quad (33)$$

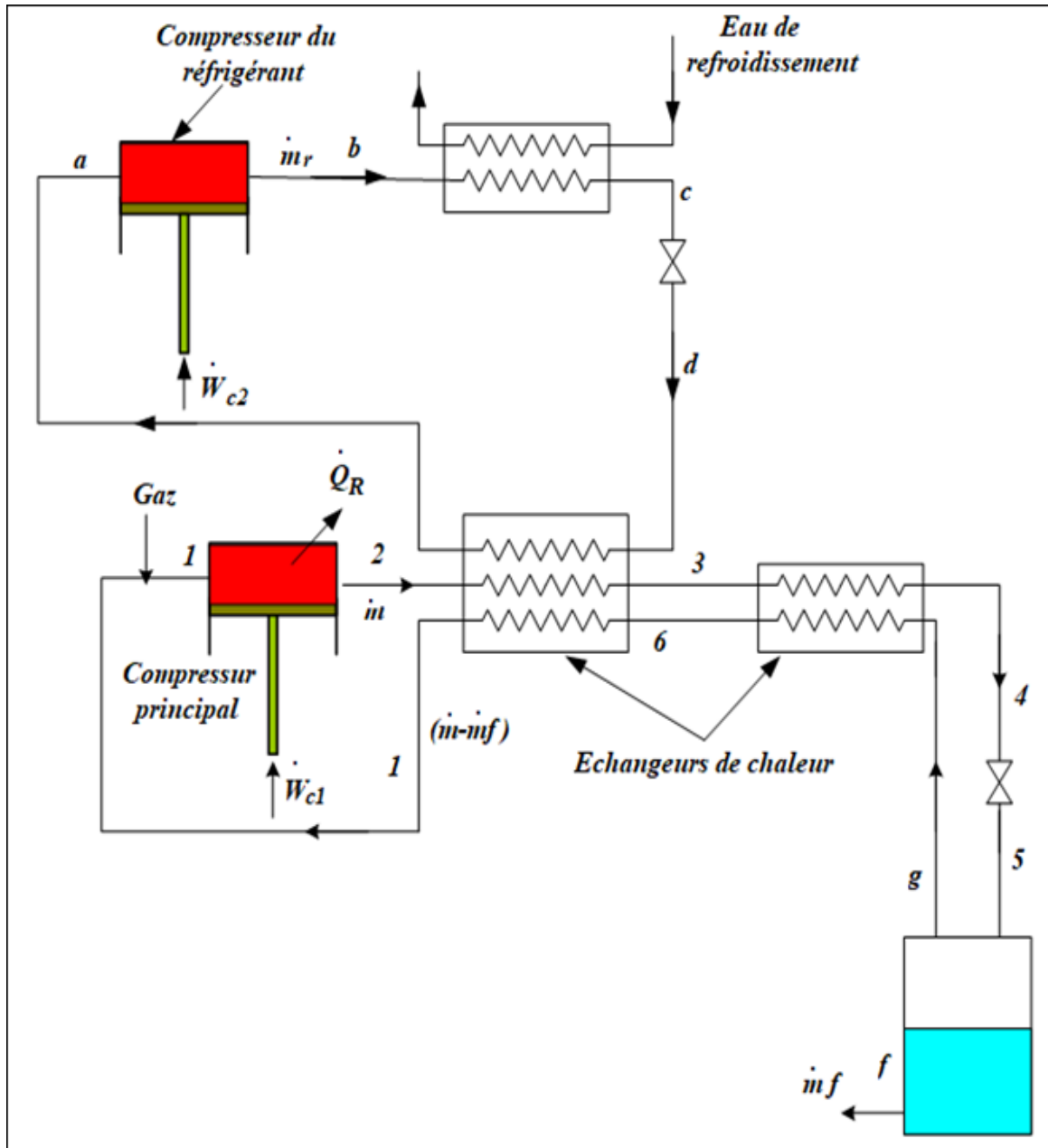
$\dot{m}_r$ is the mass flow rate of refrigerant gas

The maximum liquefied fraction for a pre-cooled Linde Hampson system is:

$$y_{max} = \frac{h_6 - h_3}{h_6 - h_L} \quad (34)$$

If the compression in the main compressor is isothermal and reversible and in the auxiliary compressor is isentropic then:

$$\frac{\dot{W}}{\dot{m}} = T_1(s_1 - s_2) - (h_1 - h_2) + r(h_b - h_a) \quad (35)$$



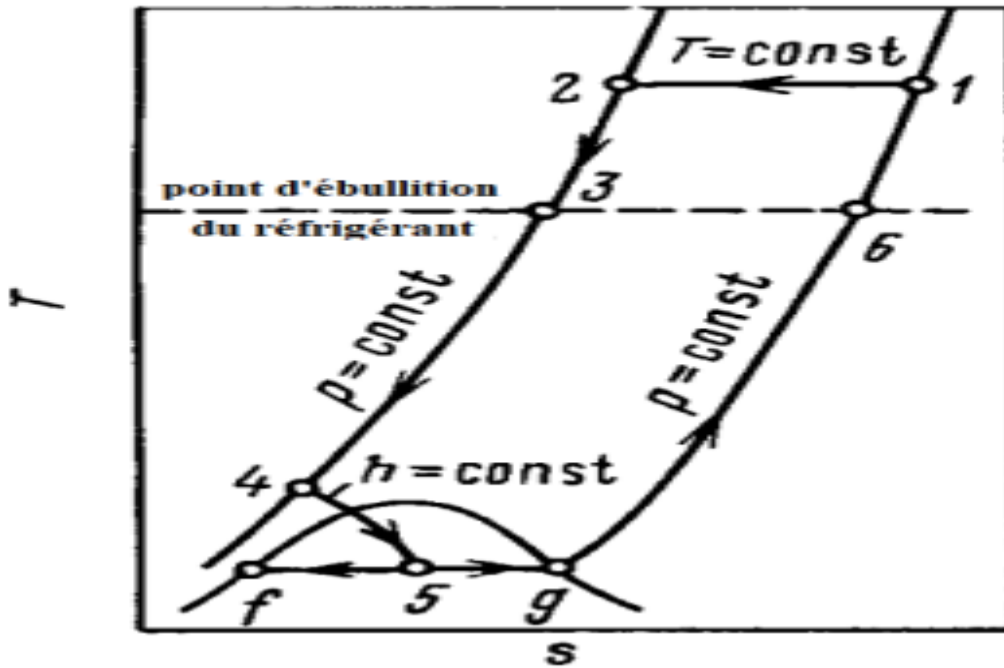


Figure 2.3 Schematic of Pre-Cooled Linde Liquefaction System and the Transformation Cycle

2.4.5 Dual pressure (double compression) Linde-Hampson process:

The simple Linde - Hampson system can be modified in other ways to reduce the total work required, although this modification will reduce somewhat the quantity of liquid obtained. Since only a small part of the gas tablet is liquefied in the simple system, we can modify it from so that part of the working gas expands by throttling at a pressure intermediate P_2 greater than the atmospheric pressure P_1 and the other part is expands to atmospheric pressure(Figure 2.4). The compression work is in function of the compression ratio, thus a reduction in the compression ratio results in a reduction in the work required [20-22]

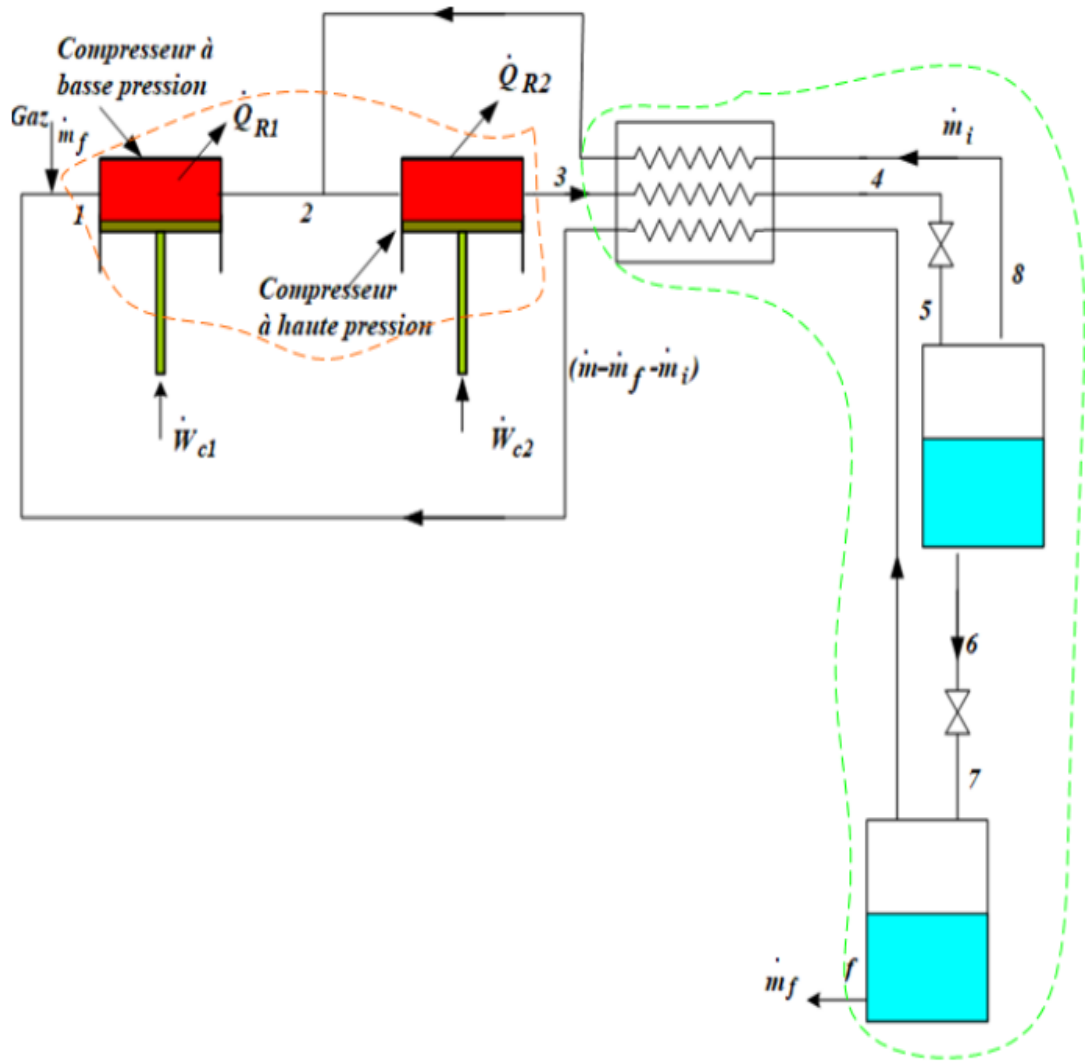
The application of the first law of thermodynamics to the whole of the heat exchanger, Joule-Thomson valve and the two tanks gives:

$$y = \frac{h_1 - h_3}{h_1 - h_L} - i \frac{h_1 - h_2}{h_1 - h_L} \quad (36)$$

With : $i = \frac{\dot{m}_i}{\dot{m}}$

$\dot{m}_i$ is the mass flow rate of gas at the intermediate pressure at point 8

$$\frac{\dot{W}}{\dot{m}} = T_1(s_1 - s_3) - (h_1 - h_3) - i \left[T_1(s_1 - s_2) - (h_1 - h_2) \right] \quad (37)$$



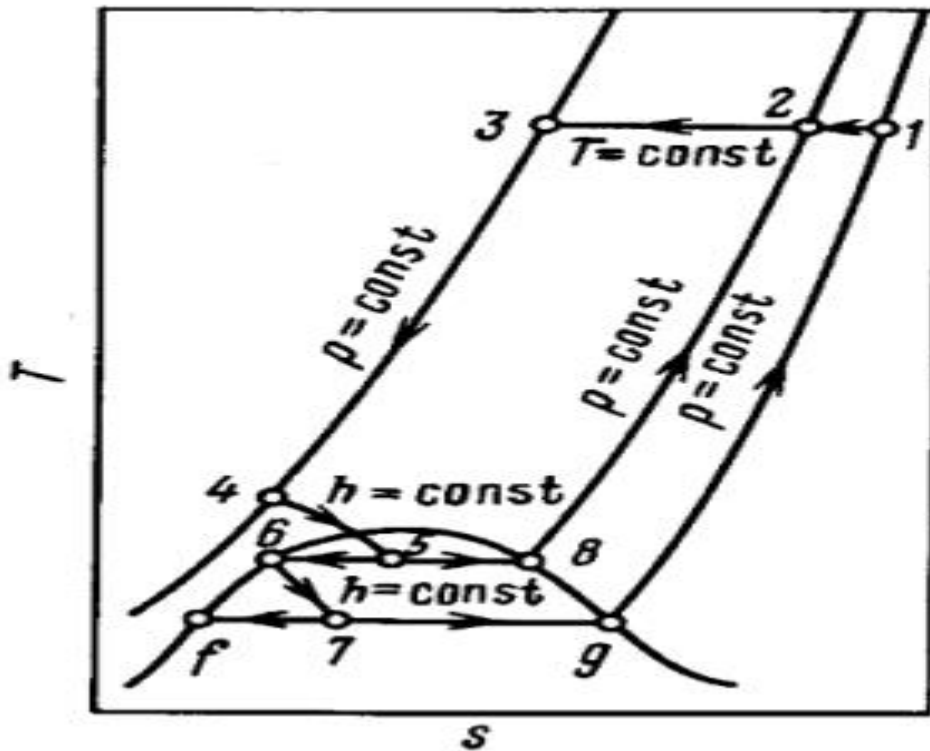


Figure 2.4 Schematic of the dual pressure Linde system and the transformations cycle

2.4.6 Pre-cooled Linde system for the liquefaction of Neon and Hydrogen

Because of its simplicity, the Linde simple system is very desirable for small-scale liquid production, however, the simple system of Linde would not work with Ne, H₂ and He because the temperature maximum inversion of these gases is lower than the ambient temperature, then the use of pre-cooling allows the temperature to be reduced gases leaving the compressor (Figure 2.5). The problem remains to choose the refrigerant used for cooling the working fluid. The refrigerant can be Air, Oxygen, Methane, Fluorine, Argon and Nitrogen. Air, Oxygen, Methane and Fluorine are not used because the risk of explosion, argon is expensive, this favors the use of Nitrogen as pre-cooling fluid for liquefaction of Hydrogen and Neon[9, 23].

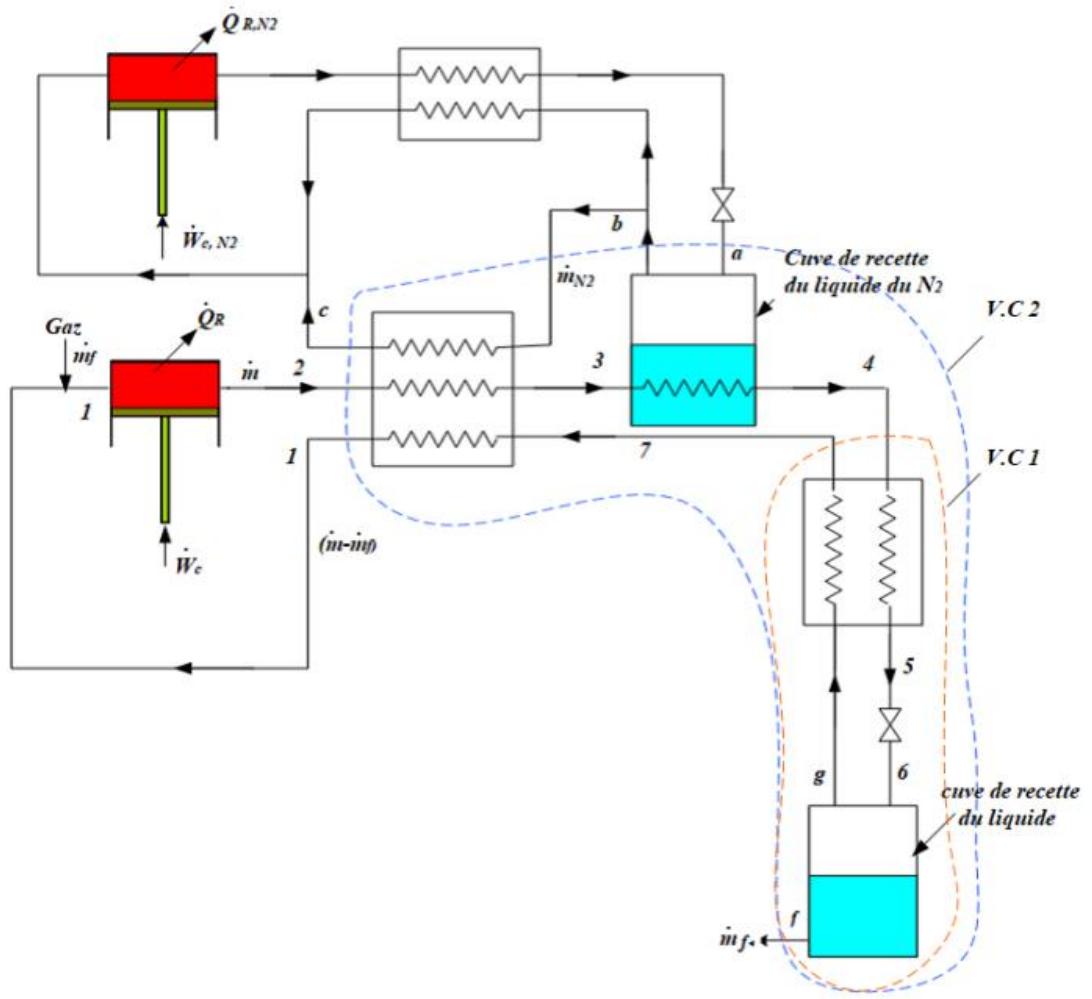


Figure 2.5 Schematic of Linde system for the liquefaction of H₂ and Ne

The application of the first principle of thermodynamics on V.C 1 gives:

$$y = \frac{h_7 - h_4}{h_7 - h_L} \quad (38)$$

The application of the first principle of thermodynamics on V.C 2 gives:

$$0 = \dot{m}_{N_2} h_c + (\dot{m} - \dot{m}_L) h_1 + \dot{m}_L h_L - \dot{m}_{N_2} h_a - \dot{m} h_2 \quad (39)$$

$\dot{m}_{N_2}$ is the flow rate of evaporated N₂ to pre-cool H₂ or Ne

Setting: $z = \dot{m}_{N_2} / \dot{m} z$

$$z = \frac{h_2 - h_1}{h_c - h_a} + y \frac{h_1 - h_L}{h_c - h_a} \quad (40)$$

2.4.7 Effect of heat exchanger effectiveness on system performance:

A non-ideal heat exchanger will have an efficiency less than 1. For the simple Linde system, the cold fluid does not leave the exchanger at condition 1 but at a lower temperature corresponding to the point 1', while the hot fluid leaves it at a temperature corresponding to the point 3' as shown by the Linde cycle in Figure 2.6[11, 19, 22]

$$\varepsilon = \frac{h_1' - h_g}{h_1 - h_g} \quad (41)$$

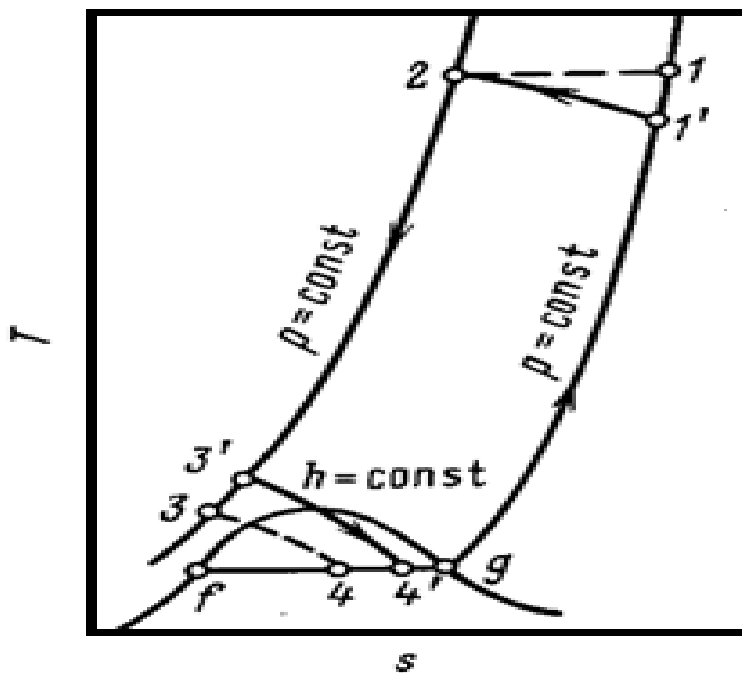


Figure 2.6 Influence of heat exchanger effectiveness on system performance

The application of the first law of thermodynamics to the entire system with the exception of the compressor we find:

$$y = \frac{h_1' - h_2}{h_1' - h_L} \quad (42)$$

$$h_1' = \varepsilon(h_1 - h_g) + h_g \quad (43)$$

$$y = \frac{(h_1 - h_2) - (1 - \varepsilon)(h_1 - h_g)}{(h_1 - h_L) - (1 - \varepsilon)(h_1 - h_g)} \quad (44)$$

2.4.8 Effect of heat input from the external environment:

The losses are due to poor thermal insulation, they reduce the liquefied fraction. Let us take the case of the simple Linde process as shown in Figure 2.6. The first principle applied to the system with heat inputs from external environment results in [2, 4, 18]:

$$\dot{Q} = (\dot{m} - \dot{m}_f) h_1 + \dot{m}_L h_L - \dot{m} h_2 \quad (45)$$

$$y = \frac{h_1 - h_2}{h_1 - h_L} - \frac{\dot{Q} / \dot{m}}{h_1 - h_L} \quad (46)$$

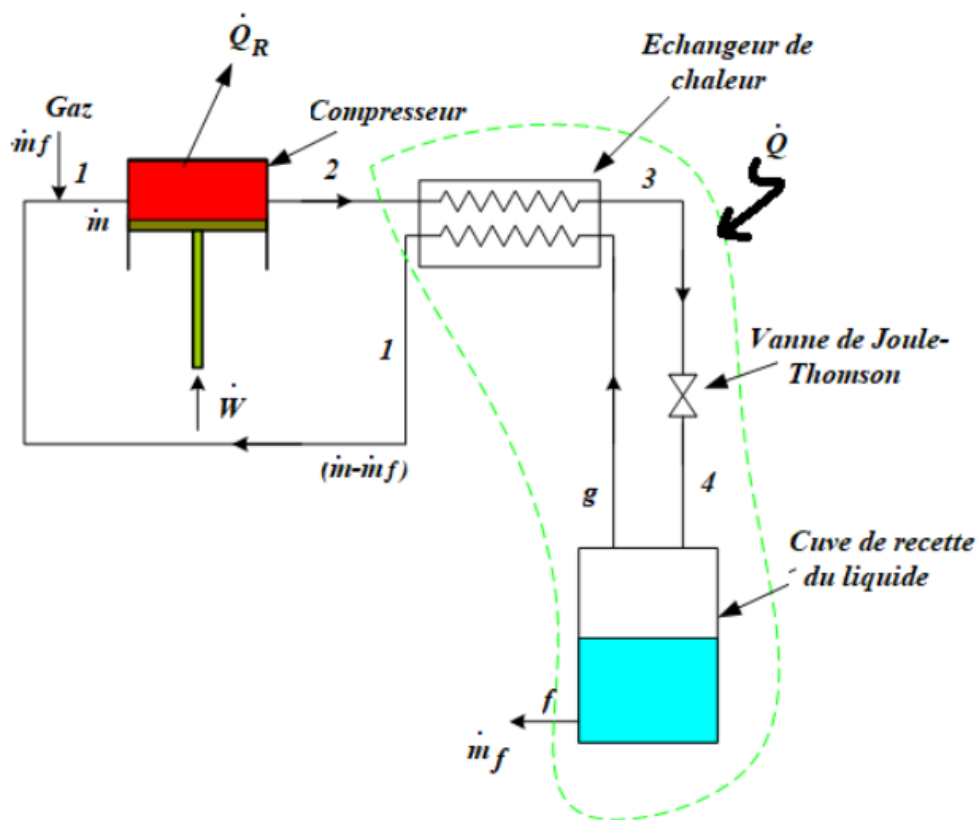


Figure 2.7 Schematic of the Linde system with heat inputs from the external environment

Chapter 3 :Cryogenic Cycles with Gas Expansion in Expanders

The cycles of this group are the most widespread in the cryogenic technique for obtaining cold and liquefying gases in heating installations medium and large production. Georges Claude (1870-1960) was able to bring to point for the first time at the beginning of the twentieth century an industrial process of liquefaction of the air with the expansion of the gas carried out in the piston expander. Depending on the gas temperature at the inlet of the expansion motor, there are three variants of connection of the expander in the system[13].

- Connection of the expander at the intermediate temperature level.
- Connection of the expander to the lower temperature level (outlet evaporator).
- Connection of the expander at the initial temperature level (outlet compressor).

3.1 Claude system

In the system the expander is connected to the intermediate level of temperature .The working gas is compressed at constant temperature to pressure P2 of approximately 4MPa (40 atm) and then passes through the first heat exchanger. Between 60 and 80% of the gas is then diverted from the main current, expanded to through a regulator and joins the gas from the return flow to the inlet of the second interchange. The gas to be liquefied cooled in the second and third exchanger is relaxed through the Joule Thomson valve until the state liquid-vapor. The liquid is withdrawn from the tank while the cold vapor is returned through the heat exchangers to the compressor. The cycle of Claude is shown in Figure 3.1 .On a T-s diagram[24].

The application of the first principle of thermodynamics to all the exchangers, expansion valve and liquid recipe tank gives:

$$0 = (\dot{m} - \dot{m}_L) h_1 + \dot{m}_L h_1 + \dot{m}_e h_3 - \dot{m} h_2 - \dot{m}_e h_e \quad (47)$$

If $x = \frac{\dot{m}_e}{\dot{m}}$ is the mass fraction of the gas passing through the expander, then the liquefied fraction can be obtained as follows:

$$y = \frac{\dot{m}_L}{\dot{m}} = \frac{h_1 - h_2}{h_1 - h_L} + x \frac{h_3 - h_e}{h_1 - h_L} \quad (48)$$

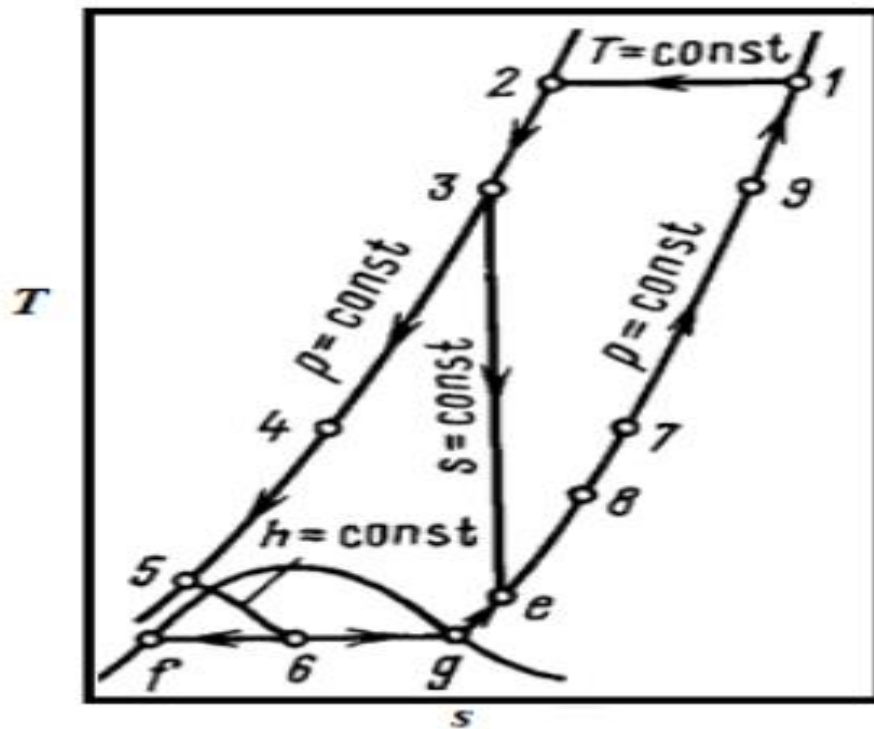
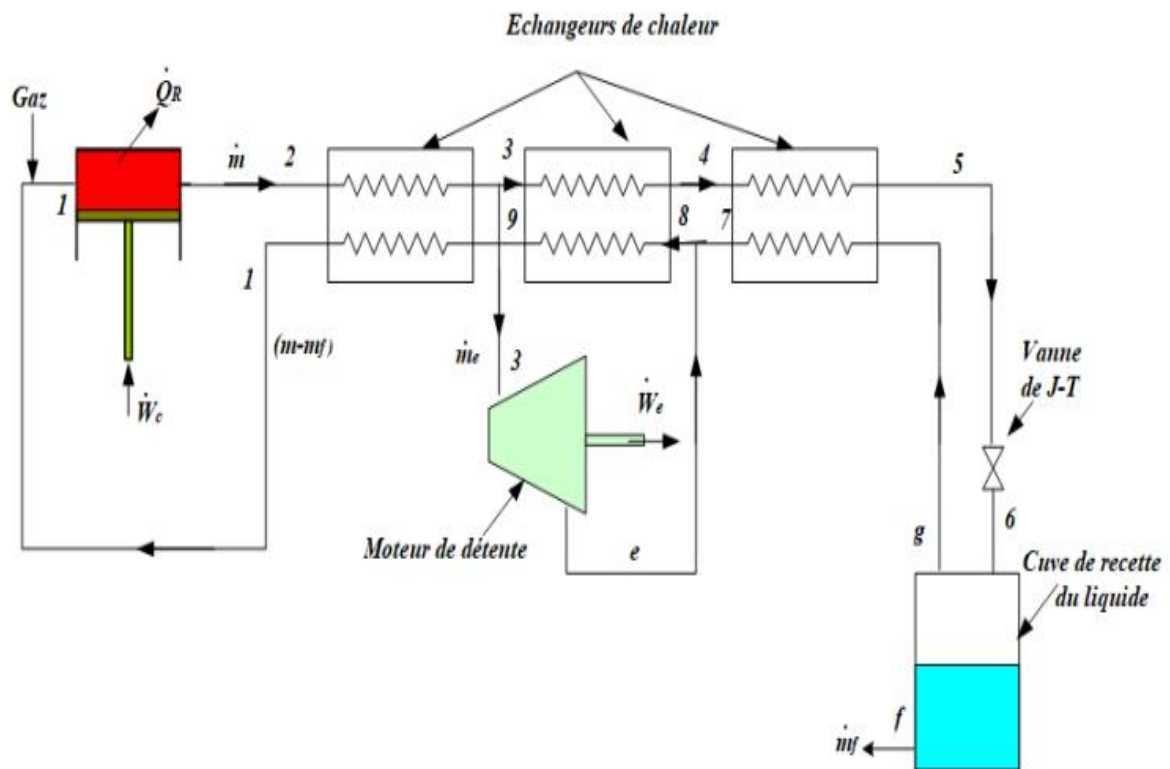


Figure 3.1 Schematic of the Claude Cycle liquefaction system and transformations

The work per unit of compressed mass necessary for the liquefaction of the gas is:

$$\frac{\dot{W}_{net}}{\dot{m}} = \frac{\dot{W}_c}{\dot{m}} + \frac{\dot{W}_e}{\dot{m}} \quad (49)$$

$$\dot{W}_e = \dot{m}_e (h_e - h_3) \quad (50)$$

$$\frac{\dot{W}_{net}}{\dot{m}} = [T_1(s_1 - s_2) - (h_1 - h_2)] - x(h_3 - h_e) \quad (51)$$

The last term of the previous equation is the reduction in energy due to the use of the work provided by the expansion motor.

3.2 Kapitza system

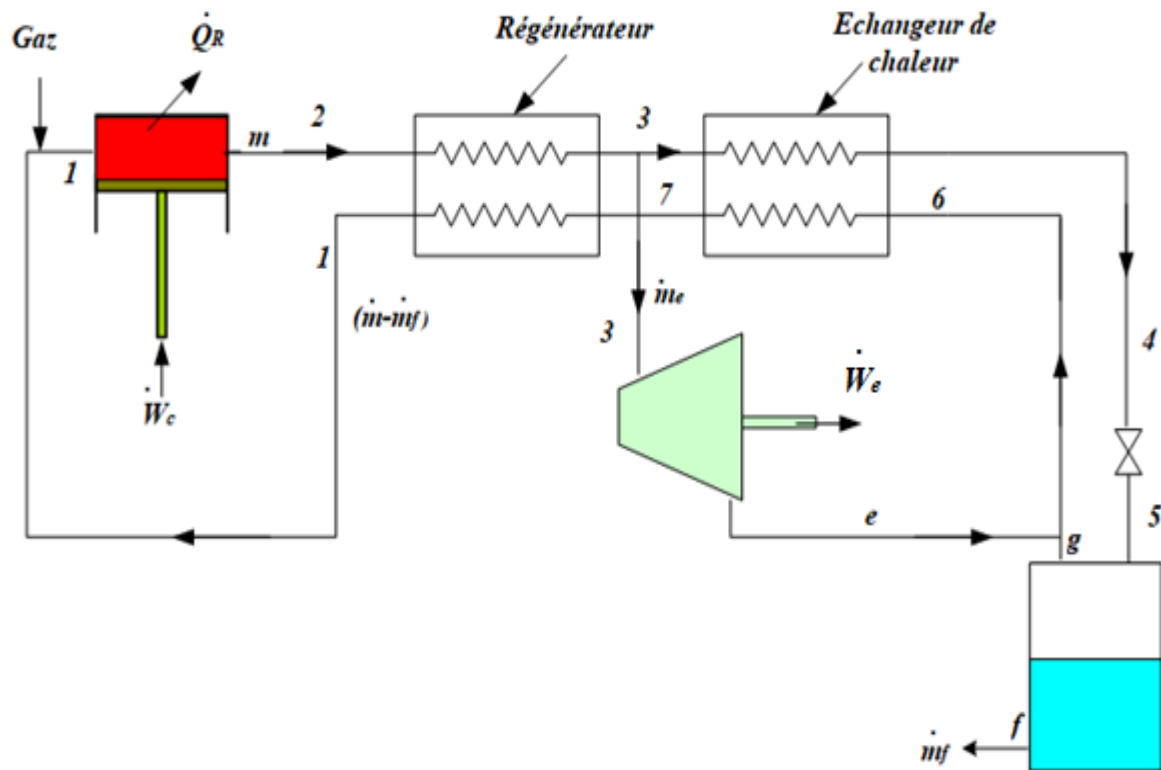


Figure 3.2 Schematic of the Kapitza liquefaction system

Invented by Kapitza in 1939 by modifying Claude's basic system by the elimination of the third exchanger and replacing the first exchanger with a regenerator. In this system the expander is connected to the lower level of temperature (evaporator outlet) as shown in Figure 3.2 . The regenerator/heat exchanger performs two different operations[25]:

- Gas cooling/heating
- Gas purification

During a cycle, a unit purifies by freezing impurities and cools the gas hot incoming. While the other unit heats the exiting gas and eliminates simultaneously the impurities frozen by evaporation. A valve is used to periodically move from one unit to another. This system was the first to use a rotating expansion valve instead of a reciprocating expansion valve. The Kapitza system operates at low pressures of around 7 atm.

The application of the first principle of thermodynamics to all the exchangers, expansion valve and liquid recipe tank gives:

$$y = \frac{\dot{m}_L}{\dot{m}} = \frac{h_1 - h_2}{h_1 - h_L} + x \frac{h_3 - h_e}{h_1 - h_L} \quad (52)$$

3.3 Heylandt system

Heylandt System is a high pressure system used in the liquefaction of the air. Typical operating pressure is approximately 200 atm. In 1949, Heylandt observed that when the Claude system operated in air with 200 atm and $x = 0.6$, the optimal value of the temperature T_3 before the engine expansion was close to room temperature, so he

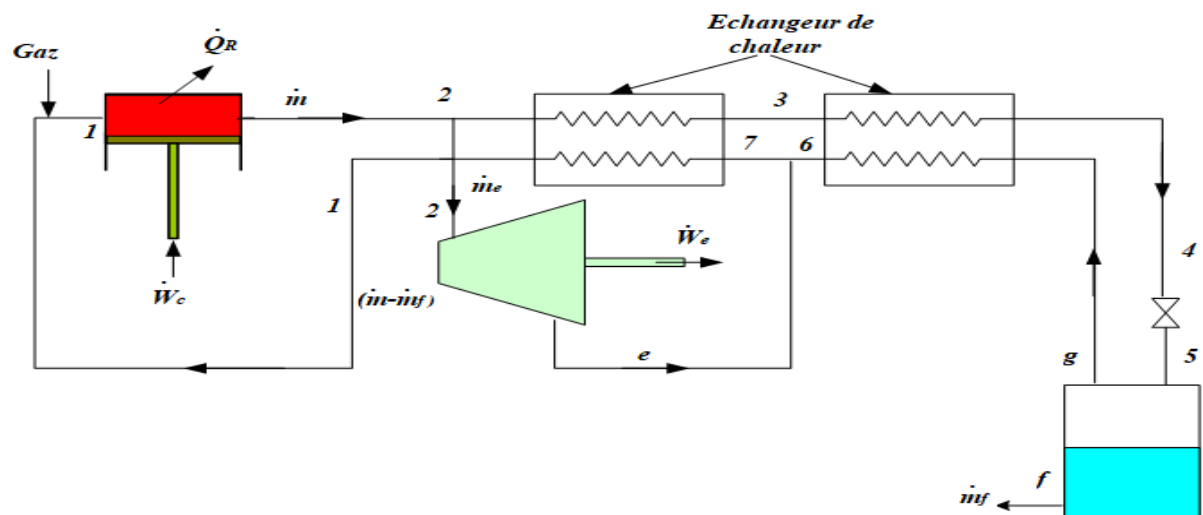


Figure 3.3 Schematic of the Heylandt liquefaction system

eliminated the first heat exchanger as presented in Figure 3.3[26-28] .

The application of the first principle of thermodynamics to all the exchangers, expansion valve and liquid recipe tank gives:

$$y = \frac{\dot{m}_L}{\dot{m}} = \frac{h_1 - h_2}{h_1 - h_L} + x \frac{h_2 - h_e}{h_1 - h_L} \quad (53)$$

Chapter 4 : Combined Cryogenic Cycles

4.1 Claude system with pre-cooling for liquefaction Hydrogen and Neon

Claude's process does not rely primarily on the Joule Thomson valve to produce low temperatures, so it can be used for liquefaction of H_2 and Ne without modification. The performance of Claude's system is improved with a pre-cooling of the working fluid using nitrogen as the fluid refrigerant (Figure 4.1)[26, 29, 30].

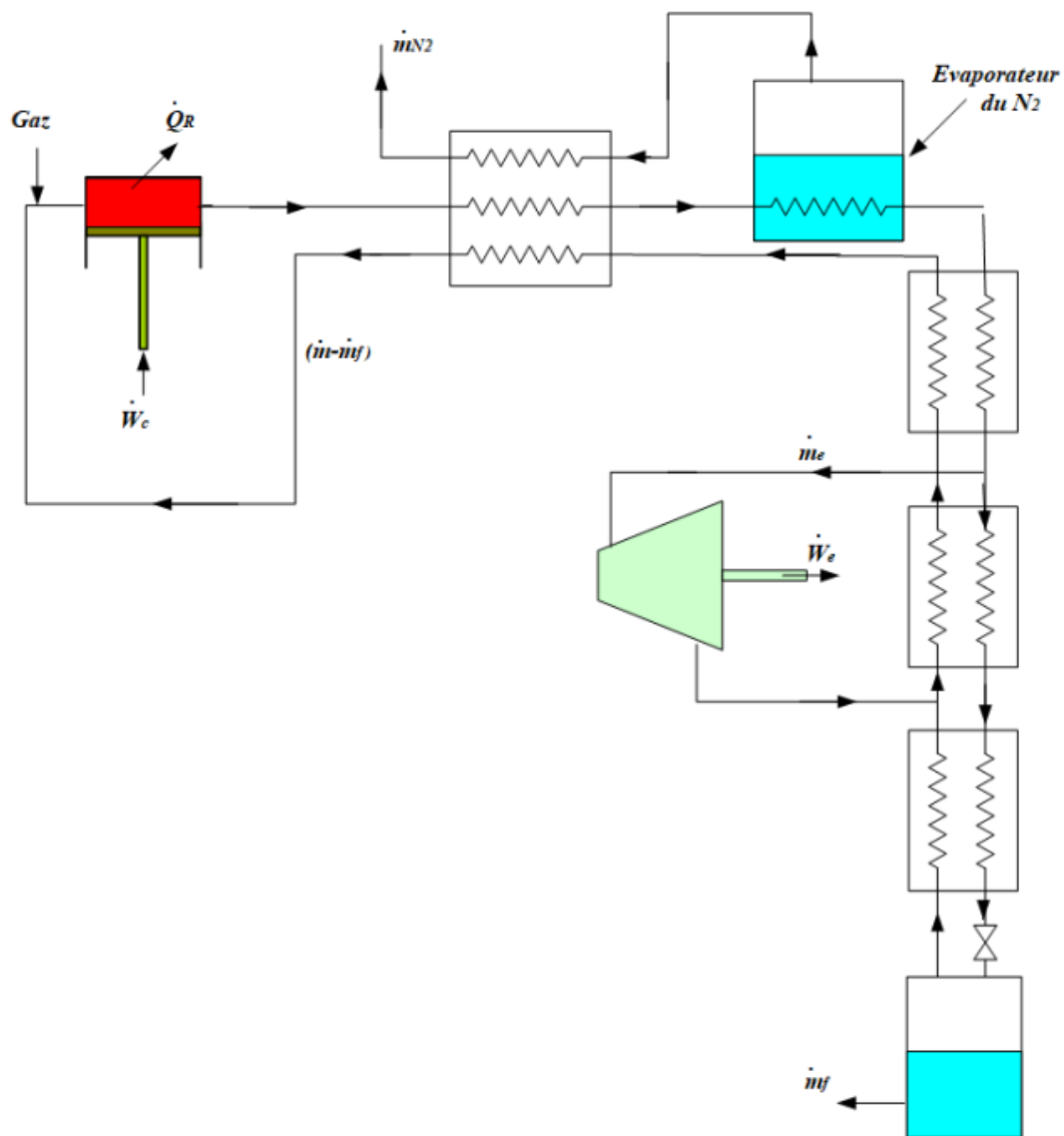
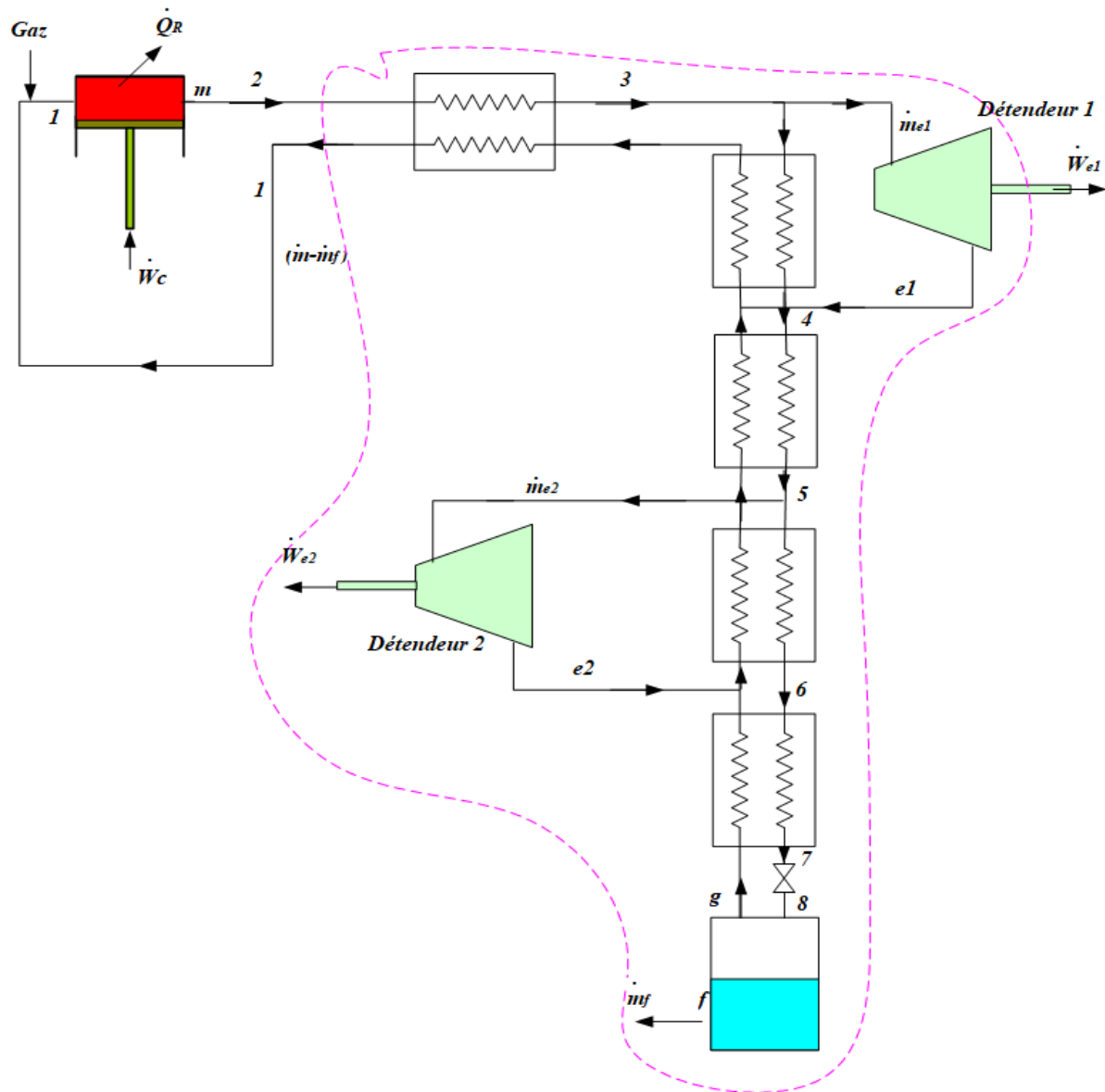


Figure 4.1 Schematic of Claude's system with pre-cooling for liquefaction of Hydrogen and Neon

4.2 Collins system for the liquefaction of Helium

It was invented in 1946 by Samuel C. Collins at the Massachusetts Institute of Technology (United States). This system is considered one of the most important achievements in cryogenic engineering (Figure 4.2). It presents an extension of the Claude's system. The system includes a compressor, a J-T valve, five heat exchangers, heat and two expansion motors. The inversion temperature of helium is around 40 K and to obtain liquid helium, T_7 (temperature at the inlet of the Joule-Thomson expansion valve) must be less than 7 K. Depending on mass flow rates and gas inlet pressure, two to six expansion motors (expander) are used [31-33] .



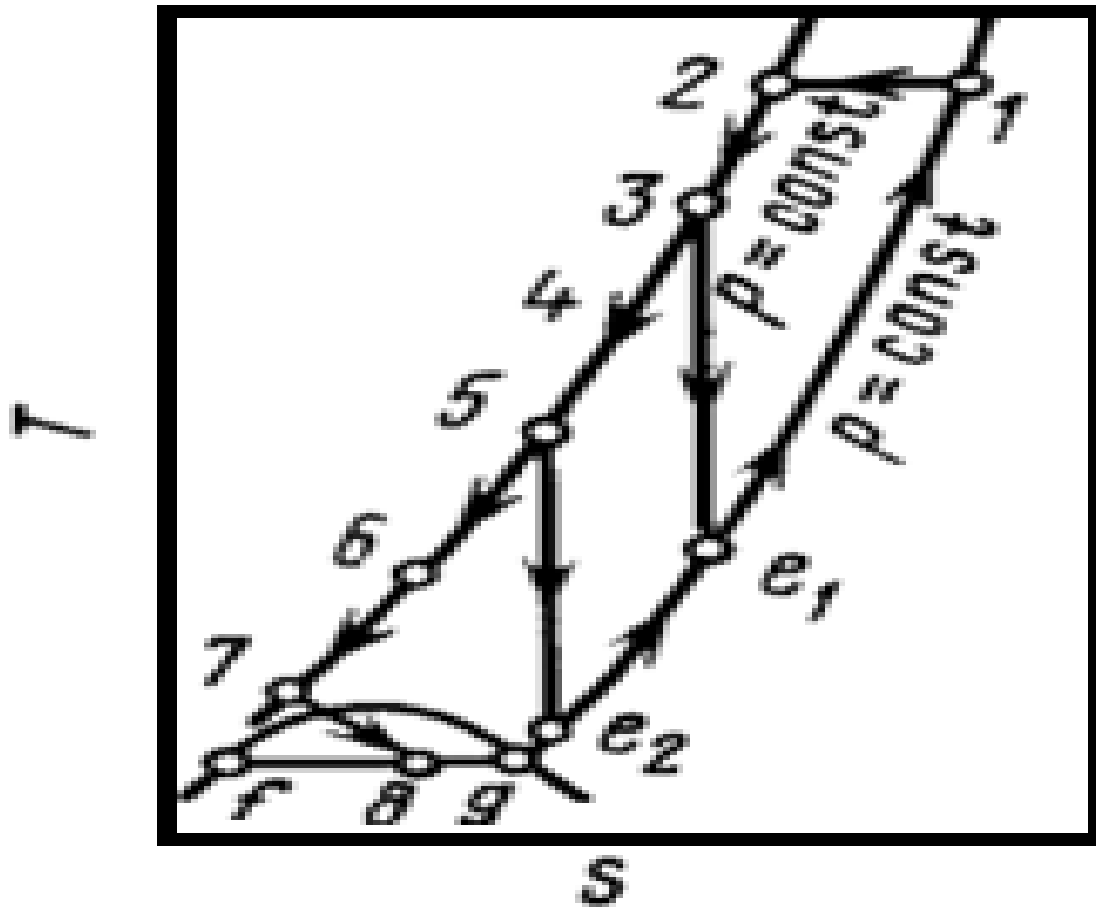


Figure 4.2 Schematic of the Collins system for the liquefaction of Helium and transformations cycle.

The application of the first law of thermodynamics to the volume of V.C control gives:

$$\dot{W}_{e1} + \dot{W}_{e2} = (\dot{m} - \dot{m}_L) h_1 + \dot{m}_L h_L - \dot{m} h_2 \quad (54)$$

$$\begin{aligned} \dot{W}_{e1} &= \dot{m}_{e1} (h_{e1} - h_3) \\ \dot{W}_{e2} &= \dot{m}_{e2} (h_{e2} - h_5) \end{aligned} \quad (55)$$

$$y = \frac{\dot{m}_f}{\dot{m}} = \frac{(h_1 - h_2)}{(h_1 - h_L)} + x_1 \frac{(h_3 - h_{e1})}{(h_1 - h_L)} + x_2 \frac{(h_5 - h_{e2})}{(h_1 - h_L)} \quad (56)$$

$$\begin{aligned} x_1 &= \frac{\dot{m}_{e1}}{\dot{m}} \\ x_2 &= \frac{\dot{m}_{e2}}{\dot{m}} \\ \dot{W}_c &= \dot{m} [T_1(s_1 - s_2) - (h_1 - h_2)] \\ \dot{W}_{e1} &= \dot{m}_{e1}(h_{e1} - h_3) \\ \dot{W}_{e2} &= \dot{m}_{e2}(h_{e2} - h_5) \\ \frac{\dot{W}_{net}}{\dot{m}} &= [T_1(s_1 - s_2) - (h_1 - h_2)] - x_1(h_3 - h_{e1}) - x_2(h_5 - h_{e2}) \end{aligned} \quad (57)$$

4.3 Effect of compressor efficiency and expander efficiency

Isothermal efficiency of the compressor[2, 26, 29]:

$$\eta_T = \frac{(\dot{W} / \dot{m})_{T=cst}}{(\dot{W} / \dot{m})} \quad (58)$$

Mechanical efficiency of the compressor.

$$\eta_{m,c} = \frac{(\dot{W} / \dot{m})_{rf}}{(\dot{W} / \dot{m})_{real}} = 1 - \frac{\dot{W}_{friction}}{\dot{W}_{real}} \quad (59)$$

Adiabatic efficiency of the expander:

$$\eta_{ad} = \frac{(h_1 - h_2)_{real}}{(h_1 - h_2)_{ad}} \quad (60)$$

Mechanical efficiency of the expander:

$$\eta_{m,e} = \frac{\dot{W}_{real}}{\dot{W}_{real} + \dot{W}_{fr}} \quad (61)$$

Total efficiency of the expander:

$$\eta_0 = \eta_{ad} \cdot \eta_{m,e} \quad (62)$$

Total efficiency of the compressor:

$$\eta_0 = \eta_T \eta_{m,c} \quad (63)$$

Considering Claude's liquefaction system, the compressor efficiency has no effect on the liquefied fraction as long as there is sufficient energy to achieve the pressure levels required for the cycle (Figure 4.3). However, work is directly related to the compressor efficiency[2, 26, 29].

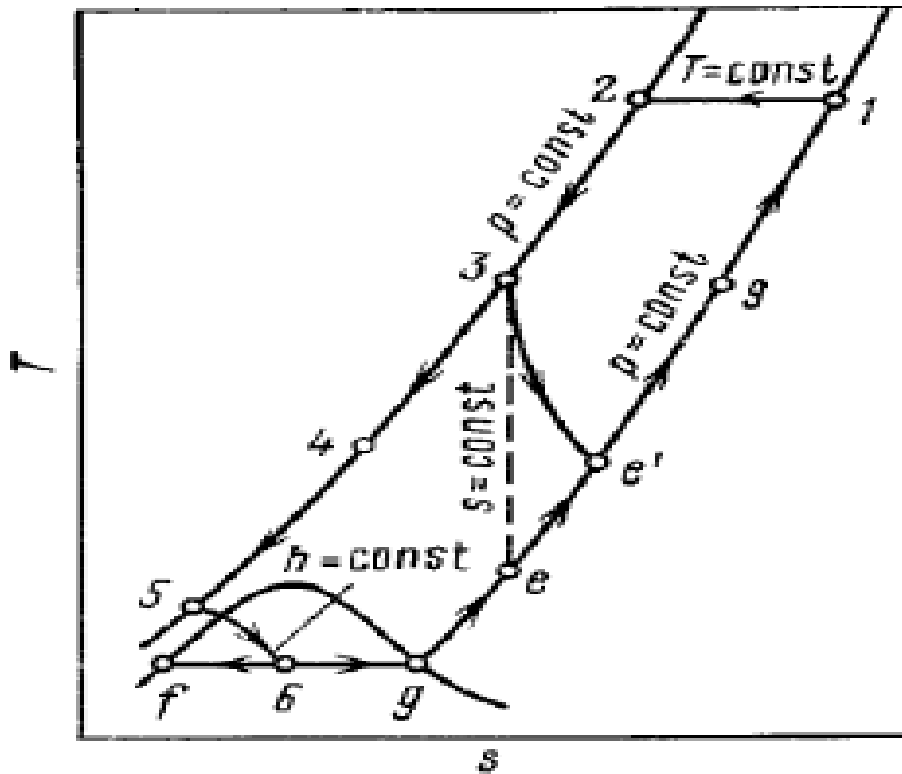


Figure 4.3 Influence of expander efficiency on system performance

$$\dot{W} / \dot{m} = \frac{1}{\eta_{c,0}} [T_1 (s_1 - s_2) - (h_1 - h_2)] \quad (64)$$

For a expander with an efficiency of less than 1

$$\eta_{ad} = \frac{(h_3 - h'_e)}{(h_3 - h_e)} \quad (65)$$

$$y = \frac{(h_1 - h_2)}{(h_1 - h_L)} + x \eta_{ad} \frac{(h_3 - h_e)}{(h_1 - h_L)} \quad (66)$$

$$\frac{\dot{W}_{net}}{\dot{m}} = \frac{1}{\eta_{c,0}} \left[T_1 (s_1 - s_2) - (h_1 - h_2) \right] + x \eta_{e,0} (h_3 - h_e) \quad (67)$$

Chapter 5: Study of Industrial Gas Liquefaction Installations

5.1 Nitrogen and oxygen liquefaction

The production of nitrogen and oxygen is based on the separation of air into its components. This cryogenic separation technique was developed more than a century ago by Carl von Linde.

Air is a mixture of several gases, consisting mainly of nitrogen (72%), oxygen (21%) and argon (0.9%). The remaining 0.1% is composed mainly of carbon dioxide and inert gases: neon, helium, krypton and xenon. Air can be separated into its components by distillation in special units[34].

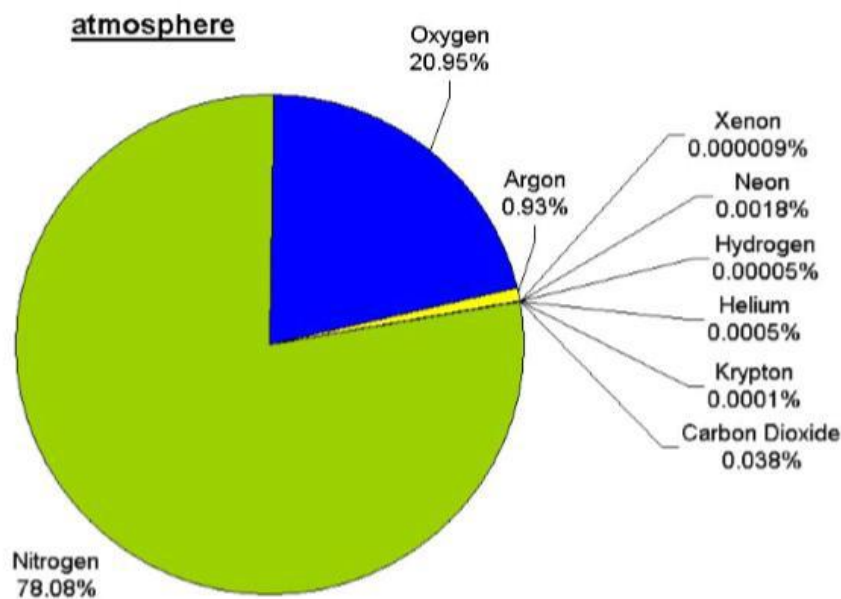


Figure 5.1 Composition of air

Cryogenic air separation process is one of the most widespread air separation processes, frequently used in medium and large scale plants. It is the preferred technology for the production of nitrogen, oxygen and argon in gas and/or liquid form[2].

The basic steps of cryogenic air separation [2, 12]

First step:

- Removal of dust particles by a mechanical air filter at the compressor inlet
- Compression of ambient air with a multi-stage turbocharger with intercoolers to a supply pressure of approx. 6 bar.

Second step:

- Cooling of the air with water in a direct contact cooler and removal of water-soluble air impurities.

- Cooling of the cooling water in a nitrogen evaporation cooler from the rectification process.
- Removal of CO₂, water and hydrocarbons from the air in periodically charged/regenerated molecular sieve adsorbers.

Third stage:

- Cooling of the air in counter-current heat exchangers to a temperature close to the liquefaction temperature of the air by gases from the rectification process.
- Additional compression in a second compressor and expansion in an expansion motor of a portion of the air.
- Expansion and liquefaction of the air portion in a liquid separator.
- Evaporation and heating to room temperature of the oxygen and nitrogen product pumped into the high-pressure heat exchangers.

Fourth stage:

Cryogenic rectification of the air to separate air by a cryogenic process, thus recovering oxygen, nitrogen and argon, a double-column rectification system is used.

- The air is introduced into the lower column with a higher pressure of approximately 5.6 bar, a separation of the cooled and liquefied air in this column into an oxygen-enriched liquid in the bottom and pure nitrogen at the top of the column.
- Liquefaction of the pure nitrogen in the condenser and evaporation of the oxygen in the bottom of the low-pressure column. The liquefied nitrogen provides the reflux for the high-pressure column and (after subcooling) for the low-pressure column.

Fifth step:

- The argon-enriched gas from the low-pressure column is converted into oxygen-free crude argon by means of a separation in the crude argon column.
- Liquid oxygen is discharged from the bottom of the crude argon column into the low-pressure column.
- Removal of the remaining nitrogen in the pure argon column.

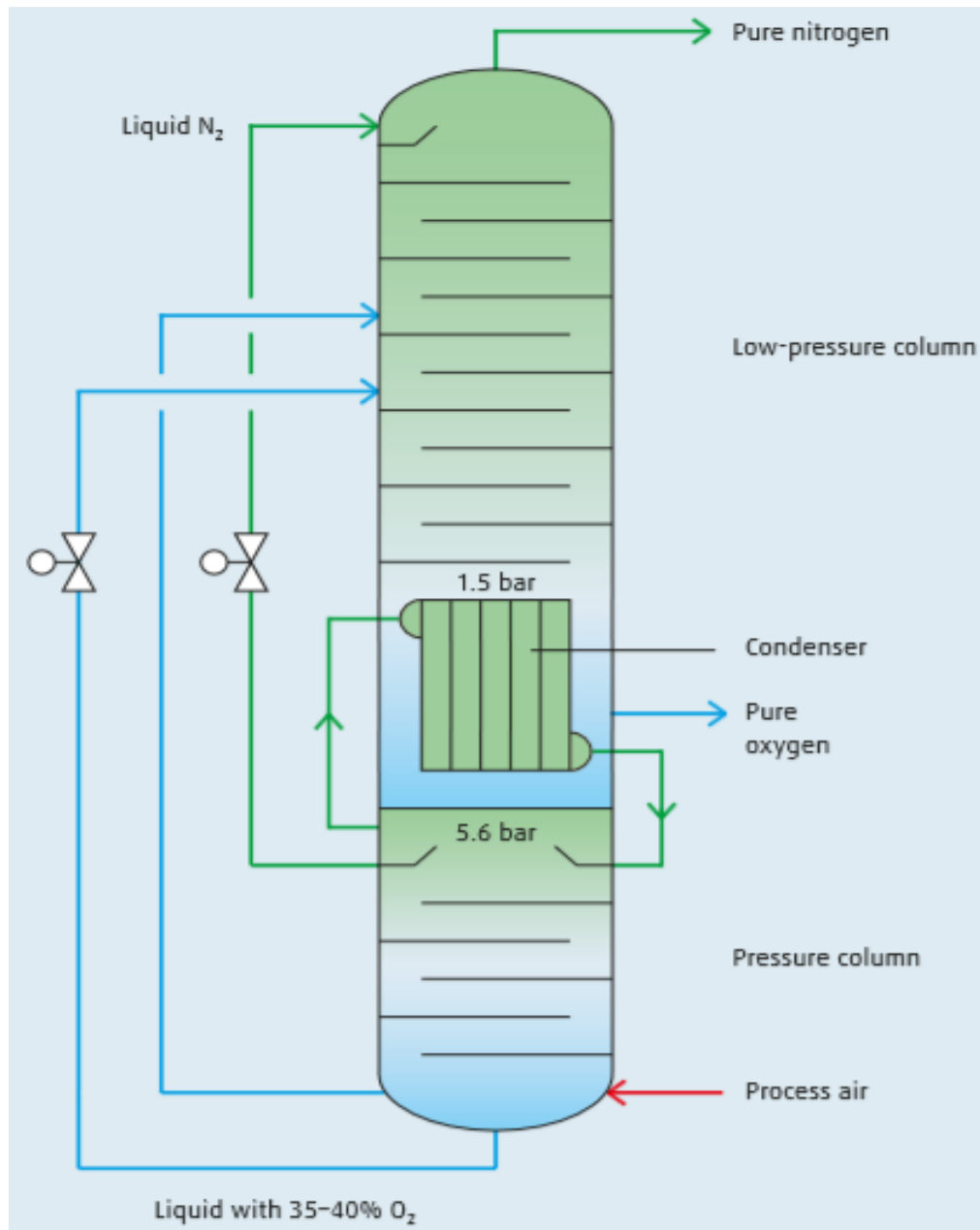


Figure 5.2 Double separation column

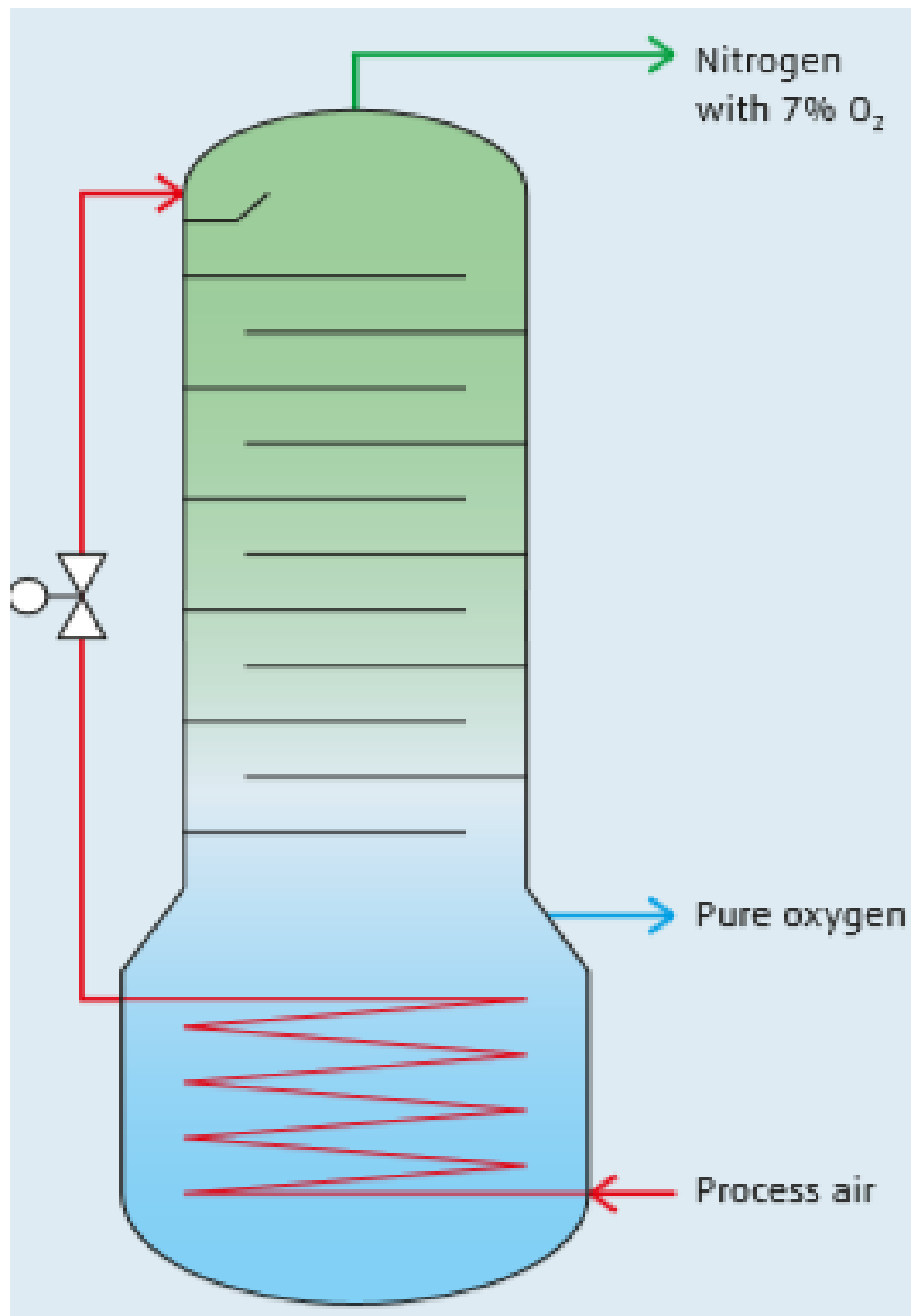


Figure 5.3 Simple separation column

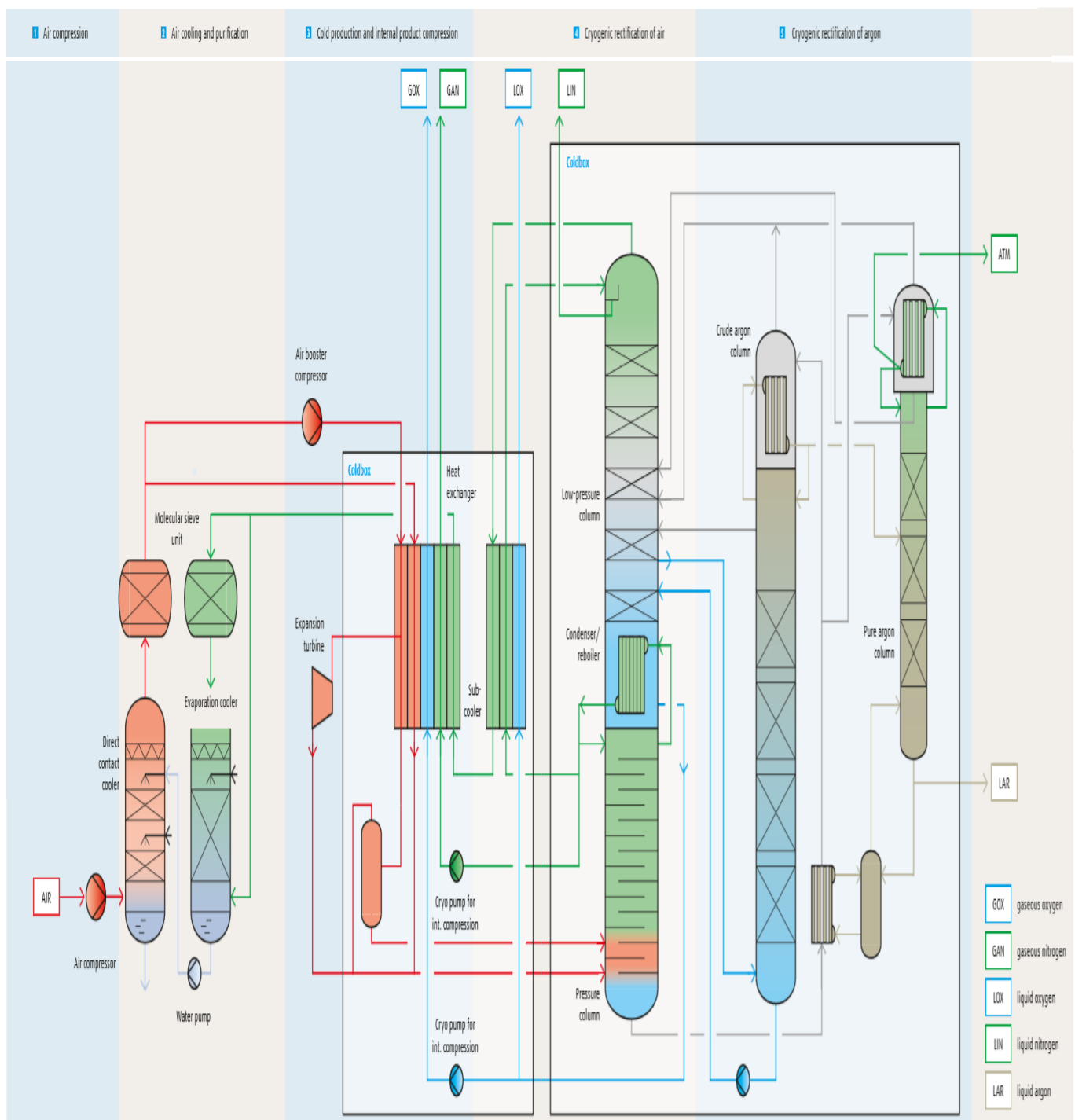


Figure 5.4 Schematic of an industrial air separation installation

5.2 Natural Gas Liquefaction Process

Natural gas (NG) plays a very important role in the energy industry. To enable the use of natural gas (NG) for consumers thousands of km away from gas production centers under acceptable pressure and volume conditions, NG is transformed into LNG (liquefied natural gas) and is transported in liquid form to the regasification center where it is vaporized and injected into the distribution networks[35].

Traditional natural gases, i.e. associated and non-associated gases from wells, have very different compositions. Table 5.1 shows the chemical composition of NG[2, 8].

Component	% mole	Component	% mole
H ₂ O	1.29	nButane	0.7
N ₂	3.32	iPentane	0.29
CO ₂	1.75	nPentane	0.29
H ₂ S	0.53	C6	0.41
Methane	81.34	C7	0.46
Ethane	5.19	C8	0.5
Propane	1.93	C9	0.34
iButane	0.41	C10	1.25

Pretreatment of raw natural gas: Dehydration of natural gas

Dehydration is a process of eliminating liquid or vapor water molecules contained in raw gas by different methods in order to avoid several problems that affect the liquefaction plant. These problems include[36, 37]:

- Risk of corrosion of pipes
- Risk of formation of hydrates.
- Risk of solidification at low temperatures.
- Reduction of the calorific value of the gas.

The dehydration process is obtained by: - Absorption of water vapor by products such as: Mono Ethylene Glycol (M. E. G), Di Ethylene Glycol (D. E. G) and Tri Ethylene Glycol (T. E. G). Adsorption of water molecules by highly hygroscopic alumina bubbles that constitute a molecular sieve.

- Removal of H₂S and CO₂ gases

Acid gases can be removed by absorption with an amine solution, Di Ethanol Amine (D. E. A.) has a high affinity for H₂S and CO₂.

- Removal of mercury

Mercury causes serious damage to heat exchangers. Mercury forms an amalgam with aluminum and in the presence of humidity at positive temperatures causes corrosion.

Mercury must be removed by adsorption in a special adsorber at the outlet of the dehydration section.

- Removal or reduction of the presence of nitrogen

Nitrogen has an effect on the calorific value (PCS) of LNG, therefore, nitrogen must be removed from NG in order to meet the LNG composition specifications. A nitrogen recovery unit whose diagram is shown in Figure 5.7 is integrated into the LNG plant to allow the removal of nitrogen by cryogenic distillation.

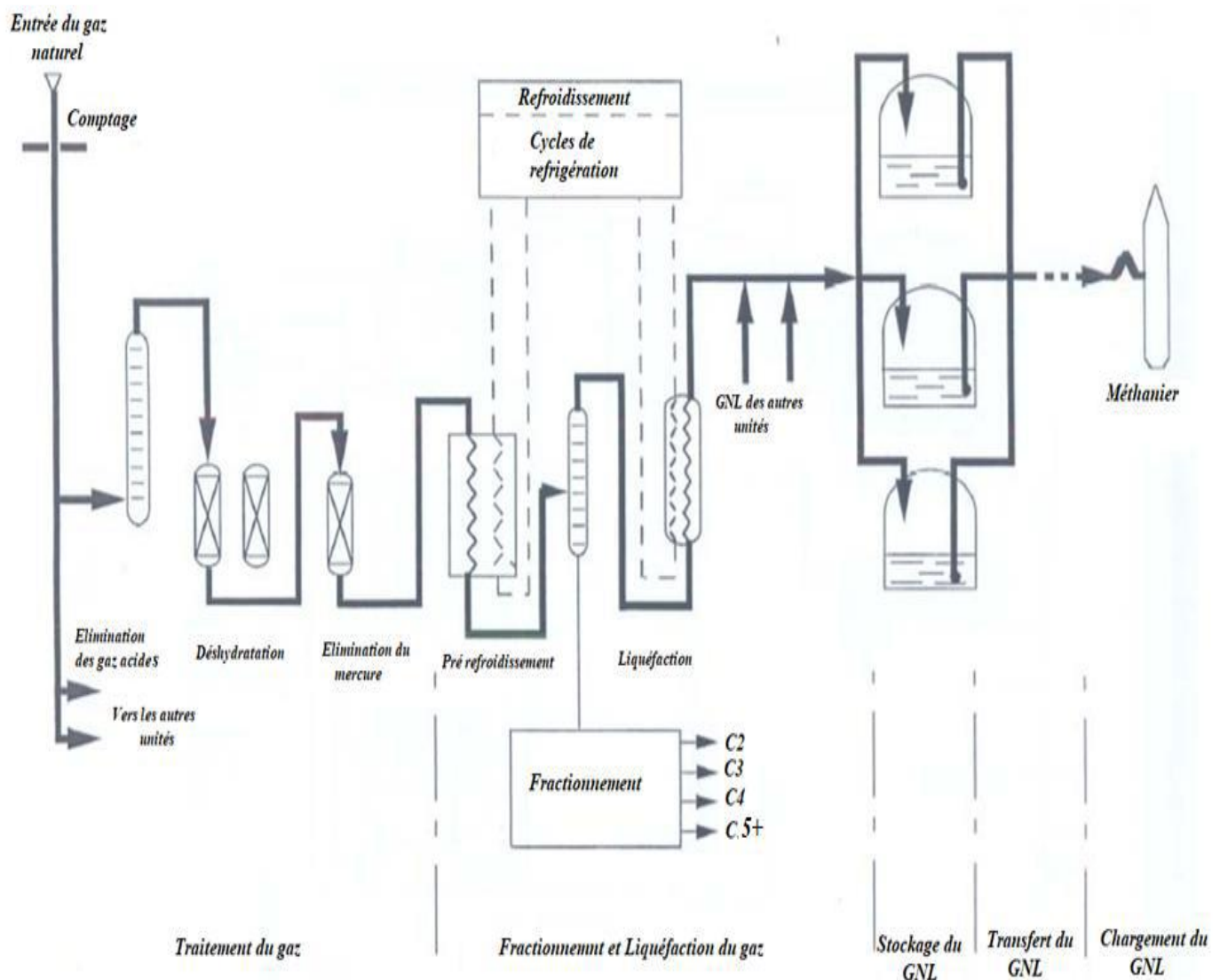


Figure 5.5 Schematic diagram of all the operations carried out to achieve the liquefaction of NG

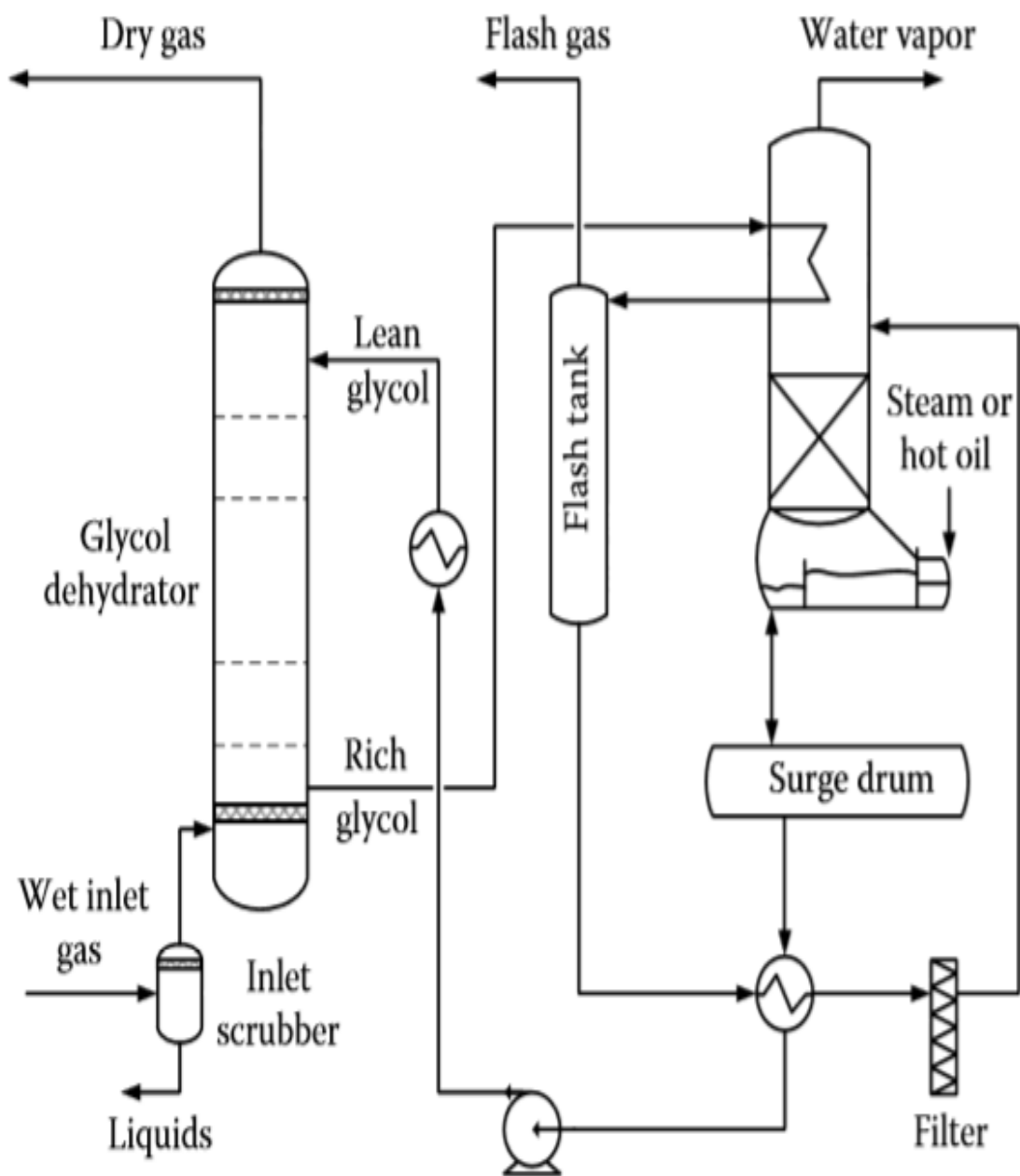


Figure 5.6 Typical schematic diagram of glycol absorption dehydration process

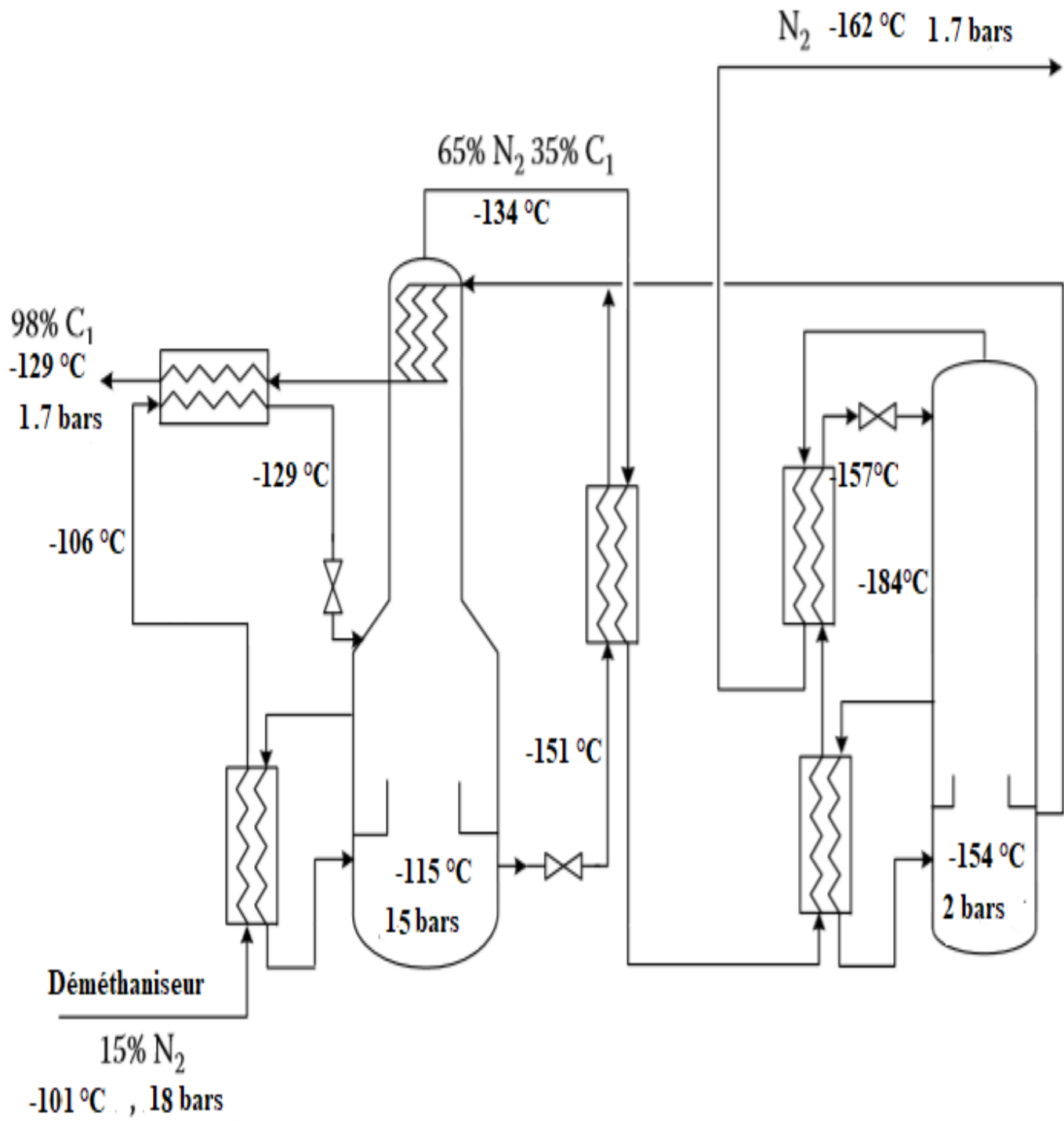


Figure 5.7 Schematic of a two-column nitrogen recovery unit (NRU)

5.2.1 Liquefaction of treated natural gas [38-40]:

- APCI process

The most common process applied in the majority of LNG units around the world. It is designed by Air Products Company Inc. The diagram of this process is represented in Figure 5.8.

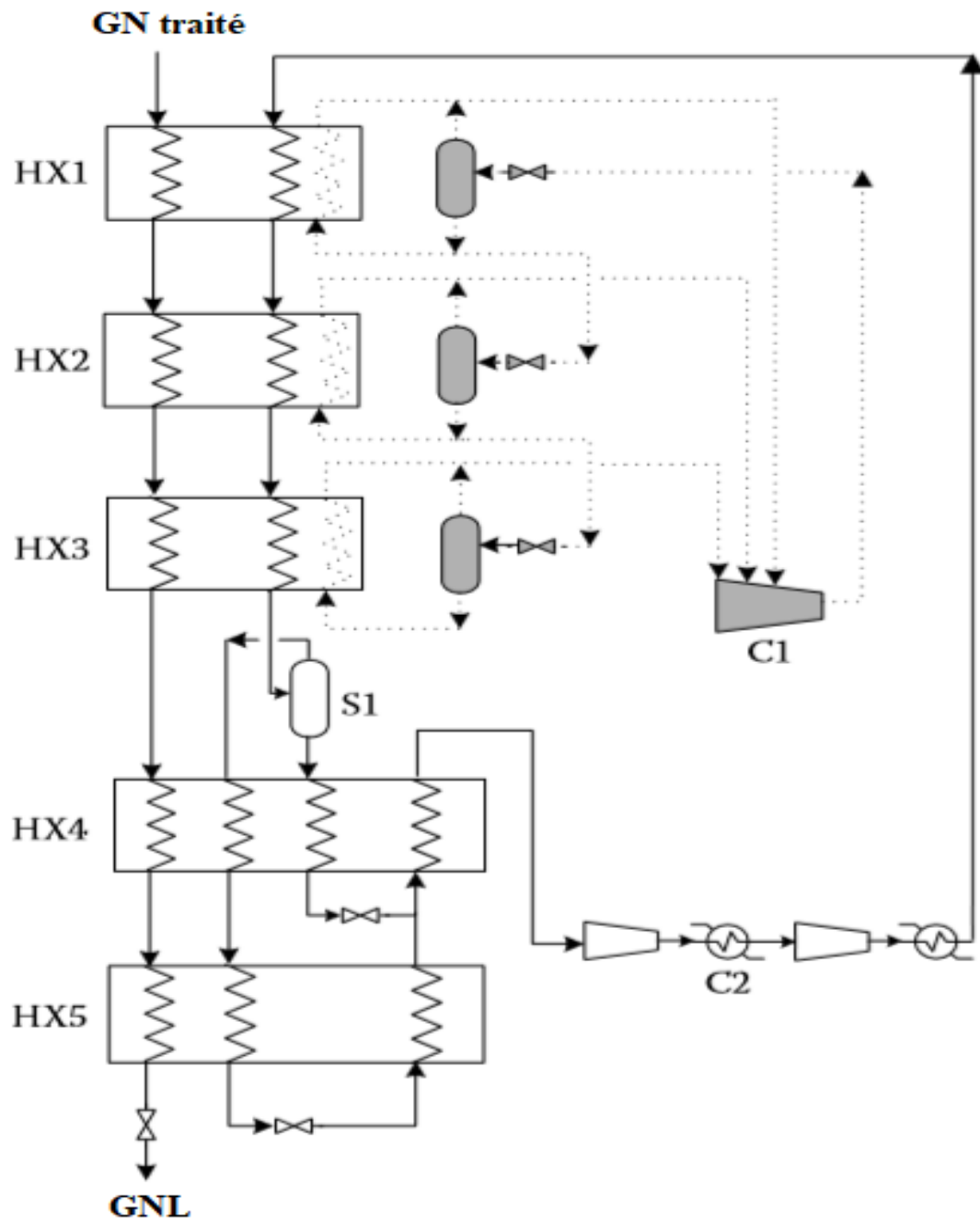


Figure 5.8 Schematic of the APCI process (propane pre-cooled mixed refrigerant system)

This process is based on two main refrigeration cycles. A pre-referral cycle using a pure refrigerant, propane, as for the cascading process and a liquefaction and sub-cooling cycle of natural gas using a mixture of four refrigerants (MCR): nitrogen, methane, propane and ethane . The propane cycle is made up of three or four compression stages. It allows you to cool natural gas up to -40°C . It is also used to cool and partially liquefy the refrigerant mixture. A centrifugal compressor C1 ensures the circulation of propane in this loop. The steam is compressed up to 15 to 20 bars and then condensed by water or air and recycle again in the evaporators. The MRC cycle (Mixed refrigerant cascade) is separated into two circuits: a first for the steam MRC and the second for the liquid MRC. The two circuits are used to liquefy natural gas from -35 to the point of cooling at -160°C .

- **PRICO (Single Mixed Refrigerant) process**

This process is carried out by the company Pritchard Corporation . The refrigerant composed of gas mixture: nitrogen, methane, propane, ethane, butane and sometimes pentane the exact composition depends on the composition of natural gas during liquefaction. The refrigerant mixture is compressed and then condensed in a water cooling exchanger. The refrigerant then undergoes a series of reductions in pressure and liquid-vapor separations to provide the cold fluid necessary in the heat exchangers in order to liquefy natural gas. The temperatures reached in the different heat exchangers depend on the composition of the refrigerant and the pressure on which the gas is initially compressed. During this cycle, natural gas crosses the heat exchangers and it is then relaxed to obtain LNG. Figure 5.9 represents an industrial example of this type of system

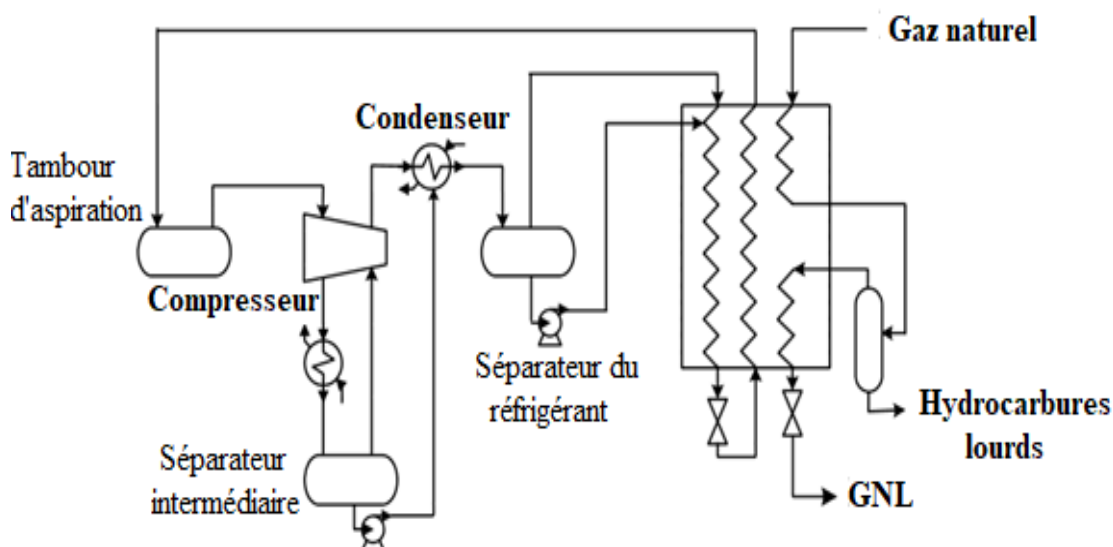


Figure 5.9 Schematic of the PRICO process

5.2.2 Fractioning section[30, 41]:

The purpose of this section is the extraction of heavy hydrocarbons from treated natural gas. It is generally of three or four columns which proceeds to fractionation by cryogenic distillation in order of condensation. These columns are:

- Demethanier: he receives the entire partially liquefied natural gas treated at the head of methane and nitrogen while the hydrocarbons produced at the foot of the column are shipped to the Detectionner.
- Detectionner: in which ethane is vaporized and the heavier cup is condensed at the bottom.
- Deproprier: in which propane is vaporized accompanied by a little ethane which is not vaporized in the deethanizer and the butane as well as the aromatics are condensed at the bottom.
- Beginning: in which the butane is vaporized, accompanied by a little propane which was not completely vaporized in the depropanator, the heavy and the aromatics are condensed in the bottom.
- Butanes "Splitter": used to obtain the n-butane and the iso-butaness

5.3 Helium liquefaction installations

Helium is extracted by distillation and fractionation of natural gas, which contains up to 6.4% helium at the Skikda site. Since helium has a lower boiling point than any other element, low-temperature, high-pressure purification processes are used to remove almost all other gases, primarily nitrogen [2].

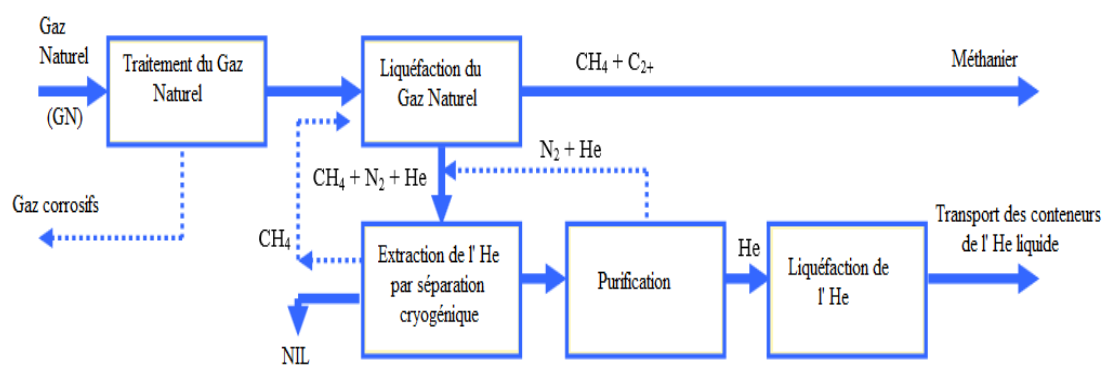


Figure 5.10 General schematic of He extraction

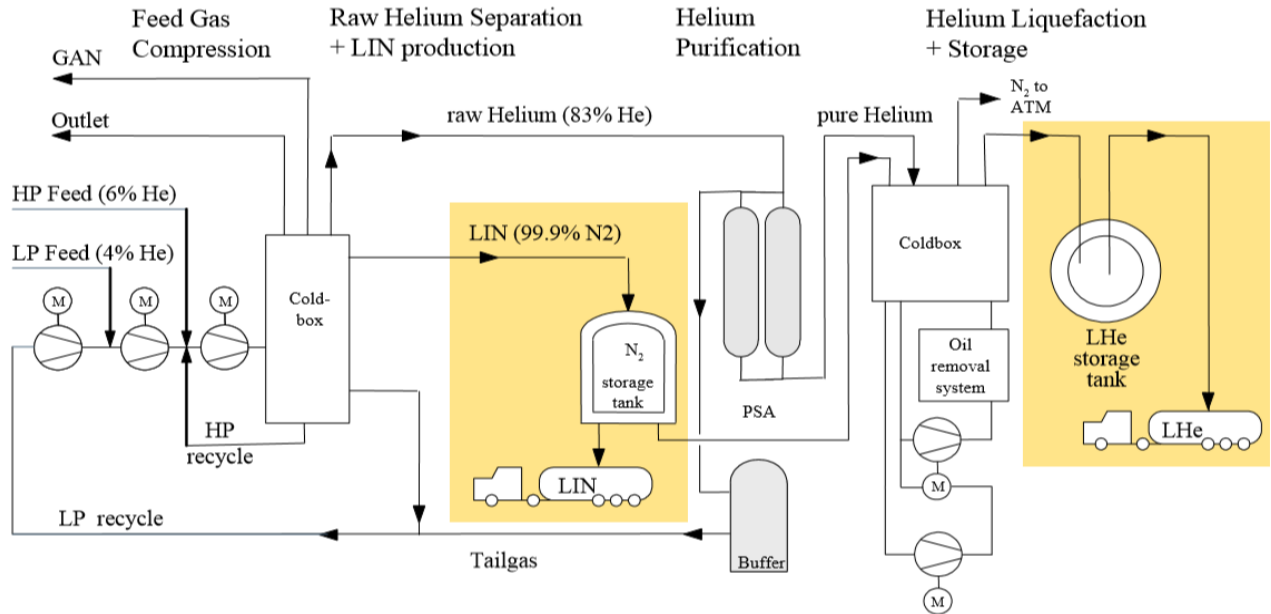


Figure 5.11 Process diagram for obtaining He in Skikda

Unit 1:

The Feed Gas Compression Unit: Three-stage compression of the two feed gases as well as pressurization of the gases from the He purification unit, LP and HP recycle gases from the raw helium recovery and liquid nitrogen (LIN) production units.

Unit 2:

The Raw Helium Separation and LIN Production Unit:

In this unit, the separation of raw helium, the recovery of raw helium and the production of liquid nitrogen take place. The gas phase leaving the cold box contains 83.5 mol% helium when sent to the purification unit.

Unit 3:

Purification Unit (The Pressure Swing Adsorption)

The PSA process is based on the phenomenon of physical adsorption, namely that highly volatile and low polarity compounds, such as hydrogen or helium, are practically unadsorbed compared to molecules such as nitrogen and hydrocarbons. It depends on two pressure conditions:

- Nitrogen and hydrocarbon adsorption is performed at high pressure to increase the partial pressure and, consequently, the loading of impurities on the adsorbent material

- Desorption or regeneration takes place at low pressure to reduce the residual load of impurities as much as possible, in order to obtain a high product purity, (99.71% pure helium in moles). There remains approximately 2800 ppm of hydrogen in the pure

helium stream discharged by the PSA unit, which must be removed by the 20K adsorber(s) in the cold box of the liquefier.

Unit 4: Helium Liquefaction Unit

The helium liquefaction unit consists of three subsystems (Figure 5.12:)

- 1 Helium Compression and Oil Removal
- 2 Cold box for liquefying helium
- 3- Liquid helium storage and filling stations

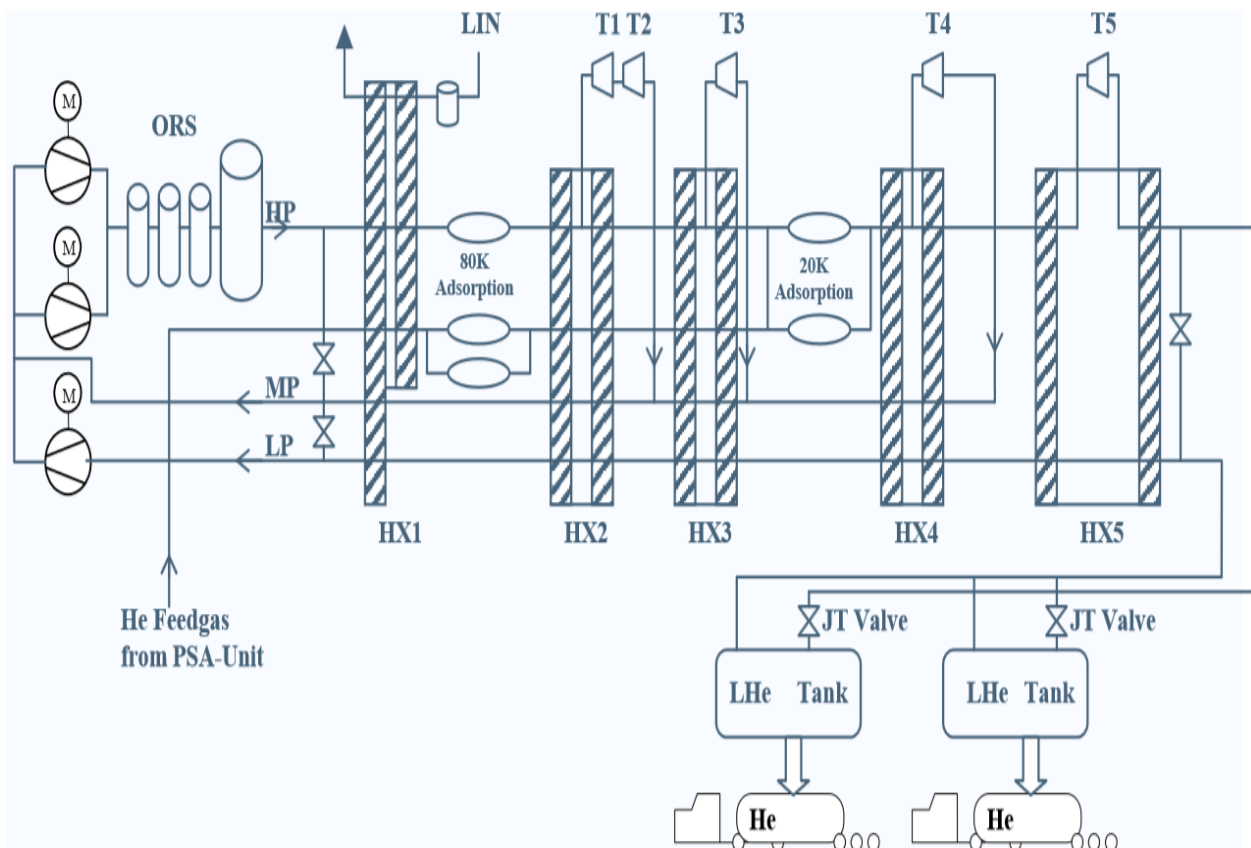


Figure 5.12 Schematic of the Helium a liquefaction unit

5.4 Hydrogen liquefaction installations

Hydrogen is the most widespread element in the universe. It exists both in water molecule and in hydrocarbons that combine hydrogen and carbon present in all living tissues of the animal and plant world. It is obtained in liquid form by electrolysis of water as well as from the reforming of natural gas and biomass. It is an energy vector that has multiple applications, particularly in chemistry for the manufacture of ammonia, in oil refining and in the metallurgical industry. In its liquid form, hydrogen is currently used in the space field for the propulsion of satellites and rockets. Hydrogen is the clean fuel of the future through its use in fuel cells[42].

Sir James Dewar obtained the first liquefaction of hydrogen in 1898, its saturation temperature is 20 K. The process was improved a few years later by the process of Georges Claude, founder of the Air Liquide Company, who perfected the compression refrigeration machine designed by Linde. Olszewski achieved his liquefaction by expanding hydrogen from 190 atmospheres after having cooled it by the evaporation of liquid oxygen and nitrogen under reduced pressure[43]. Liquid hydrogen is obtained in cryogenic installations operating according to the Linde cycle with simple throttling, using the Joule-Thomson expansion process called isenthalpic (this is a low-speed expansion of the gas which exchanges neither work nor heat with the external environment) with the prior cooling of the hydrogen gas by an external cryogenic agent and those combining both isenthalpic expansion, pre-cooling and isentropic expansion of a quantity of gas before its throttling [43].

5.4.1 Hydrogen production

Hydrogen is the most abundant element, accounting for nearly three-quarters of the mass of the universe. Hydrogen is found in the water that covers 70% of our planet's surface, and in all organic matter. Hydrogen is the simplest element in the universe. It is composed of one proton and one electron. Hydrogen is the lightest of all elements and gases; it is 14 times lighter than air. A "spill" of hydrogen gas diffuses immediately into the air and does not pollute the soil or groundwater. Hydrogen is invisible, odorless, and nontoxic. It does not cause acid rain, deplete the ozone layer, or generate hazardous emissions. Hydrogen is the primary constituent of the sun and most stars, and of interstellar or intergalactic matter[44]. Reforming natural gas by applying heat is currently the most economical process for producing hydrogen. Electrolysis produces hydrogen by using an electric current to split water into hydrogen and oxygen. Hydrogen has a high gravimetric energy power: 120 MJ/kg compared to oil (45 MJ/kg), methanol (20 MJ/kg) and natural gas (50 MJ/kg). However, it is also the lightest gas (2.016 g/mol), hence a low volumetric power: 10.8 MJ/m³ compared to methanol (16 MJ/m³) and natural gas (39.77 MJ/m³). Hydrogen therefore poses a real problem of storage and transport[45, 46].

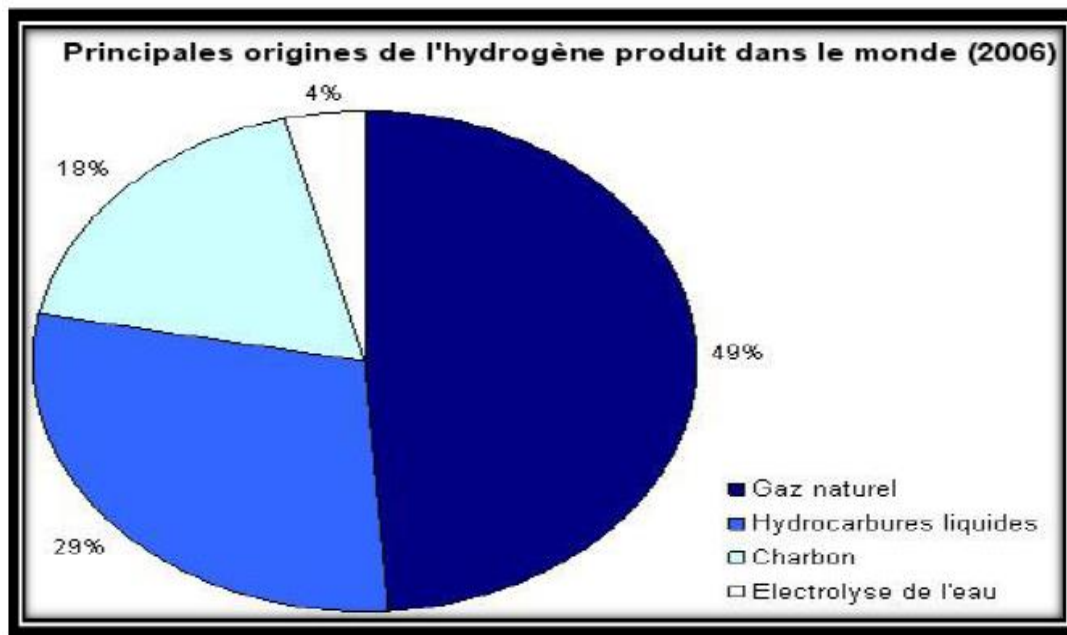


Figure 5.13 main origins of hydrogen produced worldwide

5.4.2 Industrial hydrogen liquefaction units

High Capacity Units

High liquefaction units correspond in the world to a daily production exceeding 200 tonnes. If part of this production is used by industry (oil refining, agrochemicals, materials development, etc.), another part is intended for space for which the first plant

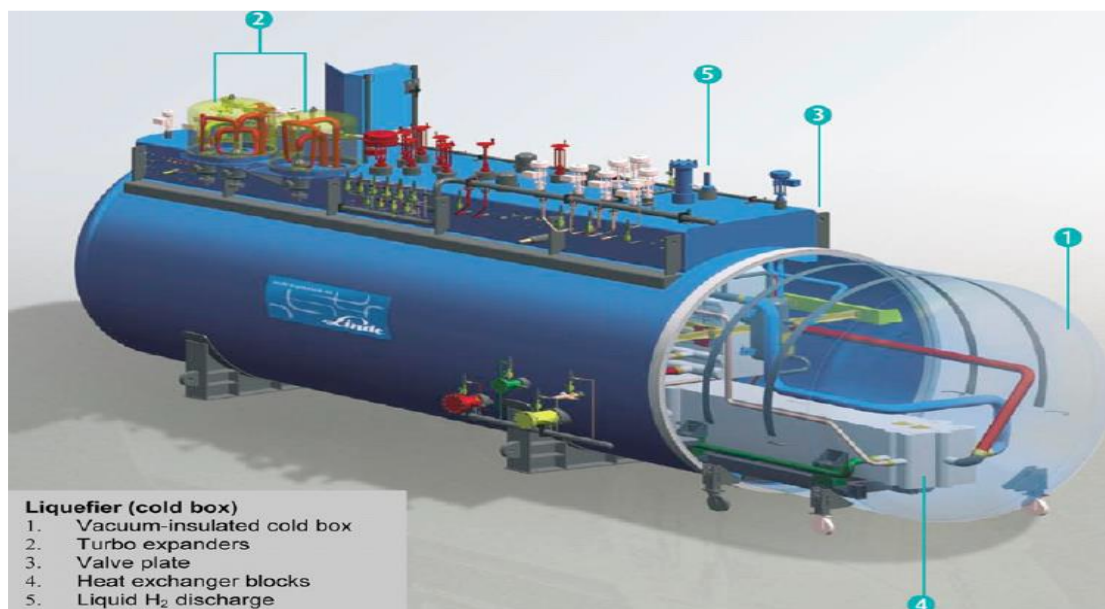


Figure 5.14 Linde liquefier in Leuna

was built in 1960 as part of the Apollo program. As for the liquefaction of hydrogen to power fuel cells, if it remains low, is constantly increasing. In the European Union, four liquefiers operate with a total production capacity of 26 t/day[47]:

- In the Netherlands, Air Products in Rozenburg producing 5.4 t/d;
- In Germany, Linde in Ingolstadt, with 4.4 t/d and in Leuna, with 5.7 t/d;
- In France, that of Air Liquide on the Waziers site in the Nord department, a unit producing 10t/d. This liquefier, the largest in Europe, is supplied with gaseous hydrogen by gas pipelines. Its production is stored in 3 independent tanks with a total capacity of 750,000 liters, a production reserved as a priority for the tests of the Ariane V program.



Figure 5.15 Air Liquide site in Waziers

In the United States, the production capacity is 182 t/day, of which 54 tonnes are produced by the Union Carbide plant in Sacramento alone. Worldwide, Air Liquide is a major player in this hydrogen liquefaction, which has installed three liquefiers since 1987[42, 45, 48]:

- In Asia, in Oita, Japan, a unit producing 1.5 t/day;
- In Canada, in Bécancour, a unit producing 10 t/day;
- In French Guiana, in Kourou, a unit producing 2.3 t/day for the aerospace launch base. This liquid hydrogen is the propellant for the cryogenic stage of the Ariane IV and Ariane V rockets: Ariane IV carried 1.9 t of liquid hydrogen and 8.8 t of liquid oxygen respectively. Ariane V carries 27 t of liquid hydrogen and 130 t of liquid

oxygen. Liquid oxygen and other gases required for the rockets' engines, nitrogen, helium and compressed air, are also produced on the same Kourou site[42].



Figure 5.16 Hydrogen liquefier at the Kourou aerospace launch site

For hydrogen mobility, in the near future, Air Liquide plans to invest more than 150 million US dollars earmarked for the construction of a large-capacity liquid hydrogen plant in California. This construction is scheduled to start in early 2019. The site will produce nearly 30 tons of liquid hydrogen per day, a volume that can supply 5,000 fuel cell electric vehicles daily. With this investment, Air Liquide will contribute to the large-scale deployment of hydrogen mobility on the West Coast of the United States because the commissioning of this source will serve the fleet of 40,000 fuel cell electric vehicles expected in California in 2022. This plant will also serve other markets in the region beyond automotive mobility, such as forklift handling and heavy-duty transportation. Once produced, liquid hydrogen is transported to the places of use by tanker trucks with a capacity of 15,000 to 53,000 litres[49].

Medium-capacity units

“Hylial” is a recent Air Liquide liquefier that can, depending on the model, produce 1 to 2.5 t of liquid hydrogen per day for mobility, laboratory, test center or microelectronic needs. It operates on the principle of helium liquefier cycles with in particular an optimized pressure ratio for its compressor, with static gas bearing turbo-expanders, with pre-cooling of the cycle and, to improve production, continuous ortho/para conversion of hydrogen. This liquefier is used in China for aerospace on two

launch sites and a study center. In Canada, it equips a technological research center on hydrogen energy[45].



Figure 5.17 Hydrogen liquefier Hylial [43]

5.4.3 Hydrogen liquefaction applied to its storage

While the density of hydrogen gas at atmospheric pressure and 20°C is 0.0838 kg.m⁻³ and 14.885 kg.m⁻³ at 220 bars in commercial gas cylinders, it is 70.9 kg.m⁻³ in the liquid state. This latter density can be reached by the gas at room temperature at a pressure of 1,820 bars (182 MPa). A value that is not suitable for practical application due to the requirements imposed by such high pressure (significant thickness of the walls of the tanks, pipes and valves). This is why, to achieve a high density, the liquefaction of hydrogen remains preferable. In fact, for gas, the compressibility curve shows an inflection at around 700 bars (70 MPa), beyond which the density increases less and less with pressure, with the consequence that beyond this pressure the gain in the quantity of gas stored decreases, while it is necessary to greatly increase the mechanical resistance of the tanks and their accessories[46]. For this reason, 700 bars was the pressure chosen to become a standard for composite material tanks that have been developed for fuel cell vehicles. At this pressure, the density of the gas reaches 39.6 kg.m⁻³, i.e. a little more than half that of the liquid. The two methods of storing hydrogen, liquid or high-pressure gas, require a certain degree of technology and it is difficult to establish a hierarchy of their dangers because both present risks and entail rigorous safety protocols. As for the energy required to reach these states, it is

significant: 22 MJ.kg^{-1} for gas compressed to 70 MPa and two to ten times more for liquefaction depending on whether it is carried out in large or small quantities. In both cases, the storage process generates a significant additional cost for hydrogen. Like all low-temperature liquids, known as cryogenic liquids, liquid hydrogen is stored in "cryostats", containers with double thermal insulation. The first prevents heat input by direct conduction by maintaining a vacuum between the double wall of the cryostat. The second, against heat input by radiation, is ensured by a stack of reflective metal sheets placed in this space between the walls[44, 49].

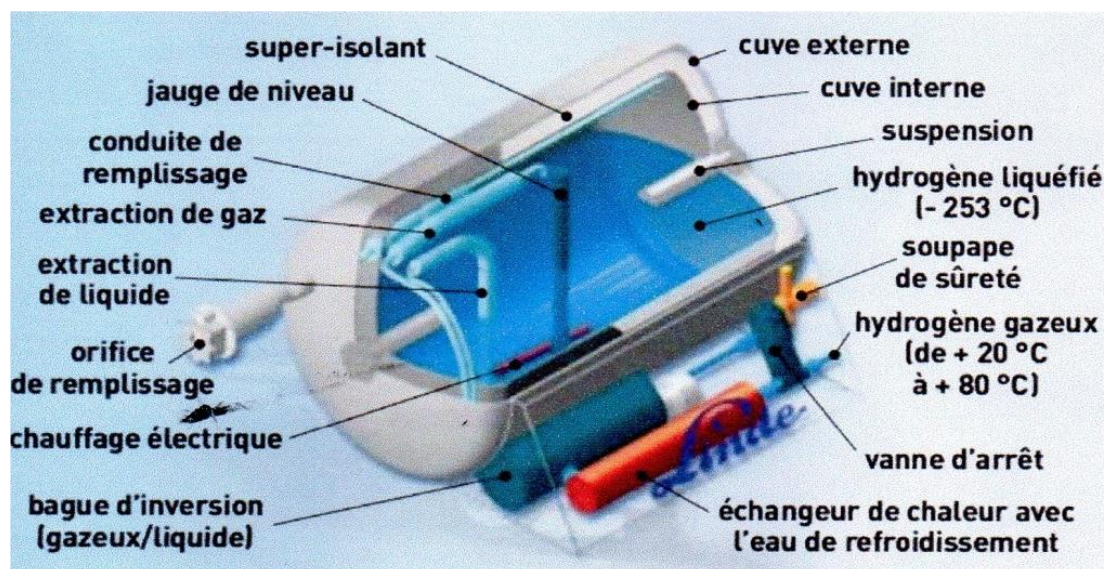


Figure 5.18 Structure of a liquid hydrogen tank

The thermal insulation of these containers, however good, is not complete [8], resulting in a slight boiling of the hydrogen due to the low heat inputs corresponding to this imperfection of insulation. A cryostat is therefore not sealed in order to allow a permanent release of gaseous hydrogen, very precisely hydrogen vapor, which prevents an excessive increase in pressure. This permanent evaporation, which corresponds to a weight loss of 0.3 to 1% per day, is one of the major drawbacks of storing liquid hydrogen. For large fixed installations, it is possible to imagine recovering this evaporated hydrogen by cryoadsorption in pressure-resistant enclosures which, heated to room temperature, will become compressed hydrogen tanks, without additional energy expenditure. In the early 2000s, this type of liquid storage was used by car manufacturers to equip some of their hydrogen car prototypes: Daimler-Chrysler (Necar 4 model), General-Motors (HydroGen1 and 3), VW (Bora HyMotion), Renault (Fever), BMW (Series 7)[42, 48]. The latter, BMW, is the manufacturer that has kept this technique the longest to power its now abandoned thermal engine. The BMW tank contained 9.5 kg of liquid hydrogen and weighed 145 kg, i.e. a weight ratio of 6.5%. A percentage close to that currently obtained with the composite material tanks mentioned above that equip fuel cell vehicles and in which the hydrogen is compressed to 350 or 700 bars. However, as we mentioned, this liquid hydrogen storage for vehicles is now

in the process of being taken up by the American manufacturer Nikola to equip its fuel cell truck prototype.



Figure 5.19 Industrial liquid hydrogen storage tanks

5.4.4 Transport of liquid hydrogen

When used in very large quantities as a basic chemical substance that most often requires a continuous supply (oil refining industry, ammonia synthesis, metallurgy and materials development), hydrogen is generally transported by gas pipeline. Transport in liquid form by truck is rather reserved for applications requiring smaller quantities, as is the case for the electronics industry, aerospace and charging stations for land mobility. Liquid hydrogen is then contained in cylindrical cryogenic tanks like tanker trucks transporting liquids. These vehicles can transport up to 3.5 t of liquid hydrogen

for a total weight of 40 t. For example, Air Liquide's fleet consists of 12 trucks in Europe and 75 in North America[44, 45].



Figure 5.20 Tanker truck for transporting liquid hydrogen

The fact that liquid hydrogen is dense and that the cryogenic tanks containing it can have very large capacities quite naturally suggests transport by sea from places that can have a large production capacity to those of high consumption. This is what the Japanese "WE-NET" and Euro-Quebec "Hydro-Hydrogen Pilot Project, EQHHPP" projects had planned. The Japanese prototype consisted of a cargo ship capable of transporting 14,000 t of liquid hydrogen contained in four spherical cryogenic tanks[43].

The basic idea of the Euro-Quebec EQHHPP project (1991 - 1995) was to transport by sea to Europe hydrogen produced in Quebec by electrolysis of water and liquefied thanks to the country's significant hydroelectric resources. It was planned that this liquid hydrogen would be contained in large spherical double-walled cryogenic tanks with a capacity of 3,000 m³ fixed on barges suitable for the high seas[48, 44].

In fact, these projects were the adaptation to liquid hydrogen of what is done for liquefied natural gas. If at the time, such maritime transport of hydrogen remained at the feasibility study stage, this is no longer the case today for Japan, which has taken up this idea to supply itself with decarbonized energy. The project consists of importing

liquid hydrogen produced in Australia by reforming lignite, of which this country has significant deposits. But this is a production that particularly emits CO₂, so it is announced that this CO₂ would be stored using the technique known as CCS, Carbon Capture and Geological Storage. To date, there is no example of an installation that stores very large quantities of CO₂ in this way because all large-scale projects seem to have been abandoned due to the additional costs they entail, the drop in overall efficiency they induce and the difficulty in finding underground storage that is acceptable from a safety perspective[46, 48].



Figure 5.21 Japanese ship project to transport liquid hydrogen from Australia

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Annexes

EX01

Answer the following questions

- .1What is the meaning of word “Cryogenics” ?
- .2Give the concept of temperature
3. What is the thermal scale range associated with the cryogenics study?

EX02:

Complete the following table

T(°C)	T(K)	T(°F)	T(°R)
0			
		-40	
	0		
			10
		100	
-30			
	90		

EX03:

We consider 1 kg of air (ideal gas) undergoing a Carnot ABCDA cycle. The temperature at point A is $T_1 = 350$ K. The pressures at A, B and C are respectively $P_1 = 1$ atm, $P_2 = 4$ atm and $P_3 = 11$ atm. We give $\gamma = 1.4$

1. Represent the cycle in the PV and TS diagrams.
2. Calculate the thermodynamic efficiency
3. Calculate the variations in entropy of air

EX04:

For real gas, prove that $T_{inv} = 2a/bR$

EX05:

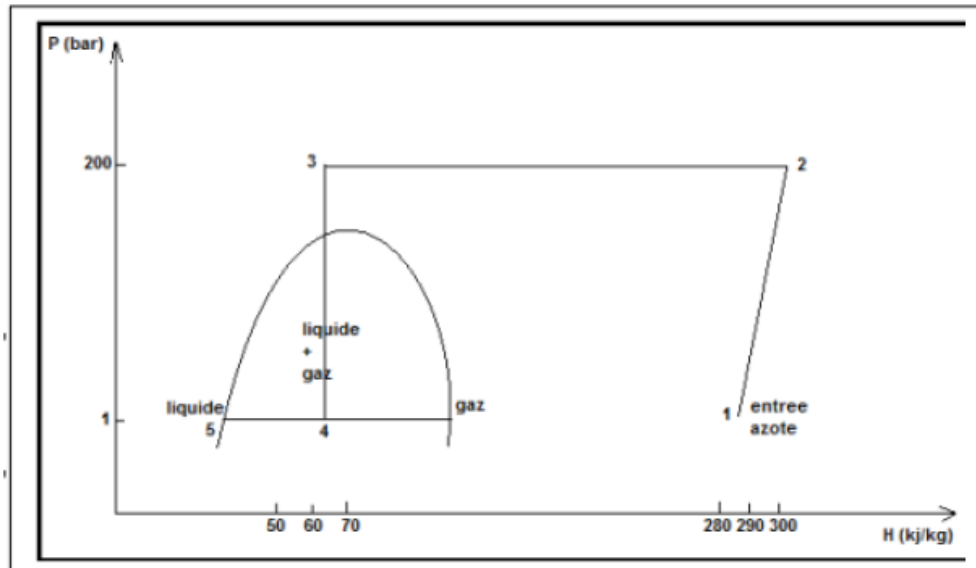
Give a comparative table between isenthalpic expansion and isentropic expansion

EX06:

The figure represents the diagram (P, H) of the cryogenic process used to produce liquid nitrogen

1 Give the diagram of the cryogenic process for the liquefaction of nitrogen linked to this diagram (P, H).

2 Explain the transformations: 1-2, 2-3, 3-4, 4-5, 4-1



EX07

Give the components of the ideal system for liquefaction

EX08:

Determine the ideal work required in KJ/Kg for liquefaction of N₂ in the initial state $P = 1 \text{ atm}$ and $T = 300 \text{ K}$. $s_1 = 4.4 \text{ J/g.K}$; $s_L = 0.4 \text{ J/g.K}$; $h_1 = 462 \text{ J/g}$; $h_2 = 30 \text{ J/g}$.

EX09:

Same question from EX02 for H₂. $s_1 = 65 \text{ J/g.K}$; $s_L = 18 \text{ J/g.K}$; $h_1 = 4190 \text{ J/g}$; $h_2 = -75 \text{ J/g}$

EX10:

Determine the fraction of liquefied gas, the work required per unit of compressed mass, the work required per unit of liquefied mass and FOM for a Linde-Hampson cycle with air as the fluid of the work. $P_1 = 1 \text{ atm}$ and $P_2 = 200 \text{ atm}$ at 300 K .

	1	2	L
$h \text{ (J/g)}$	28.47	-8.37	-406
$s \text{ (J/g.K)}$	0.10	-1.5	-3.9

EX11:

Same questions from EX04 for N₂.

	1	2	L
h	464	454	35
s	4	2.8	0.4

EX12:

Determine the fraction of liquefied gas for a Linde-Hampson cycle with air as the working fluid. $P_1 = 1 \text{ atm}$ and $P_2 = 200 \text{ atm}$ at 300 K . Efficiency of the exchanger is equal to 100%; 95%; 90%; 85%.

	1	2	L	g
P atm	1	200	1	1
h J/g	28.47	-8.37	-406	-199

EX13

A system operating according to the Linde-Hampson cycle with N_2 as working fluid 1 atm and 200 atm at 300 K . Efficiency is equal to 100% and 90%. Calculate

- 1- Fraction of liquefied gas
- 2- Work required per unit mass of compressed gas
- 3- Work required per unit mass of liquefied gas
- 4- FOM

	1	2	L	g
s	4.4	2.75	0.42	3.2
h	464	430	29	230

EX14

Determine the liquefied gas fraction and FOM for a Linde-Hampson cycle with N_2 as the working fluid and for a precooled Linde-Hampson cycle with R134a refrigerant. $P_1 = 1 \text{ atm}$ and $P_2 = 100 \text{ atm}$ at 300 K .

For N_2

	1	2	L
h (J/g)	462	445	29
s (J/g.K)	4.42	3.1	0.42

For R134a

	a	b	c
h(J/g)	390	482	26
s(J/g.K)	-	-	-

EX15

Determine FOM for a double compression Linde-Hampson cycle with Argon as working fluid and for the following intermediate pressures:

$P_2=4 \text{ atm}; P_2=20 \text{ atm}; P_2=75 \text{ atm}; P_2=100 \text{ atm}$

at $T= 300 \text{ K}$ between $P_1= 1\text{atm}$ and $P_3= 120 \text{ atm}$.

The fraction of the intermediate mass flow is equal to $i= 0.6$; $i=0.7$.

EX16

Find the liquefied fraction, work per unit mass liquefied for a simple cycle used for air liquefaction.

Given :

- $T_1=T_2=300 \text{ K}$, $P_1=1\text{atm}$, $P_2=200 \text{ atm}$.

- Heat input is estimated at 5 J/g .

	1	2	L
h (cal/g)	6.7	-1.8	-97
s (cal/g.K)	-	-	-

EX17

A double compression Linde- Hampson system is used to liquefy the argon, which enters an isothermal and reversible compressor at 285 K and 2atm . The gas is compressed to 50atm in the low pressure compressor and 160 atm in high pressure. The flow ratio $i = m_i/m$ is 0.650 . Mass flow of liquid argon of the system is 2.5 kg/s .

- Determine the power consumed by the system

EX18

In a Linde dual pressure process, the compression process is isothermal and reversible and the operating conditions are: $P_B = 30 \text{ bar}$, $P_c = 200 \text{ bar}$, $T_7 = T_2 = T_1 = 290 \text{ K}$. Calculate:

- (a) the fraction of the mixture leaving the low pressure ;
- (b) the liquefied fraction;
- (c) the value of T_3 ;
- (d) the work per unit of liquefied mass;
- (e) The FOM of the process.

$$h_9 = -97 \text{ cal/g} , h_5 = -68.2 \text{ cal/g} , h_{10} = -47.4 \text{ cal/g} , h_7 = 2.4 \text{ cal/g}$$

$$h_{11} = 4.2 \text{ cal/g} , h_6 = -48 \text{ cal/g} , h_2 = -4.8 \text{ cal/g}$$

$$s_7 = -0.223 \text{ cal/(gK)} , s_2 = -0.38 \text{ cal/(gK)} , s_1 = 0.015 \text{ cal/(gK)} ,$$

EX19

Determine the liquefied fraction y , the amount of N_2 evaporated per unit mass of liquefied H_2 , the work per unit mass compressed, the work per unit mass liquefied and the FOM for the liquefaction of Hydrogen.

$$P_1 = 1 \text{ atm} , T_1 = 300 \text{ K} , P_2 = 50 \text{ atm} , T_4 = T_7 = 70 \text{ K}$$

$$h_1 = 4200 \text{ J/g} , h_2 = 4222 \text{ J/g} , h_4 = 593 \text{ J/g} , h_7 = 726 \text{ J/g} , h_f = -256 \text{ J/g}.$$

$$s_1 = 64.8 \text{ J/g-K} , s_2 = 48.6 \text{ J/g-K} , h_a = 14.1 \text{ J/g} , h_c = 462.3 \text{ J/g}$$

EX20

Determine the liquefied fraction, the total work per unit of compressed mass, the work per unit of liquefied mass and FOM of Claude's system used for the liquefaction of nitrogen. The mass fraction of the gas passing through the expander

$$P_1 = 101.3 \text{ kPa} , T_1 = 300 \text{ K} \text{ et } P_2 = 5.066 \text{ MPa}.$$

$$x = 0.6 \text{ et } T_3 = 270 \text{ K} ,$$

$$h_1 = 462 \text{ J/g}$$

$$s_3 = s_e = 3.11 \text{ J/(gK)}$$

$$h_2 = 452 \text{ J/g}$$

$$h_3 = 418 \text{ J/g}$$

$$h_e = 238 \text{ J/g}$$

$$h_f = 29 \text{ J/g}$$

$$s_1 = 4.42 \text{ J/(gK)}$$

$$s_2 = 3.23 \text{ J/(gK)}$$

EX21

Determine y, FOM for the Collins system, helium is the working fluid. The system operates between 1 bar and 15 bars. THE flow ratios of the expansion motors are respectively $x_1 = 0.6$, $x_2 = 0.2$. The conditions for entry into the expanders are:

$$T_3 = 60 \text{ K}, P_3 = 15 \text{ bars}, T_5 = 15 \text{ K}, P_5 = 15 \text{ bars}$$

	<i>1</i>	<i>2</i>	<i>3</i>	<i>5</i>	<i>e1</i>	<i>e2</i>	<i>f</i>
<i>P(bar)</i>	1	15	15	15	1	1	1
<i>T(K)</i>	300	300	60	15	20.32	4.97	4.22
<i>h(J/g)</i>	1574	1578	329.6	81.09	120.28	36.52	10.64
<i>S(J/g/K)</i>	31.61	25.99	17.60	9.76	17.60	9.76	3.47

