جامعة محمد خيضر بسكرة
MOHAMED KHIDER UNIVERSITY OF BISKRA

CURSE OF CRYOGENIC PROCESSES

3rd year license of Process Engineering

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FOREWORD

The course on cryogenic processes for 3rd year license students specializing in process engineering is an introduction to the techniques and applications of cryogenics, which is the study of extremely low temperatures and their effects on materials. Cryogenic processes are widely used in various fields of science, industry, and medicine due to the unique properties of substances at low temperatures.

The course starts by explaining the basic principles of cryogenics, including concepts of temperature, heat transfer, and material behavior at low temperatures. It also covers different methods of producing low temperatures, such as gas liquefaction, adiabatic expansion, and the use of specific equipment like refrigerators and cryostats.

Next, the course delves into the practical applications of cryogenic processes. It looks at industrial applications like gas liquefaction and separation, storage, and transportation of liquefied gases, as well as the use of cryogenics in the manufacturing of electronics and superconducting materials. The medical field is also explored, highlighting the use of cryogenics in preserving biological samples, cryosurgery, and cold therapy.

Recent advances in cryobiology and regenerative medicine are also discussed. Lastly, the course presents the challenges and considerations associated with cryogenic processes, such as energy losses, low-temperature materials, safety, and economic aspects. It also showcases ongoing research and future prospects in the field of cryogenics.

It should also be noted that prior knowledge in TTC (Thermodynamics & Heat Transfer) and mathematics is strongly recommended. This document is the result of reading various books and documents, most of which are not cited in the bibliography. In particular, I have largely drawn inspiration from numerous documents available online.

This course consists of four main chapters in accordance with the official programme of the Ministry of Higher Education and Scientific Research:

Chapter 1: Vacuum Technology
Chapter 2: Separation and Purification Processes of Cryogenic Fluids
Chapter 3: Liquefaction Processes of Permanent Gases
Chapter 4: Cryogenic Application

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GENERAL INTRODUCTION

CRYOGENICS AND ITS APPLICATIONS

1. WHAT IS CRYOGENICS ?

A. Definition.

Cryogenics is the science and technology of producing, managing, and utilizing extremely low temperatures, typically below -150°C (123 K). The term "cryogenics" comes from the Greek words "kryos," meaning cold, and "genic," meaning producing.

B. Temperature Range.

Cryogenic temperatures are generally defined as those below the boiling points of gases such as nitrogen (-196°C or 77 K), oxygen (-183°C or 90 K), and helium (-269°C or 4.2 K).

C. History.

The field of cryogenics began in the late 19th century with the liquefaction of air and other gases, leading to the discovery of various applications across industries.

2. IMPORTANCE OF CRYOGENICS.

A. Fundamental Research.

Cryogenics plays a critical role in scientific research, particularly in understanding the properties of materials at low temperatures, such as superconductivity and superfluidity.

B. Industrial Applications.

Cryogenics is essential in various industries, including the production and storage of liquefied gases, preservation of biological samples, and the manufacturing of specialized materials that require low-temperature processing.

C. Technological Advancements.

The development of cryogenic technology has enabled significant advancements in fields such as space exploration, healthcare, and energy storage.

3. DOMAINS OF APPLICATION.

A. Scientific Research.

- ***Superconductivity*** : Superconducting materials exhibit zero electrical resistance and are used in applications like MRI machines, particle accelerators, and quantum computing.

- ***Low-Temperature Physics*** : Cryogenics allows scientists to study quantum phenomena, such as Bose-Einstein condensation and the behavior of matter near absolute zero.

B. Medical Applications.

- ***Cryosurgery*** : The use of extremely low temperatures to destroy abnormal or diseased tissue, such as in the treatment of certains cancers.

- ***Cryopreservation*** : The preservation of biological samples, such as blood, reproductive cells, and tissues, by freezing them at cryogenic temperatures.

C. Industrial Applications.

- ***Liquefied Natural Gas (LNG)*** : The production, storage, and transportation of LNG rely on cryogenic processes to maintain the gas in a liquid state for ease of handling and reduced volume.

- ***Air Separation*** : Cryogenic distillation is used to separate air into its primary components—oxygen, nitrogen, and argon—which are essential in industries ranging from healthcare to manufacturing.

D. Aerospace and Space Exploration.

- ***Rocket Propellants*** : Liquid oxygen (LOX) and liquid hydrogen (LH2) are used as cryogenic propellants in rockets due to their high energy density and efficiency.

- ***Spacecraft Cooling Systems*** : Cryogenic technology is used to cool sensitive instruments in space, such as infrared telescopes, to prevent heat interference and improve performance.

E. Food Industry.

- ***Cryogenic Freezing :*** The rapid freezing of food products using liquid nitrogen or carbon dioxide, preserving quality by preventing the formation of large ice crystals.

- ***Cold Chain Logistics*** : Cryogenics is integral to maintaining low temperatures during the storage and transport of perishable goods, ensuring freshness and safety.

F. Energy and Environmental Applications.

- ***Hydrogen Economy*** : Cryogenic technology is used in the storage and transportation of liquid hydrogen, which is a potential clean energy carrier.

- ***Carbon Capture and Storage (CCS)*** : Cryogenic methods can be employed to capture and store CO2 by cooling it to cryogenic temperatures, facilitating its liquefaction and storage.

4. FUTURE PROSPECTS

- ***Innovations in Cryogenics*** : Ongoing research in cryogenics is leading to the development of more efficient cooling systems, advanced materials with unique properties at low temperatures, and new applications in quantum technologies.

- ***Challenges*** : The main challenges include energy consumption, material durability at low temperatures, and the development of scalable systems for industrial and commercial use.

Cryogenics is a rapidly evolving field with broad applications across various industries. Its ability to manipulate materials and processes at extremely low temperatures opens new frontiers in science, technology, and industry, making it a cornerstone of modern innovation.

CHAPTER 1

VACUUM TECHNOLOGY

1. VACUUM TECHNOLOGY IN CRYOGENIC PROCESSES

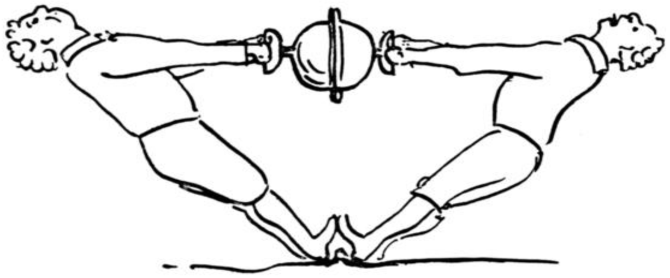
Vacuum : absence of all matter.

Absolute vacuum : a medium without elementary particles.

A space in which molecules are highly rarefied can therefore be considered a preliminary definition of approximate vacuum.

Thus, it is sufficient to use a vacuum pump to extract air from a sealed chamber to create a vacuum. The quality of the vacuum is then defined by the residual air pressure, generally expressed in pascals, millibars, or torr. Only a partial vacuum can be achieved with such a process, regardless of the temperature.

Creating a vacuum in a volume means starting from atmospheric pressure and evacuating the molecules, which lowers the pressure. The required vacuum level depends on the application : from a few mbar for vacuum handling to less than 10^-11 mbar (10^-9 Pa) for particle accelerators or surface analysis. It should be noted that a perfect vacuum does not exist, and at a pressure of 10^-10 Pa, which is not so easy to achieve, there are still 27,000 molecules per cm³.



TRYING TO SEPARATE THE TWO "MAGDEBURG HEMISPHERES"

The Magdeburg Hemispheres :

An experimental device by Otto von Guericke, mayor of Magdeburg, used to demonstrate the existence of a vacuum and the concept of air pressure.

1.1. Purpose of Vacuum

The aim of vacuum technology is to achieve pressures lower than atmospheric pressure by reducing the amount of matter present in the form of gas or vapor. Different types of pumps are used for this purpose, depending on the desired pressure. The processes implemented are primarily based on the understanding of the gaseous state. It was with the advent of the industrial era, when the understanding of heat and the atomic nature of energy became relevant questions, that the study of the gaseous state gained importance. Conducted using the mathematical and conceptual tools of the time, this study led, at the end of the 19th century, to the kinetic theory of gases, which allows for the prediction of relationships between the microscopic properties of a gas and its average behavior. With sufficiently formalized rules now available, the use of low pressures became possible on all scales, from the laboratory to industry.

1.2. Classification of Vacuum Domains

- **Rough or Industrial Vacuum (10^5 Pa to 10^2 Pa)**:
  Very large volumetric pumping rates (several hundred m^3 per hour).
  Applications: large installations, vacuum distillation, metallurgy, chemical processes.
- **Primary Vacuum (up to 1 Pa)**:
  Obtained by the first pump in the pumping system (volumetric pump).
  Allows the evacuation of 99% or more of the gases by volume.
- **Medium Vacuum (10^2 Pa to 10^{-2} Pa)**:
  Obtained by a Roots-type pump.
  Purpose: to facilitate the operation of the secondary pump.
- **High Vacuum (10^{-1} Pa to 10^{-5} Pa) or Secondary Vacuum**:
  Obtained by a secondary pump (diffusion or turbomolecular pump).
  The gas state is rarefied (molecular vacuum).
- **Ultrahigh Vacuum (10^{-5} Pa to 10^{-8} Pa)**:
  Applications: manufacturing of electronic tubes, space simulation, satellites.
- **Extreme Vacuum (below 10^{-8} Pa)**:
  Measurement and validity issues arise.
  Applications: study of matter structure (particle accelerators, etc.)

2. IMPORTANCE OF VACUUM IN CRYOGENICS

A. Role of Vacuum in Cryogenics :

- In cryogenic systems, maintaining a high vacuum is crucial to minimize thermal conduction and convection. The absence of air molecules in a vacuum reduces the thermal transfer from warmer surroundings to cryogenic components, thus ensuring the efficiency and stability of the system.

- A high vacuum reduces outgassing and contamination, which can be critical in systems where purity is essential, such as in superconducting magnets or cryogenic storage of biological materials.

B. **Benefits** :

- **Thermal Isolation** : Vacuum acts as an insulator, preventing heat transfer from external environments to cryogenic fluids or components, which helps in maintaining extremely low temperatures.
- **Prevention of Ice Formation** : A vacuum prevents the accumulation of frost or ice on cryogenic surfaces, which can occur when water vapor from the atmosphere freezes at low temperatures.
- **Operational Efficiency** : By minimizing thermal losses, a vacuum helps in reducing the consumption of cryogenic fluids and energy, leading to cost-effective operation of cryogenic systems.

C. **Applications** :

- **Cryogenic Liquefaction Systems** : In processes like liquefying gases (e.g., oxygen, nitrogen), vacuum technology is employed to enhance cooling efficiency and reduce energy losses.
- **Space Applications** : In spacecraft and satellite systems, cryogenics coupled with vacuum technology ensures stable operations of instruments and fuel storage.

3. VACUUM PRODUCTION SYSTEMS

3.1. Types of Vacuum Systems :

- **Mechanical Pumps** :
  - **Rotary Vane Pumps** : Commonly used for achieving rough vacuum levels, they are reliable and easy to maintain.
  - **Scroll Pumps** : Known for oil-free operation, ideal for sensitive applications where contamination must be avoided.
- **Turbomolecular Pumps** :
  - Used to achieve high and ultra-high vacuum levels, these pumps use high-speed rotors to remove gas molecules from the system.
- **Cryogenic Pumps** :

    - Utilize extremely low temperatures to condense gases and create a vacuum, often used in conjunction with other vacuum pumps to maintain ultra-high vacuum levels.
- **Diffusion Pumps** :
    - Use vaporized oil to capture gas molecules and are often used in high-vacuum applications, although they require careful management to avoid oil contamination.

3.2. Vacuum Measurement and Control :

- **Vacuum Gauges** : Instruments like Pirani gauges, ionization gauges, and capacitance manometers are used to measure the vacuum level and ensure the system operates within the desired range.
- **Leak Detection** :
    - **Helium Leak Detectors** : Often used in cryogenic systems, these detectors identify leaks by detecting the presence of helium, which has a small atomic size and can easily penetrate small leaks.

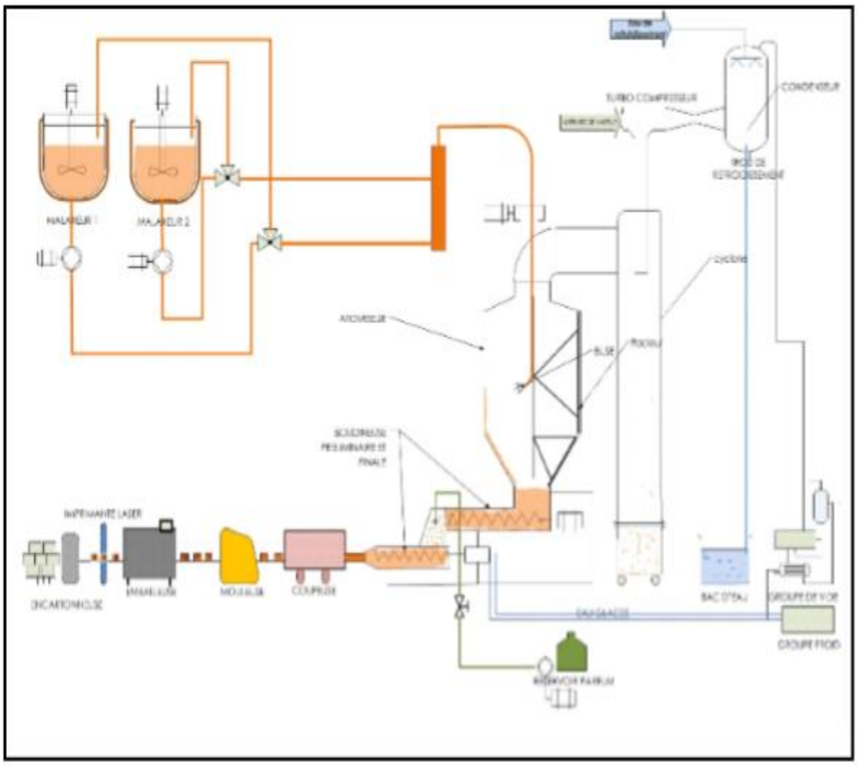
3.3. Design Considerations :

- **Material Selection** : Materials used in vacuum chambers must have low outgassing rates and be able to withstand thermal cycling between ambient and cryogenic temperatures.
- **Sealing Techniques** : The use of O-rings, gaskets, and metal seals ensures that vacuum integrity is maintained over time.
- **Pump Integration** : The integration of different pump types (e.g., backing pumps for turbomolecular pumps) and the sequence of operation are critical for achieving and maintaining the desired vacuum levels.

3.4. Example of vacuum Production Systems

Two examples of vacuum production systems are cited and studied below. The first example discusses a vacuum system in the soap manufacturing process and the second presents a vacuum system to assist the battery manufacturing process. Upon examining the two examples, it quickly becomes evident that the centerpiece of a vacuum production system is the vacuum pump.

A. Example 1 : A Vacuum System in the Soap Manufacturing Process



Soap making process diagram

The process begins with the transfer of soap from the mixer to the atomizer via a volumetric pump. Once in the atomizer, the soap is dried by a vacuum system composed of a vacuum pump and a thermocompressor that, by sending vapor through its high-pressure nozzle, creates a depression in the atomizer chamber. The dried soap then passes through a die, coming out as bars, which are subsequently cut into pieces, molded, packaged, and finally boxed.

B. Example 2 : A Vacuum System to Assist the Battery Manufacturing Process

Vacuum pump with lithium battery

To improve productivity and quality in lithium-ion battery manufacturing, several production lines are equipped with vacuum systems. These systems are used for the drying of electrodes. Each system combines a screw vacuum pump with a rotary piston fan. In battery cell manufacturing, vacuum technology can play a role in several manufacturing processes. The systems can :

- Provide the dry production environment required for electrode drying.
- Assist in cell assembly and leak detection testing.

CHAPTER 2

PROCESSES FOR SEPARATING AND PURIFYING CRYOGENIC FLUIDS

1. INTRODUCTION : ABOUT CRYOGENIC FLUIDS

As seen in Chapter 1, cryogenics encompasses all techniques for cooling a (macroscopic) sample of matter well below room temperature.

The easiest way to cool and maintain a low-temperature object or experiment (reaching temperatures much colder than 0 °C) is to use cryogenic fluids (cryogens or cryofluids), derived from gases liquefied by industrial processes.

Cryogenic fluids are liquefied gases kept in a liquid state at low temperatures. The term cryogenic means producing cold or related to low temperatures ; all cryogenic fluids are extremely cold. The boiling points of cryogenic fluids are < -150 °C. All cryogenic fluids are gases at normal temperatures and pressures. They must be cooled below room temperature before they can be liquefied through compression. Various cryogenic gases liquefy under different temperature and pressure conditions, but all have the following two properties :

- They are extremely cold
- Small amounts of liquid can occupy very large volumes when transitioning to the gaseous state.

→ Cooling with cryogenic fluid :

- Is extremely simple to implement
- Has no mechanical parts (besides the container).

However, the experiment must be continuously replenished with cryogenic fluid, which quickly becomes cumbersome… developing refrigeration machines (pulse-tube cryostats) that can operate continuously without cryogenic fluid, which are less burdensome but more complicated to use.

→ **Different Types of Cryogenic Liquids :**

Each cryogenic fluid is characterized by specific properties, but most can be classified into one of three categories :

- **Inert Gases:** These gases do not chemically react appreciably, nor do they support combustion. Examples: nitrogen, helium, neon, argon, and krypton.
- **Flammable Gases:** Some cryogenic liquids release a gas that can burn in air, such as hydrogen, methane, and liquefied natural gas.
- **Oxygen:** Many materials considered non-combustible can burn in the presence of liquid oxygen; for example, there can be an explosive reaction between the latter and organic materials.

⇒ However, the most commonly used cryogenic fluids are :

- Liquid nitrogen (N_2) between 100 and 65 K
- Liquid hydrogen (H_2) between 30 and 15 K
- Liquid helium (^4He) between 5 and 1 K
- Additionally, neon, xenon, and liquid helium (^3He) exhibit interesting properties for specific applications.

2. CRYOGENIC FLUID SEPARATION PROCESSES

The separation of gas mixtures using cryogenics applies to a whole range of molecules whose boiling point is between -40 °C and -270 °C. It can refer to several techniques used to separate gases from each other :

- either to produce several products - or to purify a single product.

Several processes can be used for the separation of cryogenic fluids ; Part of the products from the desired separation is in liquid state ; Combination : separation + liquefaction

The following table summarizes some properties of cryogenic fluids :

Gas	Boiling Point (°C)	Gas Expansion Volume
Acetylene	-84	-
Hydrogen Chloride	-85	-
Nitrogen	-195	696 to 1
Argon	-185	847 to 1
Carbon Dioxide	-78	553 to 1
Helium 3	-269	757 to 1
Helium 4	-268	757 to 1
Hydrogen	-252	851 to 1
Methane	-161	578 to 1
Carbon Monoxide	-192	-
Oxygen	-183	860 to 1
Trifluoride of Boron	-100	-

(Sources: http://www.technobio.fr/pages/Les_fluides_cryogeniques - 2051357.html)

➡In addition to distillation and fractional condensation, other separation techniques, the most commonly used industrially, can be utilized :

- Permeation
- Adsorption
- Absorption

2.1. Cryogenic Distillation

Distillation is a process for separating a mixture of liquid substances whose boiling temperatures are different. It allows for the separation of the components of a homogeneous mixture. Under the effect of heat or low pressure (ideal gas law), the substances vaporize successively, and the resulting vapor is liquefied to give the distillate. Since the 18th century, distillation operations have been carried out in industry to obtain, among other things, coke from coal or manufactured gases. These operations should more accurately be called pyrolysis : the term pyrolysis likely appeared in the 19th century to distinguish the operations of decomposition or thermolysis of an organic compound by heat to obtain other products (gas and matter) that it did not contain : in pyrolysis, the material is destroyed.

Cryogenic Distillation is carried out on a liquefied gas. The gas is compressed and then rapidly decompressed, which cools and liquefies it. By gradually reheating this now liquid gas and playing on the different boiling temperatures, its various components are separated.

Cryogenic Distillation of O_2:

The air is composed of: (See Course 'Pollution: Air, Water, Soil' (L3_GP_Semester 5))

- 78% (N_2) + 21% (O_2) + 1% (gases in small proportions: CO_2, Ar, Ne, He…) + Water vapor.
- Liquefaction temperature of O_2 = -183 °C > +13 °C to that of liquid N_2 (= -196 °C) possibility of isolating O_2 in its liquid form through cryogenic distillation!

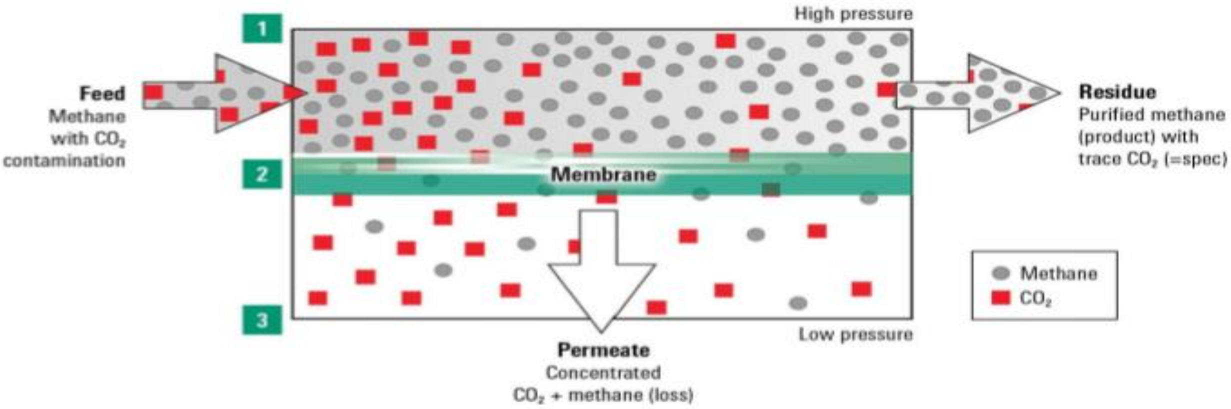
Fractional Condensation:

During separation by fractional condensation, the gas mixture is cooled in several stages during which the condensed fractions are removed. For molecules whose liquid phase is not stable at atmospheric pressure like CO_2, condensation may directly be in solid form and requires regular scraping of the support.

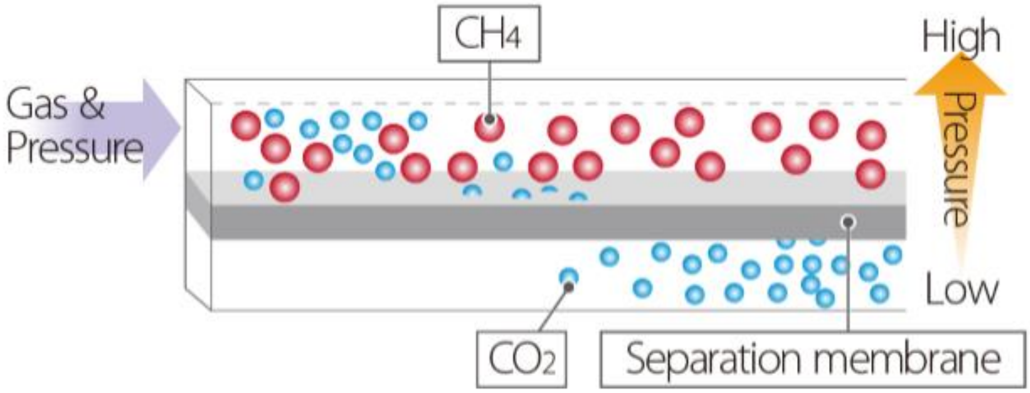
2.2. Permeation

Separation by permeation is a gas separation technique using semi-permeable membranes, which are more easily traversed by certain molecules than by others : this is called selective permeation. The selectivity of the membrane is ensured by a very thin skin supported by a more porous sublayer, or of a different nature (composite membrane) that provides the mechanical strength of the whole. The thickness of the skin = 1/100 µm to 1 µm, for a total membrane thickness = 25 to 250 µm. The equipment that allows the production of LNG is called liquefaction trains. Liquefaction plants are located as close as possible to production areas. When the gas is produced offshore, it is often brought ashore by pipeline. However, recently, offshore liquefaction systems are being developed.

In the figure below : The feed gas (e.g., CH4) enters from the side of the spirally wound membrane, allowing the smaller molecules (e.g., CO2) to traverse the multiple layers transversely. They then enter the lower pressure perforated central tube. The high-pressure non-permeable gas flow, rich in hydrocarbons and depleted in CO2, flows to the next section of the membrane modules to repeat this process until the necessary specifications for the produced gas are met. The low-pressure permeate flow rich in CO2 is collected in the central perforated tube and directed to the desired location as waste flow.



"In the figure below : During the purification of gases using a separation membrane, the difference in partial pressure across the membrane causes the permeation of the gas while allowing only the target gas to pass through."



Gas permeation presents :

- Low energy consumption.
- Compact equipment that is easy to install.
- Easy automation for installing small decentralized units.
- High operational safety.

Main Industrial Applications of permeation :

- Recovery of hydrogen from ammonia production or refining purge gas.
- Drying of air.
- Drying of hydrocarbons.
- Purification of natural gas (NG).
- Preparation of oxygen-enriched air.

3. JOULE-THOMSON VALVE

A little history

The critical temperature of ammonia is 132 °C, its condensation pressure = 10 atm (at 26 °C). Therefore, it is enough to increase the pressure of ammonia beyond 10 atm without exceeding 26 °C to obtain it in liquid state. Conversely, it is different for many other gases whose critical temperature is below ambient. For example, the critical temperature of air = -140.6 °C. No condensation will be possible without lowering its temperature below this value. For these gases, refrigeration machines will be necessary to lower the temperature below ambient.

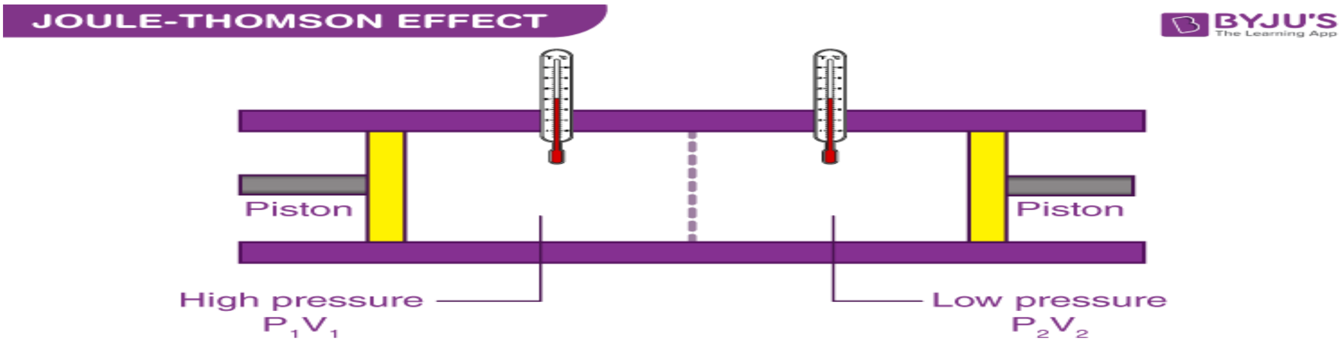
In 1852, James Prescott Joule & William Thomson (Lord Kelvin) discovered that the expansion of a real gas through a valve causes a sudden cooling, known as the Joule-Thomson effect or Joule-Thomson expansion (or Joule-Kelvin expansion).

→ **Liquefaction by Expansion**

In 1869, Thomas Andrews discovered the existence of the critical temperature and recognized the continuity of liquid and gaseous states. He demonstrated that it is impossible to liquefy a gas below its critical temperature (liquefaction point), even by infinitely increasing its pressure.

3.1.What Is Joule-Thomson Effect ?

The Joule-Thomson effect also known as Kelvin–Joule effect or Joule-Kelvin effect is the change in fluid's temperature as it flows from a higher pressure region to lower pressure.

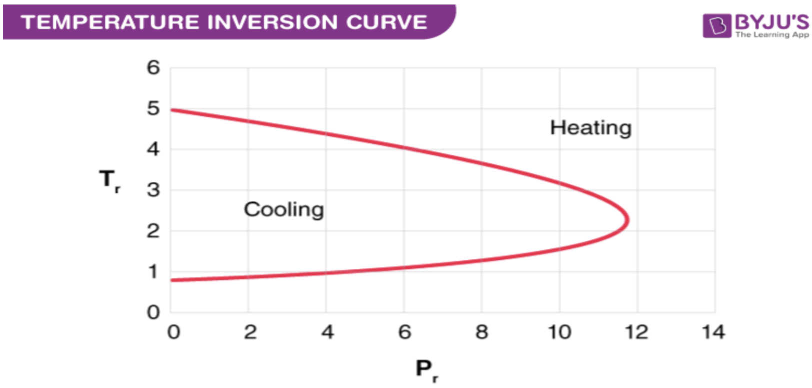


According to the thermodynamic principle, the Joule-kelvin effect can be explained best by considering a separate gas packet placed in the opposite flow of direction for restriction. For the gas packet to pass through, the upstream gas needs to perform some work to push through the packet. The work equals the volume of the packet multiplied by the times of upstream pressure.

The basic principle of Joule Thomson effect is based on the transfer of heat. Also, at ordinary temperature and pressure, all real gases undergo expansion and this phenomenon is used in the process of liquefying gases. But this does not hold good for hydrogen and helium.

3.2.Derivation of Joule Thomson Coefficient

Joule Thomson coefficient can be derived using the thermodynamic relationships and is defined as the isenthalpic change in temperature in the fluid due to pressure drop.



The temperature of a gas at which the reduction in pressure does not lead to any change in temperature is known as inversion temperature. The gas gets heated up on expansion and cools down below this temperature.

3.3.Applications of Joule-Thomson Effect

- The cooling produced in the Joule-Thomson expansion has made it a very valuable tool in refrigeration.
- The effect is applied in the Linde technique in the petrochemical industry, where the cooling effect is used to liquefy gases.
- It is also used in many cryogenic applications. For example for the production of liquid nitrogen, oxygen, and argon.
- The effect can also be used to liquefy even helium.

The Joule-Thomson effect is widely used to cool many gases to very low temperatures, making their liquefaction possible!

Then:

- Talking about Joule-Thomson expansion refers to an expansion through a valve called the Joule-Thomson valve (or J.T valve)!
- The Joule-Thomson expansion is a sudden drop in pressure during the flow of fluid through an orifice.
- A J.T valve is found in the following two cycles :
    - Refrigeration Cycle
    - Liquefaction Cycle

4. AIR SEPARATION PROCESSES

The separation of gas mixtures can refer to a number of techniques used to separate gases from each other (See the beginning of this Chapter 2). Among the gas mixtures most affected, we find air. Cryogenic distillation (See the beginning of this Chapter 2) is generally only used for very high volumes due to its non-linear cost-scale relationship, which makes the process more economical on a larger scale. For this reason, it is typically only used for separating the components of air. Air gases are frequently used in the industrial sector. These gases (mainly oxygen and nitrogen) can be processed and separated using cryogenic pumps and ultra-efficient brazed heat exchangers. All major industrial gas companies produce and market various gases and liquids produced in air separation plants. These plants, using a cryogenic distillation method (See the beginning of this chapter), divide atmospheric air into its different components : nitrogen (N_2) and oxygen (O_2), argon (Ar), and other rare inert gases. Oxygen (O_2) and nitrogen (N_2) are used for many purposes across a wide range of different industrial sectors including :

- Electronics and aerospace
- Pharmaceutical
- Petrochemical
- Oil and gas
- Chemical
- Energy
- Mining
- Steel
- Metallurgy
- Environmental protection
- Medical
- Food
- Biotechnological
- Fertilizers
- Nuclear energy

Main Equipment

Brazed heat exchangers and cryogenic pumps are integral to cryogenic air separation processes. Brazed heat exchangers, some of which are connected to distillation columns, are integrated into metal casings, commonly referred to as cold boxes, and can contain piping and insulation, protecting the equipment from external elements like rain, etc.

Air is composed of many gases :

- We can liquefy air by lowering its temperature…
- Its storage is more easily…
- The industry separates the constituents of air by distillation (see the beginning of this Chapter 2).
- Each gas is recovered when its boiling temperature is reached. Pure, the isolated gas can then be re-liquefied if necessary.

In reality, there are two main processes for air separation:

Cryogenic Process and **non-Cryogenic Process**

4.1. First Main Process : Air Cryogenic Separation

In a cryogenic air separation plant, the gases contained in ambient air are separated according to the principle of low-temperature rectification, using their different boiling points. The figure below applies the cryogenic separation principle for the following types of installations :

- Large capacity air separation unit with optional liquefaction.
- Nitrogen generators.
- Oxygen generators.

4.2. Second Main Process : Non-Cryogenic Air Separation

Non-cryogenic processes for air separation operate through pressure swing adsorption or membrane separation. The types of installations that can be used during adsorption processes are :

- **Pressure Swing Adsorption (PSA) :** This process relies on the physical adsorption qualities of specially treated molecular sieves. To ensure cost-effective production of N_2 or O_2 with purity up to 99.9% (N_2) or 93% (O_2). This air will be compressed to 10 bar, cleaned, and blown through a vessel filled with a molecular sieve.

Vacuum Pressure Swing Adsorption (VPSA): This is actually a modified PSA process. VPSA installations operate with a fan generating an overload pressure of approximately 1.5 bar and a vacuum pump used during the regeneration cycle.

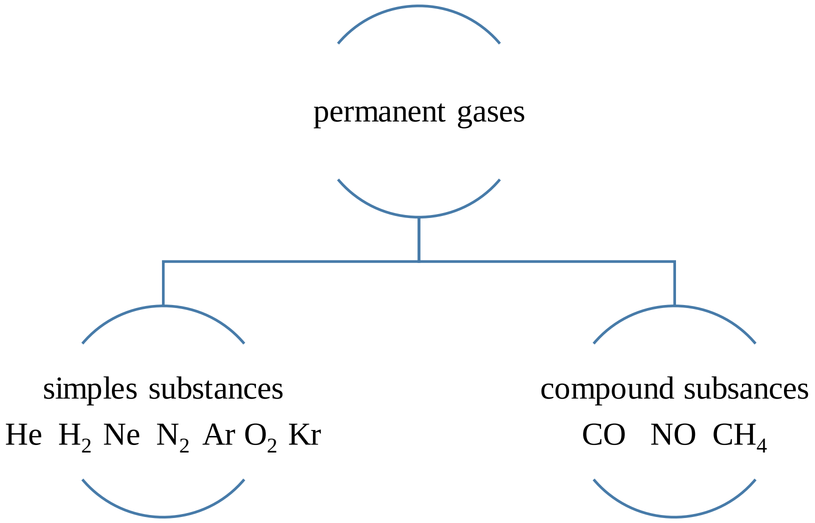
CHAPTER 3

PERMANENT GAS LIQUEFACTION PROCESSES

1. INTRODUCTION

In this chapter, we will mainly discuss some processes for the liquefaction of permanent gases, either pure or in mixtures. We will also mention some gases or gas mixtures that can be obtained in a liquid state at relatively low temperatures (between +10 °C and +40 °C) when under pressure, as well as gases or gas mixtures that remain liquid under pressure up to temperatures around +100 °C. The latter are sometimes referred to as liquid gases (such as propane, butane, ammonia…).

10 pure substances fit the previously given definition of permanent gases :



We will add 3 mixtures of gases which particularly concern the industrial field : air, natural gas (NG) and synthesis gas...

A gas is defined as any substance that exists in an expansible and compressible fluid state (gaseous state) under normal temperature and pressure conditions.

A permanent gas is a gas that cannot be liquefied by simply increasing the pressure (at ordinary temperatures, that is, without applying cold).

In more scientific language, it can be stated that any gas whose critical temperature is lower than the ambient temperature is a permanent gas. However, it must be clarified where the ambient temperature is situated. The examination of the vapor pressure curves of gases shows that, with the exception of ozone (which is difficult to encounter in a pure state due to its instability), no gas has its critical point in the temperature range between -64 °C (Kr) and +10 °C (C_2H_4). If we set the lower threshold of the ambient temperature in this range, krypton is the first gas classified as a permanent gas.

2. LIQUEFACTION OF NON-PERMANENT GASES

The most general and natural method for liquefying a gas is to cool it below its normal boiling point. Unfortunately, this temperature is often extremely low and therefore difficult to achieve. Conversely, the boiling point rises with pressure. Sometimes, it is sufficient to compress a gas to make it susceptible to liquefaction at ordinary temperatures. Thus, there are two processes to bring gases to a liquid state :

- The first is absolutely general.
- The other is not applicable in all cases.

In reality, the two methods are often combined because it is easier to produce both moderate cold and medium pressure than to achieve either very high pressure, which might not always suffice, or very vigorous cooling.

2.1. Liquefaction by cooling alone

Although this method is absolutely general, it has been used very little. However, as early as 1821, Bussy liquefied ammonia under atmospheric pressure in a tube cooled to -40 °C; three years later, he liquefied sulfur gas in large quantities in a mixture of ice and sea salt. At Bussy's time, this method could only be applied to a small number of gases due to the lack of cooling agents other than the so-called refrigerant mixtures, which only allow cooling to about -50 °C. Nevertheless, these mixtures would have sufficed for :

- Cyanogen, which liquefies at -20 °C,
- Chlorine, which transforms at -35 °C into a yellow liquid,
- Hydrochloric acid, which boils at the same temperature.

One can also obtain the necessary cold by the expansion of the gas one wishes to liquefy ; this expansion can occur in two ways :

- Either, as in the Caillelet apparatus, with the production of external work,
- Or using only internal work (Linde machine).

2.2. Liquefaction by pressure alone

Compression can also be applied alone. Thus :

- Sulfur dioxide liquefies at 7.5 °C under a pressure of 3 atm.
- At 15 °C, a pressure of 4 atm is sufficient for chlorine, 40 atm for hydrochloric acid.
- At 10 °C, hydrogen sulfide requires only 17 atm, ammonia 6.4 atm, carbon dioxide 36 atm.
- Cyanogen and nitrous oxide become liquid at 7.2 °C under respective pressures of 3.7 and 50 atm.

Thus, these eight gases were liquefied by Faraday in his first series of experiments. The Thilorier apparatus and that of Mr. Berthelot also utilize compression alone.

2.3. Liquefaction by pressure and cooling

In most experiments, both pressure and more or less vigorous cooling have been applied simultaneously. Furthermore, pressure can be produced in two distinct ways :

- Either by accumulating the gas in a reservoir using a pump,
- Or by producing in a container, through a chemical reaction, an increasingly larger mass of gas.

2.4. Use of gas pressure

This latter process was employed by Faraday in his first series of experiments, published in 1823. In one branch of an inverted V-tube, the necessary substances were enclosed to produce the gas, generally under the influence of heat. The tube being sealed at the lamp, one heats the first branch and cools the second, if necessary. As soon as the gas reaches an elastic force exceeding its maximum tension for the temperature of the cold branch, it liquefies in that branch, according to Watt's principle.

- Ammonium nitrate, heated in this tube, yielded nitrous oxide.
- Hydrochloric acid and iron sulfide provided hydrogen sulfide.

- Mercury and sulfuric acid produced sulfur dioxide, etc.

Faraday witnessed these gases liquefy at the temperatures and pressures indicated above. This method was modified in 1872 by Melsens, who liquefied various gases : chlorine, sulfur dioxide, ethyl chloride, cyanogen, hydrogen sulfide, ammonia, and hydrogen iodide.

However, until Faraday's work, gases had only been liquefied in small quantities, and none had been solidified.

3. LIQUEFACTION OF PERMANENT GASES

These six gases, which were thus named permanent gases, are :

- Oxygen,
- Hydrogen,
- Nitrogen,
- Nitrous oxide,
- Carbon dioxide,
- Methane.

As previously seen, almost all gases have been liquefied using the earliest liquefaction methods, but six gases had shown resistance with no trace of condensation, even at -110 °C and under pressures ranging from 27 to 50 atmospheres. These six gases, which were thus named permanent gases, are:
Some attempts to use pressure alone, without the aid of cold, had also been unsuccessful! The different methods of liquefaction already seen are :

- Liquefaction by cooling alone
- Liquefaction by pressure alone
- Liquefaction by pressure and cooling
- Use of the pressure of the gas

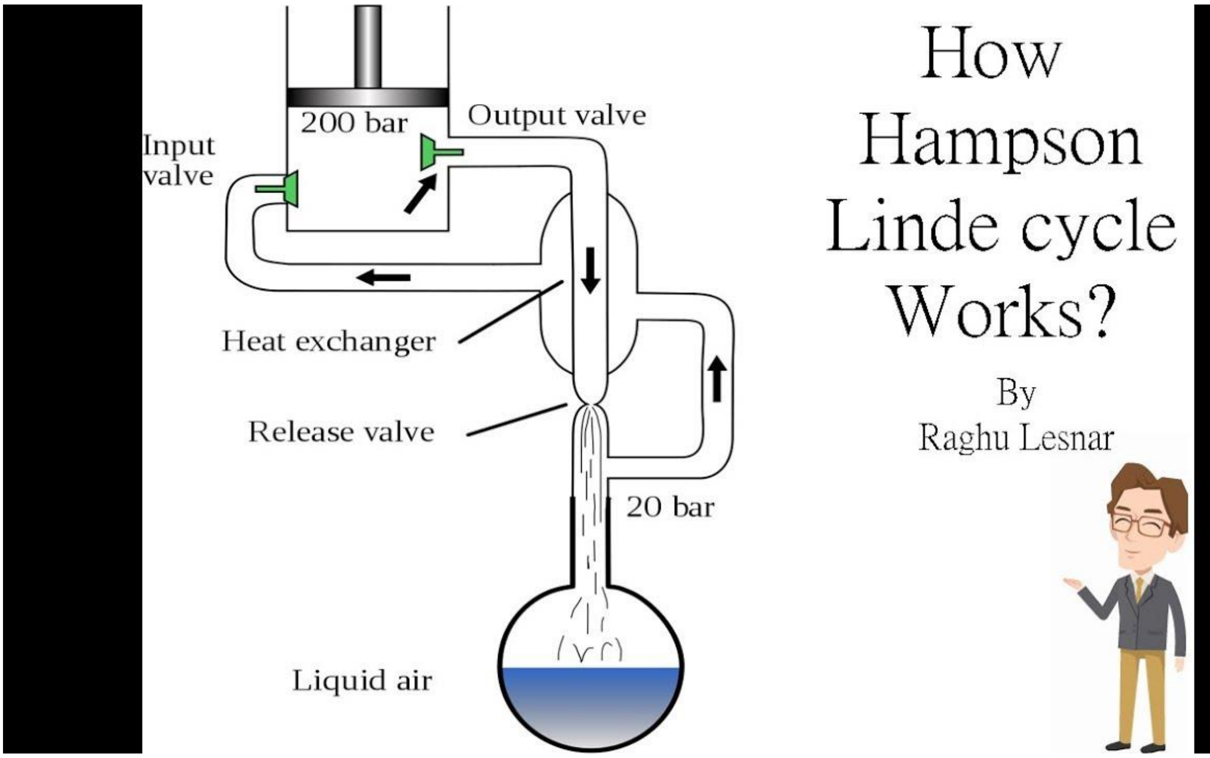
In 1845, in a second series of experiments, Faraday employed mechanical pressure combined with intense cooling. The dry gas passed successively through two pumps, which raised its pressure first to 16 or 20 atm, then, if necessary, up to 40 atm, and accumulated in a U-tube containing a small compressed air manometer : this manometer consisted of a simple divided capillary tube filled with air, closed at one end and sealed at the other with a mercury index ; the U-tube was surrounded by a refrigerating mixture of solid carbon dioxide and ether (Thilorier mixture). In some cases, the apparatus was covered with a bell jar under vacuum to reduce the temperature to about -110 °C. Most gases were liquefied or even solidified with this setup !

Some attempts to use pressure alone, without the aid of cold, had also been unsuccessful ! Aimé, in 1843, resuming an earlier experimental mode used by Perkins, submerged a gas-filled bladder in the sea, communicating with a manometric tube filled with mercury : he unsuccessfully went up to 220 atm for hydrogen and nitrogen. In 1850, Mr. Berthelot compressed oxygen to 780 atm in a very thick glass thermometer, the reservoir filled with mercury and the gas column ; by heating the reservoir, the mercury expands, penetrating the column and increasingly compressing the gas. In 1854, Natterer subjected permanent gases to a pressure of 2790 atm without success. Indeed, as early as 1822, Cagniard de la Tour, heating various liquids in a closed vessel, saw them transform into vapor with almost no change in volume. In 1845, Drion obtained similar results with sulfur gas, ethyl chloride, and ordinary ether. At the same time : Finally ! The previous methods had allowed almost all gases to be liquefied ; only six had resisted and showed no signs of condensation, even at -110 °C and under pressures ranging from 27 to 60 atm. The negative results of the preceding experiments seemed to demonstrate that an increase in pressure, even considerable, is insufficient to liquefy permanent gases. This conclusion aligns with those that can be deduced from earlier experiments. Faraday concluded from his own experiments and those of Cagniard de la Tour that it was impossible to liquefy permanent gases without resorting to vigorous cooling.

3.1. Linde-Hampson Liquefaction Process

- **Overview** :
    - The Linde-Hampson process is one of the earliest and most straightforward methods for liquefying gases, particularly air. It leverages the Joule Thomson effect, where a gas cools upon expansion without performing external work.
- **Process Description** :
    - **Compression** : The gas is first compressed to a high pressure.

  - **Pre-Cooling** : The compressed gas is then pre-cooled using a heat exchanger, typically by countercurrent exchange with cold gas leaving the system.
  - **Joule Thomson Expansion** : After pre-cooling, the gas is allowed to expand through a Joule Thomson valve, leading to a drop in temperature and partial liquefaction.
  - **Separation** : The liquid and vapor phases are separated, with the vapor being recirculated and the liquid collected as the final product.
- **Key Features** :
  - **Simplicity** : The process is straightforward and requires minimal equipment, making it cost-effective and easy to implement.
  - **Efficiency** : Though not as efficient as more modern methods, it is still widely used for small-scale applications.



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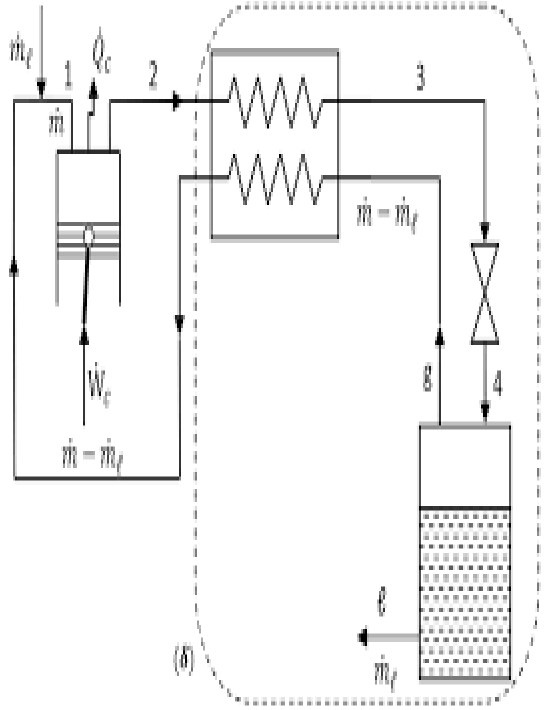


In this process, the gas compressed at high pressure in the compressor to constant temperature (room temperature) isothermal compression, The compressed refrigerant is cooled in a counter-current heat exchanger at constant pressure, then through an expansion valve the gas undergoes a second lowering of temperature (Relaxation of J-T) in the saturation zone, which allows the fluid to be partially liquefied in the liquid separation tank, the rest of the non-liquefied saturated gas undergoes isobaric heating in the exchanger heat (counter-current) before

The liquefied gas evolves in the cycle according to the following transformations :

1-2: Isothermal compression.

2-3: Isobaric cooling of the fluid.

3-4: Isenthalpic relaxation in the valve.

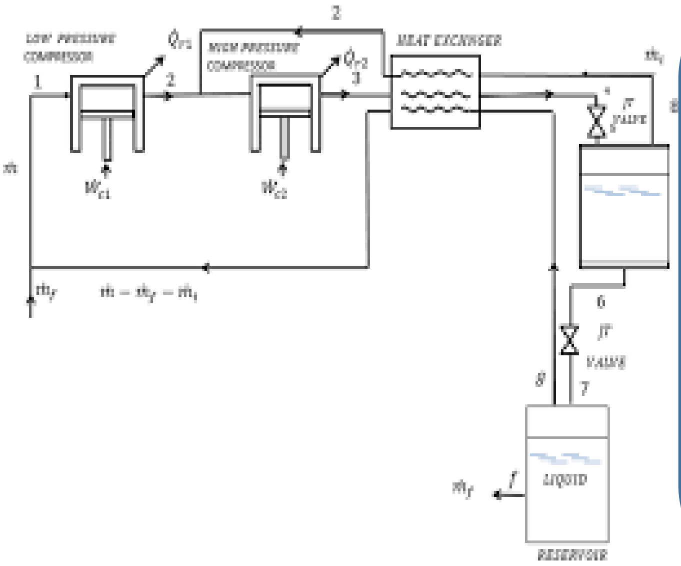
4-5: Saturated steam.

5-1: Isobaric heating of the fluid (gas) in the exchanger.

3.2. Linde-Hampson Double Compression Liquefaction Process

- **Process Improvement** :
  - This process is an enhancement of the basic Linde-Hampson process. It introduces an additional compression stage to improve efficiency by reducing the amount of work needed to achieve liquefaction.
- **Process Description** :
  - **First Compression Stage** : The gas is initially compressed to a moderate pressure.
  - **Pre-Cooling and Heat Exchange** : Similar to the basic process, the gas is pre-cooled, but with additional heat exchangers to maximize energy recovery.

  - **Second Compression Stage** : The pre-cooled gas is further compressed to a higher pressure, which increases the Joule Thomson effect during expansion.
  - **Expansion and Liquefaction** : The highly compressed gas undergoes expansion through the Joule Thomson valve, resulting in more efficient liquefaction.
- **Key Advantages** :
  - **Higher Efficiency**: The double compression stage allows for lower overall energy consumption and higher liquefaction yields.
  - **Enhanced Cooling**: More effective use of pre-cooling and heat exchangers leads to better temperature control and process stability.



To improve the performance of the Linde cycle it is necessary to increase the liquefaction rate and ensure that the gas leaving the exchanger is at a room temperature. The LINDE double choke system contains :

- Two compressors
- Two throttle valves
- Two tanks
- A counter-current heat exchanger

3.3. Claude's Liquefaction Process

The Linde cycle uses isenthalpic expansion which has two drawbacks : firstly the expansion work is lost, and secondly cooling cannot be achieved if the fluid thermodynamic state is such that the Joule Thomson expansion leads to a temperature lowering.

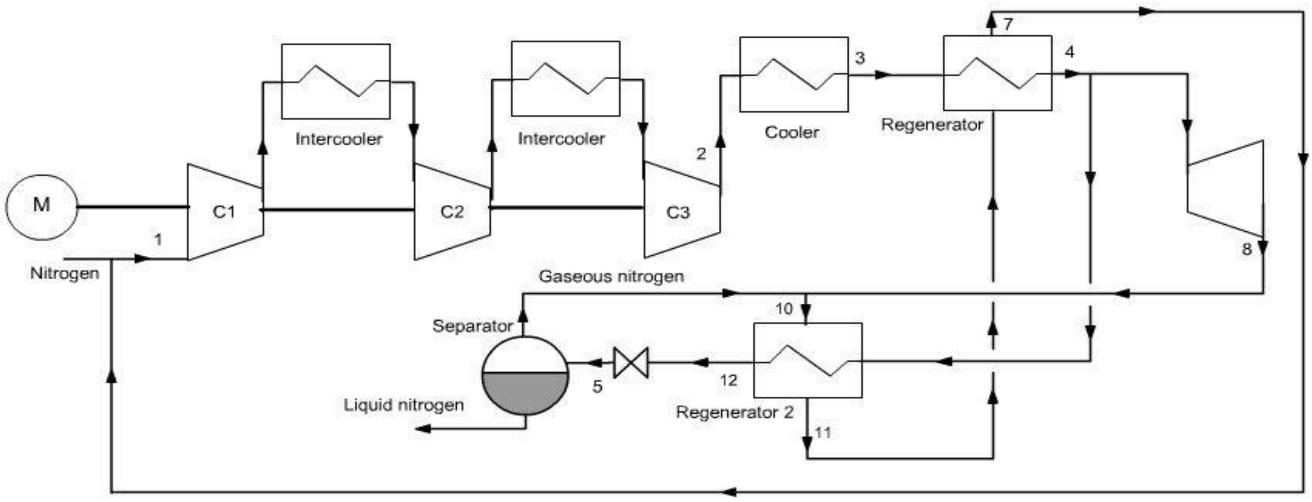
Claude has proposed a cycle that involves a turbine and an expansion valve and has the peculiarity that the plant operates with a single fluid compressed at a single pressure level, as shown in Figure below. The Claude cycle has been used in many air liquefying facilities.

- **Overview** :
    - The Claude process is a more advanced method of gas liquefaction that incorporates both isentropic (adiabatic) expansion and the Joule Thomson effect. It is particularly effective for liquefying gases that require very low temperatures, such as hydrogen and helium.
- **Process Description** :
    - **Initial Compression** : The gas is compressed to a high pressure, similar to the Linde-Hampson process.
    - **Pre-Cooling** : The compressed gas is pre-cooled using heat exchangers, often involving regenerative cooling from the cold exhaust gases.
    - **Expansion Engine** : The pre-cooled gas is then expanded isentropically through an expansion engine (turboexpander), which cools the gas significantly by doing work on the surroundings.
    - **Joule Thomson Expansion** : After the isentropic expansion, the gas undergoes a further pressure drop through a Joule Thomson valve, leading to additional cooling and liquefaction.
    - **Phase Separation** : The resulting mixture of liquid and vapor is separated, with the vapor being recycled and the liquid collected.
- **Key Features** :
    - **Efficiency** : By combining isentropic expansion with the Joule Thomson effect, the Claude process achieves higher efficiencies and lower final temperatures than simpler processes.
    - **Complexity** : The process requires more sophisticated equipment, such as expansion engines, but offers greater control over the liquefaction process.
- **Applications** :
    - **Liquefaction of Hydrogen and Helium** : Due to its ability to reach very low temperatures, the Claude process is commonly used for gases that are difficult to liquefy.

Claude thus achieves separation by fractional distillation of oxygen, nitrogen, and argon. The cold necessary for the industrial liquefaction of air is obtained through expansion, taking advantage of the following two properties of the Joule-Thomson effect :

- The temperature drop caused by the expansion is proportional to the difference between the initial and final pressures.
- The energy expended during compression is proportional to the logarithm of the pressure ratio, meaning that the expenditure is the same for compressing a mass of gas from 1 to 10 atm or from 10 to 100. In the latter case, for the same energy expenditure, the temperature drop after expansion is ten times greater than in the former.

The advantage of this cycle is that the compression ratio can be significantly lower than in the case of the Linde cycle. One of the difficulties is that the expansion machine can only operate with good efficiency if the fluid remains in the vapor zone or retains a high quality. Therefore, the originality of the Claude cycle is to combine isentropic expansion in the turbine with isenthalpic expansion in the only expansion leading to the liquefaction of the gas.



The beginning of the cycle is the same as that of Linde: compression of gas to liquefy, then cooling to about room temperature (1–3). The gas then passes through a regenerator which allows it to cool at about -105°C (3–4). The flow is then divided, about 15% being expanded in a turbine (4–8). The main flow passes through a second regenerator of which it is released at very low temperature (4–12). It undergoes isenthalpic expansion (12–5) and the liquid phase is extracted. The vapor is mixed with the flow exiting the turbine, and serves as a coolant in the second regenerator (10–11), then in the first (11–7) before being recycled by mixing with the gas entering the cycle.

The advantage of this cycle is that the compression ratio can be significantly lower than in the case of the Linde cycle. One difficulty is that the expansion machine cannot operate with good efficiency if the fluid remains in the vapor zone or keeps a high quality. The originality of the Claude cycle is to combine isentropic expansion in the turbine, and isenthalpic expansion only in expansion leading to the gas liquefaction.

CHAPTER 4

CRYOGENIC APPLICATIONS

1. WHAT IS CRYOGENIC TECHNOLOGY ?

Before we discuss cryogenic applications in detail, first, a brief introduction, what exactly is cryogenic technology, and what makes a material or application "cryogenic" ?

Cryogenic engineering is the field that deals with **extremely low temperatures** and the **chemical reactions** that take place in the process. The focus is on the liquefaction of industrial gases. Around a temperature of -160°C, gases take on a liquid form, and from this temperature and below, are referred to as "cryogenic".

A large number of industries use liquefied industrial gases, which are kept liquid using cryogenic technology. Some of the industries that rely significantly on cryogenics include the :

- *Automotive industry*
- *Electronics industry*
- *Food industry*
- *LNG industry*
- *Marine industry*
- *Medical industry*
- *Pharmaceutical industry*
- *Scientific research*
- *Space industry*
- *Hydrogen industry*
- *Air separation industry*

Each of these industries work with specific applications that use different liquid gases at different temperatures. Four liquid gases we typically see within many sectors are:

- ***Liquid nitrogen*** (with a boiling point of -195.8°C). Liquid nitrogen is widely used in the *automotive industry*, *electronics industry*, *food industry*, *medical industry*, and *pharmaceutical industry*, where it is used for the cryogenic cooling of materials. As liquid nitrogen can be extracted from ambient air, it is a relatively environmentally friendly and affordable gas. This makes it a popular gas used by many manufacturers.
- ***Liquid hydrogen*** (with a boiling point of -252.9°C). As can be read in our blog on liquid hydrogen, this popular gas is widely used as a renewable fuel and energy carrier in, among others, the (road) transportation sector.
- ***LNG***, or liquefied natural gas (with a boiling point of -162°C). LNG is a popular fuel widely used in the road transport and *marine industries*.

- ***Liquid helium*** (with a boiling point of -268.9°C). Helium is essential in *scientific research* and is regularly used in the *medical industry*.

2. DISCOVERY OF SUPERCONDUCTIVITY

2.1.Introduction to Superconductivity :

Superconductivity is a quantum mechanical phenomenon where a material exhibits zero electrical resistance and the expulsion of magnetic fields when cooled below a characteristic critical temperature.

This discovery was made by Heike Kamerlingh Onnes in 1911 when he observed that mercury lost all electrical resistance at 4.2 K (-269°C).

2.2.The Role of Cryogenics :

Cryogenics is essential for achieving the extremely low temperatures required to induce superconductivity. Liquid helium, with a boiling point of 4.2 K, is often used to cool materials to their superconducting state.

The development of cryogenic technology has enabled the exploration of superconductivity in various materials, including high-temperature superconductors which function at higher temperatures (though still cryogenic).

2.3. Applications of Superconductivity :

- **Magnetic Resonance Imaging (MRI)**: Superconducting magnets are used in MRI machines to create strong, stable magnetic fields, allowing for detailed imaging of soft tissues in the body.
- **Particle Accelerators** : Superconducting magnets are crucial components in particle accelerators, such as the Large Hadron Collider (LHC), where they guide and focus particle beams with high precision.
- **Power Transmission** : Superconducting cables can carry electricity with zero losses over long distances, which has potential for revolutionizing power grids.

3. CRYOGENIC APPLICATIONS

The very first cryogenic applications, cryogenic technology does not stand still. There is continuous research into new techniques, applications, and possibilities for the most efficient use of liquid gases. But where did it all begin ? What did the first cryogenic applications look like ?

As might be expected, the development of cryogenic applications began with research surrounding the production and storage of liquefied gas. Thus, in 1892, not long after various gases were first liquefied, James Dewar developed his well-known **dewar**. The dewar is a storage container for extremely cold gases that is still widely used today.

A few decades later, the focus shifted to the large-scale production of industrial gases. A strong example of an important development in this field was the construction of the first **air separation plant** for oxygen in 1902. This new technique, discovered by Carl Von Linde, was seen as a major breakthrough in cryogenics.

As large-scale production of industrial gases took off, cryogenic applications were developed and deployed in various industries. To name a few examples :

- Around 1960, liquid nitrogen was first used for food refrigeration on a commercial basis in **large-scale freezing systems**.
- In 1961, liquid hydrogen and liquid nitrogen were used in the **U.S. rocket Atlas Centaur.**
- During the same period, several developments also took place in the medical field. For example, the first cryoprotectants were used in 1946 and 1959 to **cool medical tissue**. In 1961, **cryosurgery** was performed for the first time, and in 1983, the first cryogenic techniques were used for **Magnetic Resonance Imaging (MRI).**

The above applications represent only a small selection of all cryogenic applications discovered and developed over the past century. Some have remained, others have been replaced, and new applications are added every year.

An Atlas-Centaur rocket on Pad 36A at Cape Kennedy for a fueling test in preparation for the AC-3 launch in June 1964.
Source: NASA, Glenn Research Center

Cryogenic applications in 2023

In 2023, cryogenic technology will become an indispensable part of a good number of industries. Many manufacturing processes are now dependent on liquid gases, and cryogenic infrastructures are getting both better and more sophisticated.

Further on in this blog, we will elaborate on some recent discoveries in cryogenics and possible cryogenic applications in the future. First, however, we want to briefly discuss cryogenic applications that will be fully established and widely produced and used by 2023.

3.1.Cryogenic applications in the medical and pharmaceutical industry

Two interrelated industries in which cryogenic applications will be widely used in 2023 are the *medical* and *pharmaceutical industries*. In both industries, the **preservation of tissue in optimal form** is vital, whether it be **medicines** or **biological materials**.

Cryogenic freezing systems

The cryogenic freezer is one of the oldest and most widely used *cryogenic freezing* systems in the *medical* and *pharmaceutical industries*. In standard *cryogenic freezers*, **liquid nitrogen** is injected into the system, **creating cold vapors**. These vapors envelop the product to be cooled and bring it to the desired low temperature.

Many substances, such as certain drugs, blood cells, stem cells, and eggs, can be frozen using a “regular” *cryogenic freezer* or a so-called *control rate freezer*. However, this does not apply to all substances. Sometimes the preservation of specific components is so important that other techniques are needed. In this case, *freeze drying* – or *lyophilization*– may offer the solution.

Freeze drying is a refrigeration process in which water is removed from a substance after it has been frozen and placed in a vacuum. This process is used to freeze food, pharmaceutical/biopharmaceutical bulk ingredients, proteins, collagen, peptide, oligonucleotide, chemical API, enzymes, and mAbs.

Storage of materials and cryogenic liquids

Obviously, the *medical* and *pharmaceutical industries* use many other cryogenic applications. For example, small biological samples are stored in CRFs and storage containers, where they can be kept for an extended period of time while they remain at optimum quality. This process is called *sample storage*.

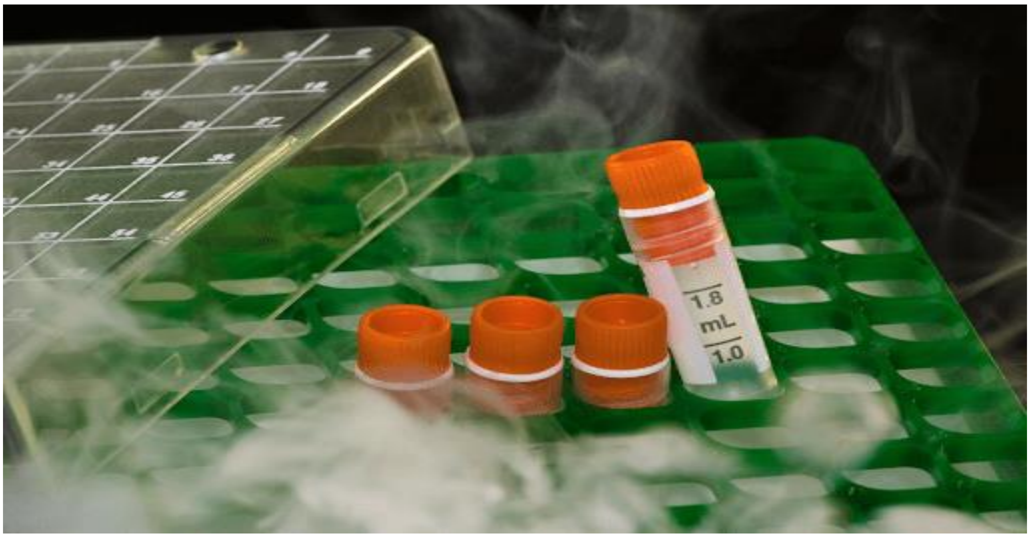
Sample storage takes place in small vials, which are cooled in liquid nitrogen to approximately -135°C. The extreme cold stops virtually all biological activity and theoretically minimizes sample degradation over the long term.

Finally, within many medical facilities, we also see the aforementioned *cryogenic storage dewars* and *nitrogen filling stations.* These stations are placed near a tank in or outside of a building and allow for quick retrieval of several liters of liquid nitrogen for use.

Cryogenic health treatment with the cryosauna

Before we move on to the *food industry*, here’s another popular application that is strongly related to the *medical sector*: the cryosauna. A treatment in this sauna, called **cryotherapy**, exposes the body to cryogenic temperatures for several minutes for an overall health boost.

Usually, a cryosauna is cooled with liquid nitrogen vapor or air cooled by electricity. The application looks like a large cabin, with a dewar containing liquid nitrogen next to it (or inside of it).



Cryogenic sample storage

3.2.Cryogenic applications in the space industry

The space industry not only makes widespread use of cryogenic applications but would look completely different without cryogenic technology. For example, cryogenic gases are used as fuel, and liquid helium is used to cool detectors so that they can take highly accurate measurements in space.

- ***Cryogenic rocket engines***

A cryogenic rocket engine makes use of a **cryogenic fuel** and **oxidizer**, usually consisting of **liquid oxygen** (at -183°C) and **liquid hydrogen** (at -253°C). This technology was first used in the famous American rocket **Atlas-Centaur** and contributed significantly to NASA's success in reaching the moon with **the Saturn V rocket**.

- ***The cryogenic test chamber***

Cryogenic applications are also indispensable in launch preparation. The **cryogenic test chamber** is an example of a cryogenic application that prepares satellites and rockets for departure. In this chamber, cryogenic temperatures are used to research the extent to which all functions of a satellite or engine remain active under **extreme temperature variations**.

IISRO Propulsion Complex (IPRC), a rocket engine test facility

3.3.Cryogenic applications in transportation

Perhaps foremost among the industries in which liquid gases are increasingly included in the development of new applications is the transportation sector.

Mainly **hydrogen** forms the basis of the current efforts toward **sustainability** in both road transport and shipping, and there are plenty of hydrogen-powered cars, trucks, and ships in development.

Some examples of cryogenic applications within the transportation industry include :

- **Passenger cars** with an engine that runs on liquid hydrogen. In 2001, BMW launched the Mini Hydrogen, which is considered one of the first liquid hydrogen-powered cars. Currently, more and more hydrogen cars are emerging on the market, mainly using a hydrogen fuel cell.
- The development of **trucks** with hydrogen fuel cells or tanks for liquid hydrogen. A good example is Daimler's Mercedes-Benz GenH2 Truck, currently under development.
- The use of LNG as a fuel primarily for **trucks** and **cargo ships**. LNG (*liquid natural gas*) is now widely available and is regarded as a fuel that is just a bit more sustainable than common diesel fuel.
- **A refuelling station** for LNG or hydrogen.

Hyundai NEXO, a self-driving car with a hydrogen fuel cell

3.4.Cryogenic applications in scientific research

One of the very first industries to experiment with cryogenic techniques, and thus cryogenic applications, is *scientific research*.

By cooling magnets with cryogenic gases to almost absolute zero, they can, depending on the material, be made superconducting, and generate enormous forces with relatively small sizes. And these enormous forces are the subject of extensive research.

Some examples of cryogenic projects in *scientific research* include experiments with **particle accelerators** and **large superconductors**. At the same time, the effect of **extreme temperatures** is monitored.

Because it is one of the coldest and most powerful cryogenic gases, **liquid helium** is often used as a coolant in scientific experiments.

Dozens of industries

Obviously, the above list of industries and applications is far from complete. Other industries in which cryogenic applications are used include the electronics industry, automotive industry, **chemical industry**, and **metal industry**.

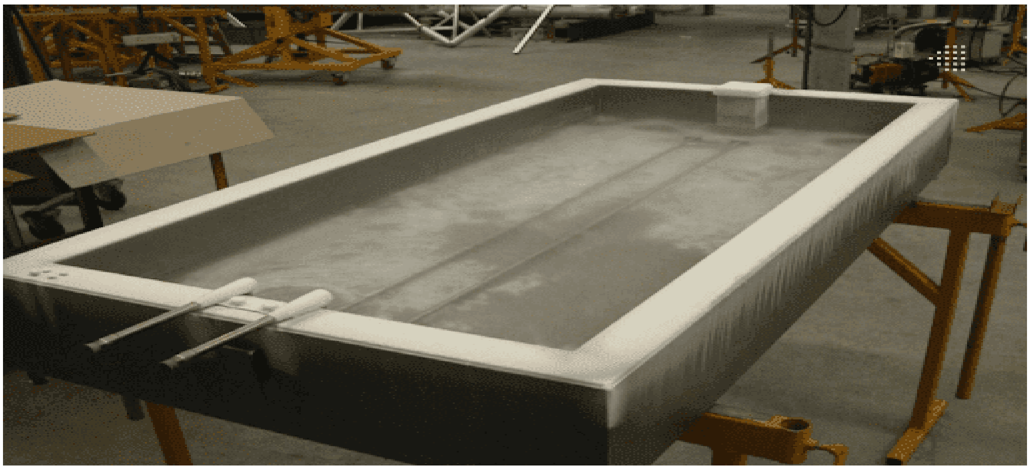
The electronics industry uses nitrogen-cooled test chambers for testing computer chips.

3.5. Application in the Food Industry

A second industry that relies intensely on cryogenic applications is the food industry. Cooling food, while it is at its best quality, is crucial within this industry. Cryogenic refrigeration systems have proven to be the ultimate method for this.

- **Cryogenic Freezing** :
  - Cryogenic freezing is a rapid freezing process that uses liquid nitrogen (at -196°C) or carbon dioxide to freeze food products quickly. This process minimizes ice crystal formation, preserving the texture, flavor, and nutritional value of the food.
  - It is particularly useful for high-value foods like seafood, fruits, and ready-to-eat meals, where quality preservation is crucial.
- **Benefits of Cryogenic Freezing** :
  - **Speed** : The rapid freezing process prevents the formation of large ice crystals that can damage cell structures, leading to better preservation of food quality.
  - **Flexibility** : Cryogenic systems can be adapted for various food types and production scales, making them suitable for both industrial and smaller-scale applications.
  - **Energy Efficiency** : Compared to mechanical freezing, cryogenic freezing can be more energy-efficient, particularly for small batches or specific high-value products.
- **Cryogenic Grinding** :
  - This process involves using liquid nitrogen to cool materials, such as spices or herbs, to make them brittle for easier grinding into fine powders. It helps retain volatile flavors and aromas that could be lost during traditional grinding methods.
- **Packaging and Storage** :
  - Cryogenics is also used in packaging and storage to extend the shelf life of perishable foods. Modified atmosphere packaging, combined with cryogenic cooling, helps maintain the freshness and safety of food products during transportation and storage.
- **Emerging Technologies** :

  - **Cryogenic Dehydration** : A technique that combines freezing and vacuum drying to remove moisture from food products while preserving flavor, color, and nutrients better than conventional dehydration methods.
  - **Cold Chain Management** : Cryogenic systems are integrated into the cold chain logistics to maintain the required low temperatures from processing to delivery, ensuring food safety and quality.



Cryogenic cooling trays with liquid nitrogen, into which foods are immersed for super-fast cooling

4.THE FUTURE ROLE OF CRYOGENIC APPLICATIONS

Cryogenic applications have undergone tremendous changes over the past century, and research is ongoing. What does the future of cryogenic application look like ? What role will cryogenics play in 2023 and beyond ?

Looking at the projects currently under development as well as the mission and vision of major parties in the cryogenic industry, two themes stand out for the near future : **further technical development of cryogenic applications** and the use of **cryogenic techniques to make various industries more sustainable.**

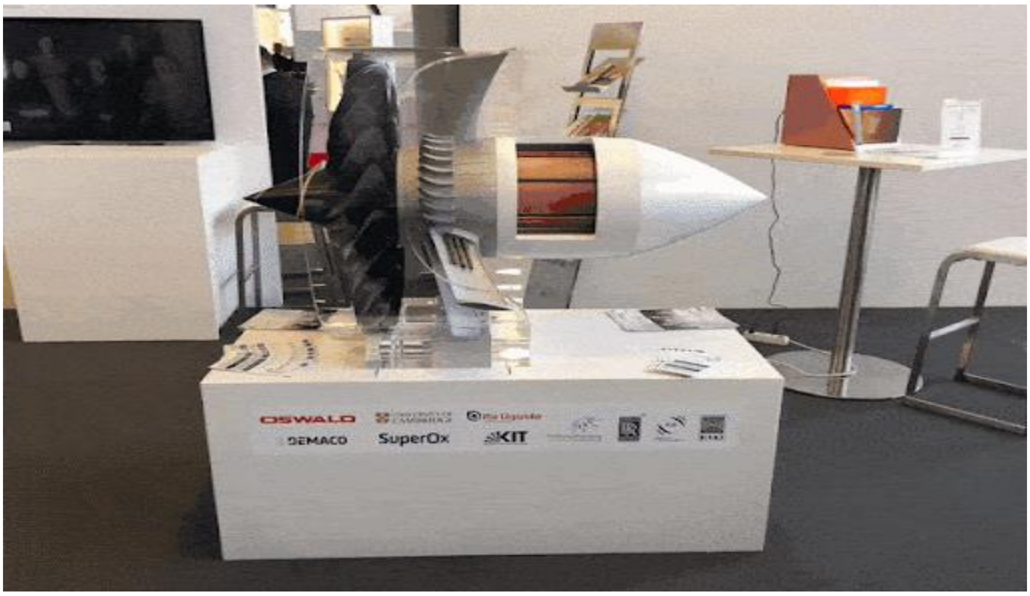
Some new cryogenic applications that we expect to see more and more in the future include :

- New cryogenic applications in the *medical industry*, such as **open MRI devices, magnetoencephalography** based on SQUID detectors to map the brain’s response to stimuli, and **compact accelerators for proton therapy**, are helpful in some cancer treatments.
- The further development and scale-up of hydrogen-powered road transport. **Hydrogen-powered passenger cars** will be made more accessible, **hydrogen-powered freight**

transport is expected to take off, and work is underway on **combustion engines running on liquid hydrogen.**

- The development of sustainable aircraft engines based on cryogenic techniques. Several aircraft are currently under development with lightweight, **superconducting engines**, and the prototypes are expected to be produced by 2030.

Energy transportation using liquid hydrogen. As we move more and more to renewable energy worldwide, it becomes essential to transport this energy internationally. After all, not every country has equal access to solar, wind, and other renewable energy sources. Converting this energy into liquid hydrogen using **electrolyzers** makes it significantly easier to transport it over long distances.



A mock-up of the ASuMED engine : a superconducting aircraft engine co-developed by Demaco.

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13. DE SAINT OMER DUNKERQUE. Département Génie thermique et énergie. 2010 – 2011. - CRYOGENIC ENGINEERING Second Edition Revised and Expanded
14. THOMAS M. FLYNN CRYOCO, INC. LOUISVILLE, COLORADO, U.S.A.2005.
15. R.F. BARRON, « Cryogenic Systems », 2nd Edition, Oxford University Press, NY, 1985.
16. PETIT, « Oxygène, Azote, Gaz Rares De l'Air », Techniques De l'Ingénieur, Traité Génie Et Procédés Chimiques, J 6020,1973.
17. F. Ayela, P. Decool, J.L. Duchateau, P. Gandit, F.Kircher, A.Sulpice,L.Zani, « Températures Cryogéniques Et Fluides », Techniques De l'Ingénieur, R2811, 2004.
18. A. Rojey, B. Durand, C. Jaffret, S. Jullian et M. Valais, « Le gaz naturel », Ed. Technip, 1994.
19. P. Wuittier, Tome II, « Raffinage et génie chimique », Edition Technique, France 1972.
20. Engineering Data Book, « Physical properties », Section 23, Edition1994.
21. R.C. Reid, J. M. Prausnitz, T. K. Sherwood, « The Properties of gases and liquids », Third Edition Mc. Graw Hill 1977.
22. K.D. Timmerhaus, T.M. Flynn « cryogenic process engineering », Springer Science, business media, LLC 1989.
23. Réda KHAMA, « CRYOGENIC PROCESSES », Course support intended for third year students of the Process Engineering academic degree, Batna university, Algeria.

Semestre :6
Unité d'enseignement : UED 3.2
Matière1 : Procédés cryogéniques
VHS: 22h30 (Cours: 1h30)
Crédits : 1
Coefficient : 1

Objectifs de l'enseignement:

Présenter les différents procédés dans le domaine du froid et de la cryogénie ; Quelques applications dans le domaine des basses températures.

Connaissances préalables recommandées:

Phénomènes de transfert de chaleur ; Thermodynamique et les outils mathématiques (équations différentielles et calcul intégral).

Contenu de la matière:

Introduction générale : La cryogénie et ses domaines d'applications **(1 semaine)**

Chapitre 1 : (2 semaines)
Technologie du vide : Importance du vide en cryogénie ; Systèmes de production du vide.

Chapitre 2 : (4semaines)
Procédés de séparation et de purification des fluides cryogéniques : Procédé de séparation : système idéal ; Procédés de séparation – Rectification ; Rôle et description de la vanne de Joule Thomson ; Procédés de séparation de l'air.

Chapitre 3 : (5 semaines)
Procédés de liquéfaction des gaz permanents : Procédé de liquéfaction Linde-Hampson ; Procédé de liquéfaction Linde-Hampson à double compression ; Procédé de liquéfaction de Claude.

Chapitre 4 : (3 semaines)
Applications cryogéniques : Découverte de la supraconductivité ; Application dans l'agroalimentaire.

Mode d'évaluation:

Examen: 100%.

Références bibliographiques:

1. R.F. BARRON, « Cryogenic Systems », 2nd Edition, Oxford University Press, NY, 1985.
2. PETIT, « Oxygène, Azote, Gaz Rares De l'Air », Techniques De l'Ingénieur, Traité Génie Et Procédés Chimiques, J 6020,1973.
3. F.Ayela, P. Decool, J.L.Duchateau, F.Gandit, F.Kircher, A.Sulpice,L.Zani, « Températures Cryogéniques Et Fluides », Techniques De l'Ingénieur, R2811, 2004.
4. A. Rojey, B. Durand, C. Jaffret, S. Jullian et M. Valais, « Le gaz naturel », Ed. Technip, 1994.
5. P. Wuittier, Tome II, « Raffinage et génie chimique », Edition Technique, France 1972.
6. Engineering Data Book, « Physical properties », Section 23, Edition1994.