1

Introduction

Generally, refrigeration technology is the engineering science of how to cool a corresponding cooling object to a temperature below the ambient temperature and/or how to keep it cold continuously at this low temperature for the required time. Usually, the cooling is done by means of a special device – a refrigerator. Typical examples of refrigerators known from our everyday life are household refrigerators, chest freezers, and air conditioners.

Cryotechnology (from the ancient Greek κρύος (*kryos*) – cold, ice) is a part of refrigeration technology covering the range of very low temperatures (see Figure 1.1). In terms of numbers, probably, the most successful commercial cryosystem is the superconducting magnet at the core of an magnetic resonance imaging (MRI) system, as found in most large hospitals today. Other typical examples of cryosystems are helium liquefier, air separation plant, or liquid hydrogen storage.

Principally, the cryotechnology consists of two large areas: (i) technologies for use/application of very low-temperature cold and (ii) that for generation of cryogenic cold (see Figure 1.1). The latter is called cryogenics (also from ancient Greek κρύος (*kryos*) – cold, ice and γενεά (*geneá*) – generation, or γένεσις (*génesis*) – origin), which is literally translated as "deep cold generation." A typical example of a **cryogenic** system is a helium liquefier. In contrast, a superconducting magnet at the core of MRI systems, as mentioned above, is a typical example of a cryo application.

In English-speaking community, the terms "cryogenic" and "cryogenics" are used often as synonym for "cryo" and "cryo technology": a cryo application can be referred to as a "cryogenic application," although no active cold generation takes place within such systems.

In cryogenic engineering, it is common to specify and define the temperature $\boldsymbol{T}$ in degrees Kelvin (K) as absolute temperature instead of relative temperature Θ usually measured in degrees Celsius (°C). The conversion is simple and is performed as follows:

$$\mathrm{T}\,(\mathrm{K}) = \Theta\,(^{\circ}\mathrm{C}) + 273.15$$

$$\Theta\,(^{\circ}\mathrm{C}) = T\,(\mathrm{K}) - 273.15$$

Process Design for Cryogenics, First Edition. Alexander Alekseev.

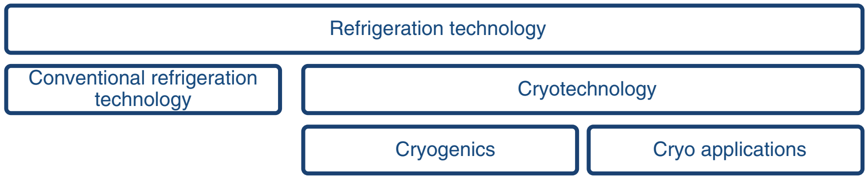

Figure 1.1 Refrigeration technology.

The use of degrees Kelvin has the advantage of eliminating negative temperature values. The zero point is the absolute zero point. "That frees us from annoying minus signs and subtractions," as Kurt Mendelssohn writes in [1].

According to the definition established during the 13th Congress of the International Institute of Refrigeration in Paris (1971), the formal boundary between conventional refrigeration and cryotechnology is a temperature of 120 K (approx. −153 °C), which corresponds to the liquefaction temperature of natural gas. This definition is to be considered in historical context – at that time, the first large natural gas liquefaction plants were being built, the business around liquefied natural gas (LNG) was booming, and technologies for this temperature level were emerging.

Although this 120 K-level definition was formally established, the discussion about the borderline between the cryo and the conventional refrigeration is still ongoing. The discussion as such does not generate any useful, applicable knowledge, but it provides an indication of what is the most emerging cryogenic application at the moment. For example, in the 1990s, when the first applications based on the so-called high-temperature superconductors (HTSCs) (see Section 1.2) were intensively developed, a lively debate revolved around the question of whether to reset the boundary temperature to the critical temperature of the best high-temperature superconductive materials.

Recently, the gas industry prefers to consider the temperature of 217 K (approx. −56 °C) as a practical boundary between cryotechnology and conventional refrigeration technology. This temperature corresponds to the triple point of carbon dioxide (CO_2) and is attributed to increasing commercial value of this gas. The technology and the logistics chain for CO_2 supply on an industrial scale closely resemble those of liquid oxygen or liquid nitrogen, and therefore liquid CO_2 is often considered a cryogenic gas.

From a process design perspective (since this book is about process design), it would make sense to define the differentiation criteria based on thermodynamic process used in a plant. For example, a system based on a Joule–Thomson process or a mixed fluid Joule–Thomson process, Brayton process, Claude process, or cascade with more than two stages would be allocated to cryogenics, whereby a system based on the Rankine process or its derivates would be considered as conventional refrigeration technology.

This book is focused on cryogenics and cryogenic processes for temperatures below 120 K, according to the formal definition of cryogenics.

1.1 Historical Background

The era of cryogenics began with the liquefaction of oxygen, which was reported by two scientists – Louis Paul Cailletet and Raoul Pierre Pictet – in December 1877, independently from each other.[1] It was a classical example of a disruptive development causing a considerable acceleration in corresponding science, in this case in cryogenics.

The oxygen liquefaction realized by Pictet and Cailletet was an exceptional achievement and must be highly honored. Science historians have pointed out the phenomenon that "at any given time there is a consensus among scientists of a given field regarding the fundamental hypotheses of their discipline" (see [2]). The "standard" theory at that time postulated that all known gaseous substances could be categorized into two groups:

- gases which can be liquefied by compression and cooling, such as chlorine, ammonia, sulfur dioxide, hydrogen sulfide and
- gases which cannot be liquefied at all, regardless of pressure and temperature conditions – the so-called "permanent" gases such as nitrogen, oxygen, or hydrogen.

This thermodynamic rule was accepted by most engineers/scientists without doubt. Only a minority – scientists like Pictet and Cailletet – dared to disbelieve and question the established theory. The exceptional achievement of Pictet and Cailletet was not only about the oxygen liquefaction, but it was more about breaking the rules.

After the announcement of the successful liquefaction of oxygen, the theory of permanent gases was suddenly (literally overnight) no longer valid. From this moment on, it was evident that *all* gases could be liquefied, without exception. The race for the liquefaction of permanent gases and thus "the quest for absolute zero" was opened at this moment. Only five years later, in April 1883, Karol Olszewski and Zygmunt Wroblewski (Cracow, Poland) succeeded in producing liquid air and later liquid nitrogen. This operation required a temperature of 77 K (−196 °C), 14° lower than the temperature of liquid oxygen (91 K ≈ −182 °C). It took another 15 years until hydrogen, with a boiling temperature of 20.1 K (−253 °C), was liquefied by James Dewar in London (1898). Ten years later (1908), Heike Kammerlingh Onnes was able to produce liquid helium in Leiden (Netherlands (NL)). The boiling temperature of helium is 4.2 K (≈−269 °C). This opened the domain of extremely low temperatures to scientists.

Further developments in cryogenics in the following years were dominated primarily by two communities:

- Physicists and chemists, who made amazing and groundbreaking discoveries such as superconductivity or superfluidity (see Table 1.1) and
- Innovators like Carl Linde, George Claude, or Samuel Collins, who launched commercial products, mostly cryogenic systems or cryogenic hardware components, and created the demand and market for cryogenic applications. Several examples are listed in Table 1.2.

1 This event is described in detail in [1].

Table 1.1 Milestones in cryogenic + science.

Year	Discovery/event	Temperature (K)	Scientist(s)
1911	Superconductivity	4.2	Heike Kammerlingh Onnes
1933	Meißner–Ochsenfeld effect	4.2	Walther Meißner, Robert Ochsenfeld
1938	Superfluidity	<2.7	Peter Kapitsa (original: Capiţa)
1957	Superconductivity (Bardeen-Cooper-Schrieffer (BCS)) theory	—	Bardeen, Cooper, Schrieffer
1972	Superfluidity in ^3He	0.002	David Lee, Robert Richardson, Douglas Osheroff
1986	High-temperature superconductivity	>35	Johannes Bednorz, Alexander Müller
2003	Nobel prize for physics	—	Vitaly Ginzburgh, Alexei Abrikosov, Anthony Leggett
2017	Nobel prize (chemistry) for cryo-electron microscopy	>4.2	Joachim Frank, Jacques Dubochet, Richard Henderson

Table 1.2 Milestones in cryogenic engineering.

Year	Innovation	Inventor(s)
1893	Dewar flask	James Dewar
1895	Industrial air liquefaction	Carl Linde
1902	Low-temperature piston expansion machine and Claude cycle	George Claude
1905	Industrial air separation	Carl Linde
1938	Centrifugal expander for air separation	Peter Kapitsa
1947	Industrial helium liquefaction plant	Samuel Collins
1952	Stirling cooler	J.W.L. Köhler
1957	Atlas rocket with liquid hydrogen as fuel	NASA, I am not sure about the name
1958	Superinsulation	I am not sure about the name
1958	Mixed gas cycle for natural gas liquefaction	A.P. Klimenko
1963	Gifford–McMahon cooler, pulse tube cooler	E. Gifford, R. Longsworth
1990s	Joule–Thomson expansion machine	I am not sure about the name
1990s	Cold compressor	I am not sure about the name
1990s	Structured packing for air separation plants, especially for cryogenic argon separation	Linde AG, I am not sure about the name

The discussion about which group – scientists with their discoveries, or innovators with their inventions – created a greater contribution to our culture is a confusing one. In reality, both these groups were linked so closely to each other that it is almost impossible to distinguish between them: the physicist James Dewar was also a great innovator. The same applies to Heike Kammerlingh Onnes or Peter Kapitsa, who not only discovered superfluidity, but also built the first industrial air separation plant with a turbo expander. Carl Linde, who founded the air separation industry, invested an immense amount of time in the development of an equation of state (similar to van der Waal's equation). From the author's point of view, both groups – scientists and innovators – emanated unbelievable creative impulses, and both groups were extremely "cool" (in the cryogenic sense).

1.2 Cryogenic Applications

Cryogenics is normally not of prime concern to its users. Instead, it is a sort of utility only for a primary application (for example, steelmaking). Two typical functions delivered by cryogenics are shown in Figure 1.2: either it provides a cooling capacity or it supplies the main application with the required industrial gases such as nitrogen, argon, oxygen, and hydrogen.

Use case cooling capacity: The cooling capacity can be provided directly by a cryogenic refrigerator or indirectly in form of a liquefied cryogen (refrigerant), such as liquid helium or liquid nitrogen, which is filled into the corresponding device and usually evaporates during the operation of the application.

Use case gas supply: there are two options available:

1. **Remote cryogenic plant**: The required gas is produced and liquefied in a corresponding remote cryogenic production plant or facility, and the customer is supplied with compressed or liquefied gas (liquid oxygen, liquid nitrogen, etc.) by pipelines, trucks, or other transport methods. The delivered liquefied gas is evaporated on the customer's site to provide the gas to the main application. This method is used for small and medium gas quantities (up to 20 t/d),
2. **On-site cryogenic plant**: an appropriate cryogenic production plant is installed on the customer's site directly. It supplies the application with the required amount of gas. This option is economically more feasible for large amounts of gas.

Almost all industrial gases can be produced by a non-cryogenic method as well. The decision for or against the cryogenic option is always based on techno-economic considerations according to the given requirements and conditions. The cryogenic system is usually a cost-intensive option. It is competitive only

- if the alternative technical solution is not able to deliver the required product quality (for example, the gas purity) or
- if high gas amount/flow produced by means of a large-scale cryogenic plant is required. Since the "economy of scale" works well in this case, a very competitive specific product cost can be easily achieved.

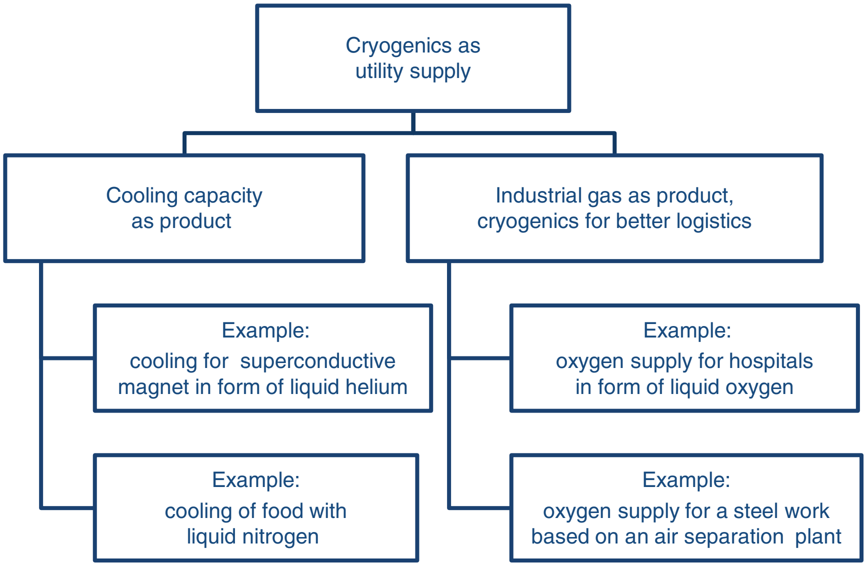

Figure 1.2 Cryogenics as utility.

Several typical cryogenic applications are briefly described in this chapter as a rough overview. For a deep dive into this topic, the book [3] is recommended.

1.2.1 Natural Gas Liquefaction

The largest cryogenic systems in the world are the so-called "base-load natural gas liquefaction plants." The natural gas is mainly liquefied for logistics reasons: the density of the LNG is roughly 600 times higher than the density of natural gas under normal conditions; therefore, the transport of natural gas in form of LNG over longer distances provides a reasonable economic option in comparison to other transport methods, for example by means of a pipeline. A further valuable advantage of LNG transport is its flexibility in terms of geography: it is possible to supply customers at different destinations in different countries using the same ship. The pipeline-based logistics (the alternative option) does not provide a comparable flexibility.

In former times, the LNG industry was based primarily on individual, more or less self-contained projects that required immense capital investment (in the range of double-digit billions of US dollars) and which therefore were fraught with high risk. In the meantime, "the industry has proven its reliability and stability under different market and economic conditions. Currently, demand growth and high energy prices, coupled with advances in technology, are driving more planned and proposed LNG projects than at any point in history," according to [4].

1.2.2 Cryogenic Air Separation

The second-largest cryogenic systems are air separation plants. With a double-digit number of plants installed or replaced annually, the air separation industry represents the largest market for cryogenic systems. Medium-size systems (10 000–90 000 m^3/h oxygen) dominate this market. These systems are used for production of oxygen, nitrogen, argon, neon, and xenon, at high purity and in large quantities. Modern metallurgy, especially steel production processes, cannot be realized without oxygen, nitrogen, and argon, and oxygen production is an integral part of every steel plant. In similar fashion, the chemical industry in its present form is inconceivable without oxygen, hydrogen, and nitrogen supplies. These gases are essential for ammonia production and for bleaching of pulp, gas-to-liquid processes, and general partial oxidation methods. Large quantities of high-purity nitrogen are used in the electronics industry and chip production, where it is not only applied as a process and carrier gas, but also used for purging purposes. Air separation plants produce not only gaseous products, but also cryogenic liquids like liquid nitrogen and liquid oxygen for numerous applications in the food and beverage industry, welding, chemistry, and so forth.

1.2.3 Helium Plants

40–50 years ago, the availability of liquid helium was very limited. However, recently it has become a sort of commodity: today every large university owns a helium liquefier and maintains its own local liquid helium infrastructure for research purposes. The global helium supply infrastructure is well developed: large amounts of helium are produced, liquefied, and shipped successfully from one continent to another.

1.2.4 Aerospace

Space launch vehicles require large quantities of liquid oxygen as an oxidizer for almost all types of fuel. Therefore, cryogenics plays an essential role in the space industry. Another cryogenic substance – liquid hydrogen – is still used as fuel for heavy rockets, such as the European Ariane, US-based Atlas V, and Chinese Long Marche. However, the newest commercial space launchers do not use liquid hydrogen. This fuel is being replaced with more common substances like kerosene due to better economics, availability, and easier logistics. The development of the reusable "Falcon" or "Antares" rocket families confirms this trend. The use of liquid (or solid) methane (cryo-option) as rocket fuel is discussed as an attractive option for future rockets.

1.2.5 Physics

Cryogenics plays a considerable role in high-energy physics. Large particle accelerators and fusion research systems, especially, include large cryo components such as:

- superconducting magnets and cavities,
- cryovacuum pumps for generation of high vacuum,
- detectors, targets, and further scientific instruments cooled to cryo temperature.

The most prominent projects of the last decade were the massive Large Hadron Collider (LHC) particle accelerator at CERN in Geneva and the Wendelstein 7X stellarator in Greifswald. The International Thermonuclear Experimental Reactor (ITER) fusion reactor in France will be the largest scientific machine upon its completion. It consists of a significant cryogenic system for cooling of gigantic magnets and vacuum pumps.

Moreover, there are many medium- and small-size scientific cryo-based machines (accelerators, cold neutron sources, neutrino detectors) available in almost every major urban area in the world.

1.2.6 Medical Applications

The most successful cryogenic commercial application ever realized is the MRI tomograph found in many medical institutions. The core of this instrument is a superconducting magnet submerged in liquid helium. The modern version of the MRI device includes an additional integrated cryocooler, which helps to reduce the evaporation rate of liquid helium and therefore extend the recharging interval of the magnet with liquid helium. When inside the MRI instrument, this cooling option can be noticed as an audible pulse approximately once per second.

Medical oxygen is used for treatment of patients with respiratory problems (including asthma or COVID).

Blood plasma and other biological samples are usually stored at low temperatures (cryopreservation) in special cryo storage devices (vessels or cabinets).

A relatively new application is the production of extremely sensitive bio-based pharmaceuticals (such as special bacteria, probiotica, lipid-rich substances, and similar) via cryo-based freeze–drying technology. It ensures very gentle handling of substances with minimized destruction of these living objects and guarantees acceptable shelf life.

1.2.7 Liquid Hydrogen for Hydrogen Economy

Liquid hydrogen is seen as an important part of the logistics chain in the future hydrogen-based economy. From today’s perspective, it is still a great vision. It is still difficult to predict when this vision will become reality. The hydrogen-based economy will require a completely new infrastructure and a considerable investment (billions and billions) in its development. Therefore, it is considered to be a long-term project.

1.2.8 Devices Based on High-temperature Superconductors for Electrical Engineering

Devices based on HTSC – ceramic materials without electrical resistance at temperatures below 100 K – are regarded as an interesting option for some special tasks in electrical engineering.

- HTSC-based motors or generators are not only extremely efficient and compact, but they also have a broader load range and the fastest ramping capability. These machines can be used in the maritime sector (or other bulk transport) in the future due to extremely high specific power density.

- Another unique device is an electrical cable based on HTSC for power transmission and distribution. It is a compact system, which allows a virtually invisible power supply without power limitations, without thermal losses, and without electromagnetic emissions. This could be an attractive solution for power supply in densely populated areas like cities, where bulky overhead lines are no longer imaginable today and the installation of conventional copper underground cables is too expensive due to the large footprint required.
- The next interesting HTSC-based device is the fault current limiter developed for safe disconnection (and protection) of the grids and grid segments in case of an electrical fault. The HTSC-based design is an extremely fast-acting system. It allows safe and reliable operation of electrical grids at close to maximum load. It also helps to reduce the overdesign margin (the standard option today) and creates a more sustainable and economical grid solution.

The commercial success of all these applications is still unclear due to the high competitiveness of existing technology, at least in terms of cost. But increasing urbanization and electrification of cities (e-mobility, digitalization, air conditioners, etc.) create more and more opportunities for HTSC applications.

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