



A Brief History of Refrigeration

1. Refrigeration in the pre-refrigerating-equipment era

Natural Ice

People living in temperate zones soon realized that perishable foods kept much better in winter than in summer. The use of “natural refrigeration” began in the distant past and lasted a very long time: early in the 20th century, the natural-ice market was still bigger than the man-made ice market. Naturally produced ice (i.e. that produced without refrigerating equipment):

- originated in cold regions and was transported over large distances;
- or originated in rivers, lakes and ponds, where freezing took place during winter in temperature regions. Once harvested, this ice had to be stored in ice-storage facilities with thermally insulated walls.
- or was produced by man using natural cooling. In countries with clear skies, ice was produced in open ponds. Thermal radiation from the water made it possible, under certain atmospheric conditions, to achieve sufficient cooling to form ice.¹

Refrigerating mixtures

The chilling effects of the addition of certain salts to water was discovered, no doubt by accident, in the distant past. Ibn Abi Usaibia, an Arabic writer, appears to have been the first to mention the use of these type of mixtures in India during the 4th century.

An Italian physician called Zimara mentioned the use of water chilling using potassium nitrate in Padua in 1530 and Blas Villafranca, a Spanish physician, recorded similar practices in Rome in 1550. It was later demonstrated that by mixing snow and salts, even lower temperatures could be achieved. These phenomena were described by Battista Porta in 1589 and Tancredo in 1607.

2. Pioneers and scholars

In the 17th century, heat and cold fuelled reflections conducted by scholars and philosophers such as Robert Boyle (1627-1691) in England and Mikhail Lomonosov (1711-1765) in Russia. Over the same period, following Galileo's initial research, many studies were performed in the thermometry field by illustrious scholars: Guillaume Amontons (1663-1705) in France, Isaac Newton (1642-1727) in England, Daniel Fahrenheit (1686-1736), a German who worked in England and The Netherlands, René de Réaumur (1683-1757) in France and Anders Celsius (1701-1744) who invented the centesimal-scale thermometer in Sweden in 1742.

William Cullen (1710-1790) observed that when ethyl ether evaporated, it was accompanied by a fall in temperature. In 1755, he succeeded in obtaining a small quantity of ice by evaporating water under a bell jar. His disciple and successor, the Scotsman Joseph Black (1728-1799), clarified the notions of heat and temperature, and can be considered as being the founder of calorimetry. Several French scholars excelled in this domain: Pierre Simon de Laplace (1749-

¹ Using a suitably cautious approach, Professor Trombe was able to cool black surfaces exposed to a clear sky at temperatures of 30 - 35 K below the ambient temperature. During the the 5th century the Greek Protagoras reported that Nile-Valley Egyptians made ice in this way by placing containers on the roofs of their houses.

1827), Pierre Dulong (1785-1838) and Alexis Petit (1791-1820), Nicolas Clément-Desormes (1778-1841) and Victor Regnault (1810-1878).

Research conducted by the Scotsman James Watt (1736-1819) on the steam engine, research on gases performed by the physicists Boyle (in England), Edme Mariotte (1620-1684) then Jacques Charles (1746-1823) and Louis Joseph Gay-Lussac (1778-1850) (in France), and experimental work performed by the American Benjamin Thomson (1753-1814), paved the way to the emergence of thermodynamics. The Frenchman Sadi Carnot (1796-1832) was the first to enter the limelight, in 1824, when he published his famous treatise that was to prove to be the starting point for the second law of thermodynamics. During the 19th century, a great deal of research was devoted to various refrigerating systems, and thermodynamics was a fast-growing discipline thanks to studies performed by the following, among others: James Prescott Joule (1818-1889) in England, Julius von Mayer (1814-1878), Herman von Helmholtz (1821-1894), and Rudolph Clausius (1822-1888) in Germany, Ludwig Boltzmann (1844-1906) in Austria and William Thomson (Lord Kelvin) (1824-1907) in England. Other famous physicists were drivers of the development of thermodynamics during the 20th century.

3. The advent of refrigerating systems

Refrigerating systems fall into two main categories: those that require mechanical energy or its equivalent in order to operate (these are called *mechanical refrigerating systems*), and those consuming essentially thermal energy (these are called *thermal refrigerating systems*).

3.1. Mechanical refrigerating systems

These systems can be divided into two main categories:

- vapour-compression systems using liquefiable vapour,
- gas-cycle systems.

Vapour-compression systems

The working fluid of the refrigerating cycle, the *refrigerant*, vaporizes in an *evaporator*, producing useful cooling. The vapour produced is aspirated and compressed by a *mechanical compressor*. It then returns to the *condenser* where it is liquefied. The liquid formed returns to the evaporator via a *regulator* (or *expansion device*). This is by far the most widely used system.

The American Oliver Evans (1755-1819) was the first to describe this cycle, in 1805. However, it was Jacob Perkins (1766-1849), an American working in England, who first patented a machine based on this cycle (in 1835); the machine ran on ethyl ether. The first compression machines that proved to be successful on an industrial scale were developed by James Harrison (1816-1893), a Scotsman who had emigrated to Australia; Harrison patented his inventions in 1855, 1856 and 1857). Harrison's machines were manufactured in England, and were capable of producing ice or cooling brine (*a secondary refrigerant*). The refrigerant used was still ethyl ether.

Two new refrigerants then came into use:

- *dimethyl ether*: the Frenchman Charles Tellier (1828-1913) introduced this refrigerant.
- *carbon dioxide* (CO_2) was used by the American Thaddeus Lowe (1832-1913). It then fell into disuse, but is now experiencing a comeback.
- *ammonia* (NH_3), was first investigated by Tellier (in 1862), but it was the American David Boyle (1837-1891) and above all the German Carl von Linde (1842-1934) who were the first to apply it on a broad scale in the industrial field. It is still used.
- *sulphur dioxide* (SO_2) was first implemented by the Swiss physicist Raoul Pierre Pictet (1846-1929) and fell into disuse just before the Second World War.
- *methyl chloride* (CH_3Cl) was first employed by the Frenchman C. Vincent in 1878, and remained in use for many years: use ceased in the 1960s.
- *fluorocarbon refrigerants* were developed as safe (non-toxic and non-flammable) refrigerants; following research conducted by Swarts, (in 1893-1907) in Ghent, an American team at Frigidaire Corporation, headed by Thomas Midgley, developed the first

fluorocarbon refrigerants, in 1930. The first CFC, R12 (CF_2Cl_2) came onto the market in 1931, and was followed by the first HCFC, R22 (CHF_2Cl), in 1934, then in 1961, the first azeotropic mixture, R502 (R22/R115).

In 1974, two US Nobel prizewinners, F. S. Rowland and M. J. Molina, published disturbing findings: they suspected that the chlorine released by halogenated hydrocarbons was adversely affecting the ozone layer. This is why the Montreal Protocol (1987) on ozone-depleting substances and its subsequent amendments banned CFCs and HCFCs. Other halogenated (but not chlorinated) refrigerants are now used: these include pure HFCs such as R134a, HFC mixtures (R410A, R407C, R404A, etc.), these being refrigerants with varying global-warming impacts. "Natural" refrigerants, including ammonia, hydrocarbons, water and CO_2 , are being introduced or are making a comeback; use of these refrigerants involves more constraints but their global-warming impacts are non-existent or low.

Components of compression systems have also been considerably improved over the years. The heavy, slow and voluminous pistons used late in the 19th century have gradually given way to faster, lighter equipment. New types of compressors have been developed over the years: A. Lysholm developed a screw compressor with twin rotors in Sweden (1934), B. Zimmern developed a screw compressor with a single rotor in France in 1967, the scroll compressor was developed in the 1970s (this technology was patented by the Frenchman Léon Creux in 1905), and centrifugal compressors were developed (following fundamental research performed by the Frenchman Auguste Rateau in 1890, and that conducted by the American Willis Carrier in 1911).

Soon after these systems started to be used, ways of reducing refrigerant leakage were sought, and hermetic refrigerating units were developed in order to address this problem. The first unit of this type was a strange one invented by Father Audiffren in France, in 1905. Hermetic units are now widely used.

Heat exchangers (condensers and evaporators) have also been improved and are now much lighter.

Systems using gas cycles

In these systems, the working fluid does not undergo phase change during the refrigerating cycle: it remains in the gaseous phase. The compressed gas heats up, then is cooled under pressure down to the ambient temperature, then is expanded, leading to cooling.

The first open-cycle "air machine" was invented by John Gorrie (1803-1855), an American physician, in order to cool brine to a temperature of -7°C (Gorrie patented successive versions in 1850 and 1851). Based on the hot-air motor developed by the Scottish pastor Robert Stirling in 1837, Alexander Kirk (1830-1892), a Scottish mechanical engineer, developed a closed-cycle machine that produced, over a 10-year period starting in 1864, temperatures of -13°C . The German Franz Windhausen (1829-1904), the American Leicester Allen (1832-1912) and the Frenchman Paul Giffard (1837-1897) all played key roles in the development of this technology.

The development of these systems was hampered by their reduced efficiency (with respect to vapour-compression systems) in the refrigeration, freezing and air-conditioning fields. However, they are used in most cryogenic cycles in order to liquefy gases and produce low temperatures.

Thermoelectric systems

In 1834, the French physicist Jean Charles Peltier (1785-1845) discovered that the passage of continuous current through a junction of two metals triggered cooling in one metal and a temperature rise (through heat absorption) in the other junction. Thermoelectricity was for a long time considered as simply a scientific curiosity, but developed during the period ranging from the 1940s to the 1960s during which knowledge of semi-conductors expanded. However, although

this technology seemed promising initially, it has not achieved extensive penetration and is relatively little used today.

3.2. Thermal refrigerating systems

These refrigerating systems consume thermal energy and fall into the following categories:

- absorption systems,
- adsorption and thermochemical systems,
- ejection systems.

Absorption refrigerating systems

Although these systems are far less widely used than compression systems, they are the only thermal refrigerating systems that are currently encountering a degree of development. In these systems, instead of using a mechanical compressor to circulate the refrigerant, a pump is used to circulate an absorbent liquid, the quantity of which, in terms of absorbed refrigerant, depends on the temperature and the pressure. The mechanical work is very reduced; however, this system requires heat.

The “father” of these systems was the Frenchman Ferdinand Carré (1824-1900), who in 1859 patented the first continuous absorption machine using ammonia/water (with water as absorbent) as the working pair. These machines were almost immediately operational. It was only in 1913 when the German Edmund Altenkirch started investigating them, that the thermodynamic properties of these systems began to be elucidated, and studies were performed throughout the first half of the 20th century. Work performed by the Italian Guido Maiuri on these systems, and studies performed by the Swedes von Platen and Munters on the absorption-diffusion cycle of pumpless absorption refrigerators (in 1920) are noteworthy. In the US during the 1940s, water-lithium bromide absorption systems, with water used as refrigerant, came into use; this type of system is based on a modified Carré cycle and has been widely used in the air-conditioning field.

Although discontinuous absorption refrigerating systems were among the first absorption systems to be developed (e.g. the water-chilling system invented by Edmond Carré² in 1866) but encountered very little success.

Adsorption and thermochemical adsorption systems

These systems were developed much later, essentially during the first half of the 20th century. The operating principle, based on the thermal effects accompanying the physical sorption or desorption of a gas on a solid (adsorption systems), or the forming or the breakdown of chemical compounds using a gas refrigerant (thermochemical systems), and is naturally discontinuous. These systems are little used but are being widely investigated.

Ejection refrigerating systems

Although water is not the only refrigerant that can be used, the first ejection systems, developed in 1908, operated on water (in the form of steam). The Frenchman Maurice Leblanc (1857-1923) was the inventor of this system.

This system operates using cooled water that changes into vapour at low pressure; the vapour is then aspirated using an ejector that is fed by a steam jet supplied by a boiler. The ejector comprises a combining nozzle – raising the flow rate of the jet reduces the pressure, enabling the desired degree of suction to take place – then a delivery nozzle – the gradual increase in diameter of the nozzle reduces the flow rate and the pressure is raised again. This system has specific application niches but is far from widely used.

² Ferdinand Carré's brother

4- A few salient dates in the gas liquefaction and very-low-temperature refrigeration fields – cryogenics

The cryogenic field is generally considered as comprising temperatures below 120 K (-153.15°C).³

- 1877: Louis Cailletet, in Paris, then Raoul Pictet, in Geneva, liquefied (in a transitory manner) oxygen.
- 1883: K. Olszewski and S. Wroblewski liquefied (durably), in Kraków, oxygen (boiling point $T_{eb} = 90$ K) and nitrogen ($T_{eb} = 77$ K).
- 1895: Carl von Linde, in Germany, obtained, using Joule-Thomson expansion (using a valve, without external work), 3 litres of liquid air per hour.
- 1898: Liquefaction of hydrogen ($T_{eb} = 20.4$ K), in London, by James Dewar.
- 1902: Georges Claude liquefied air using equipment with an expansion device, with external work.
- 1908: Helium liquefaction ($T_{eb} = 4.2$ K), in Leiden, by Heike Kamerlingh Onnes.
- 1911: Accidental discovery of mercury supraconductivity by Kamerlingh Onnes in Leiden; Kamerlingh Onnes began using the term “supraconductivity” in March 1913.
- 1926: Separate descriptions of a cooling process using adiabatic demagnetization by W. F. Giauque (Canada) and P. Debye (The Netherlands).
- 1931: Demonstration of the existence, in Leiden, of point λ (2.17 K) by W.H. Keesom and K. Clusius: – Helium I (normal) – Helium II (superfluid).
- 1933: First experiments on adiabatic demagnetization by Giauque in Berkeley (USA) (0.53 – 0.25 K).
- 1931 – 1938: Series of studies on helium superfluidity: Burton, A.D. Misener, H. Jones, P. Kapitza, J. G. Daunt, K. Mendelssohn, F. London, L. Tisza.
- 1956: Nuclear adiabatic demagnetization (13 μ K): Kurti, Robinson, Simon and Spohr (Oxford).
- 1965: Dilution cooling of ^3He in ^4He (2 mK): B.S. Neganov (USSR); De Bruyn Ouboter and K. W. Taconis (The Netherlands).
- 1983: Cooling of copper electrons (20 nK) by O. Lounasmaa (Finland)
- 1986: O. Lounasmaa: at around 1 nK, silver becomes a magnet.
- 1986: J. G. Bednorz and K. A. Muller discovered “high-temperature” superconductivity (35 K).

³ Note that 0°C = 273.15 K (K pour kelvin), temperature expressed using the Kelvin absolute scale.