HISTORICAL SUMMARY OF CRYOGENIC ACTIVITY PRIOR TO 1950[*]

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ABSTRACT

Cryogenics is the science and technology dealing with temperatures less than about 120 K, although this historical summary does not adhere to a strict 120 K definition. The techniques used to produce cryogenic temperatures differ in several ways from those dealing with conventional refrigeration. In practice these two areas often overlap and the boundary between conventional and cryogenic refrigeration is often indistinct. Significant reductions in temperature often have very pronounced effects on the properties of materials and the behavior of systems.

Many cryogenic applications have developed as the refrigeration techniques prior to 1950 have improved, although many applications still face stiff competition from ambient temperature phenomena because of the associated refrigeration problems. This review shows how the development of new applications over the past 50 years is closely tied to the advances in cryogenic refrigeration prior to 1950.

KEYWORDS: **A**ir separation, cryocoolers, cryogenics, cryopumping, cryosurgery, freezing, liquefied natural gas, refrigeration, review, superconductivity, thermal noise.
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INTRODUCTION

Temperature affects processes and material properties more than any other variable, such as pressure, magnetic field, electric field, etc. The ability to harnessing and apply these temperature effects is a unique feature of mankind, and it has contributed to great advances in our civilization. Mankind has discovered abundant uses for high temperatures, beginning in prehistoric times with the use of fire for warmth, light, and cooking. Later, but still more than 20 centuries ago, mankind learned to forge tools and make crude pottery using heat from fires. As civilization advanced and higher temperatures could be achieved, stronger metals, such as iron, could be forged into tools, and much stronger pottery and china could be produced by the higher temperature firing (sintering) of clay. The industrial revolution ushered in the steam engine and the ability to generate tremendous power for efficient manufacturing and transportation. The enhancement of chemical reactions at higher temperatures has been exploited for the production of vast amounts of new and improved materials in the last century or so.

High temperature applications began rather early in the history of civilization due to the ease of producing increasingly hotter fires. In contrast, mankind's use of low temperatures has greatly lagged that of high temperatures because of the greater difficulty in producing low temperatures. Low temperature applications were limited for many centuries to the use of naturally occurring ice. The practice of using natural ice to treat injuries and inflammation was carried out by Egyptians as early as 2500 BC,[1] and Chinese began to use crushed ice in food around 2000 BC. Although ice was first created artificially in the laboratory in 1755, it was not until near the mid 1800s with the development of the steam engine and practical compressors in the industrial revolution that artificial ice could be produced in sufficient quantities to replace natural ice cut from lakes. Until then the sole use of low temperatures was with natural ice for food preservation and a few medical procedures.

The science of thermodynamics was just beginning to develop around 1850, which related heat, work, and temperature. Though the concept of absolute zero at -273 °C was put forward in the mid 1700s, the means of reaching temperatures much below 0 °C were not known or possible until the development of thermodynamics and high-pressure reciprocating compressors around 1850. Thus, nearly all understanding and uses of low temperatures have occurred in the last 150 years. Prior to that time, laboratory techniques for reducing temperatures relied on the liquefaction of a small quantity of gas at high pressure in a thick-wall glass tube surrounded by ice, followed by a rapid expansion of the vapor phase to atmospheric pressure through a valve. The temperature of the remaining liquid phase then dropped to its normal boiling point. Faraday used this one-shot process on several gases, beginning in 1823 with chlorine (normal boiling point of 239 K).[2] Over the next several decades nearly all of the gases were liquefied at the ice point under sufficient pressure. Ethylene, with a critical temperature of 282 K and a normal boiling point temperature of 169 K, yielded the lowest achievable temperature with this technique. Those known gases such as methane, carbon monoxide, oxygen, nitrogen, and hydrogen, that could not be liquefied by this technique, even with pressures up to 40 MPa (400 atm.), were called 'permanent' gases.

In a 1834 British patent Jacob Perkins, an American who had moved to England, showed how to carry out the Faraday process of liquefaction and expansion continuously.[3] That was the beginning of today's vapor-compression refrigerators, shown schematically in Figure 1. The Perkins refrigerator was designed for use with ethyl ether, although the actual refrigerator
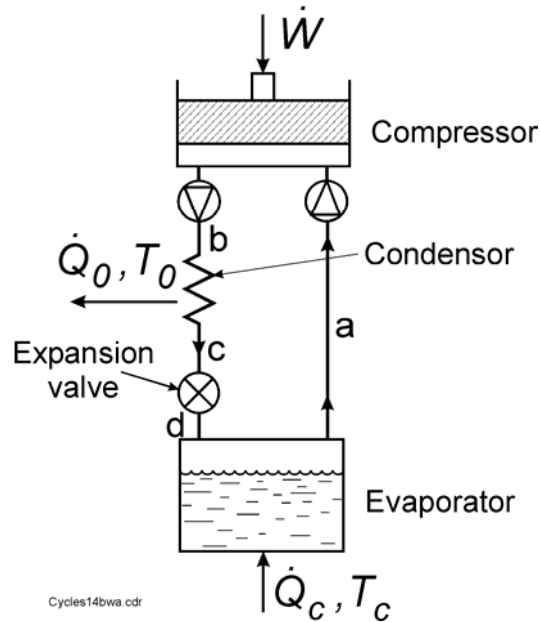
Figure 1. Schematic of the vapor-compression refrigerator in which liquid forms at location c under high pressure before expanding to low pressure at *d*.

built by John Hague and shown in Figure 2 used caoutchoucine, a distillate of India rubber readily available at that time, to produce small quantities of ice soon after 1834.

New applications of cryogenics are made possible whenever some lower temperature is achieved. The difficulties and problems associated with achieving a particular temperature
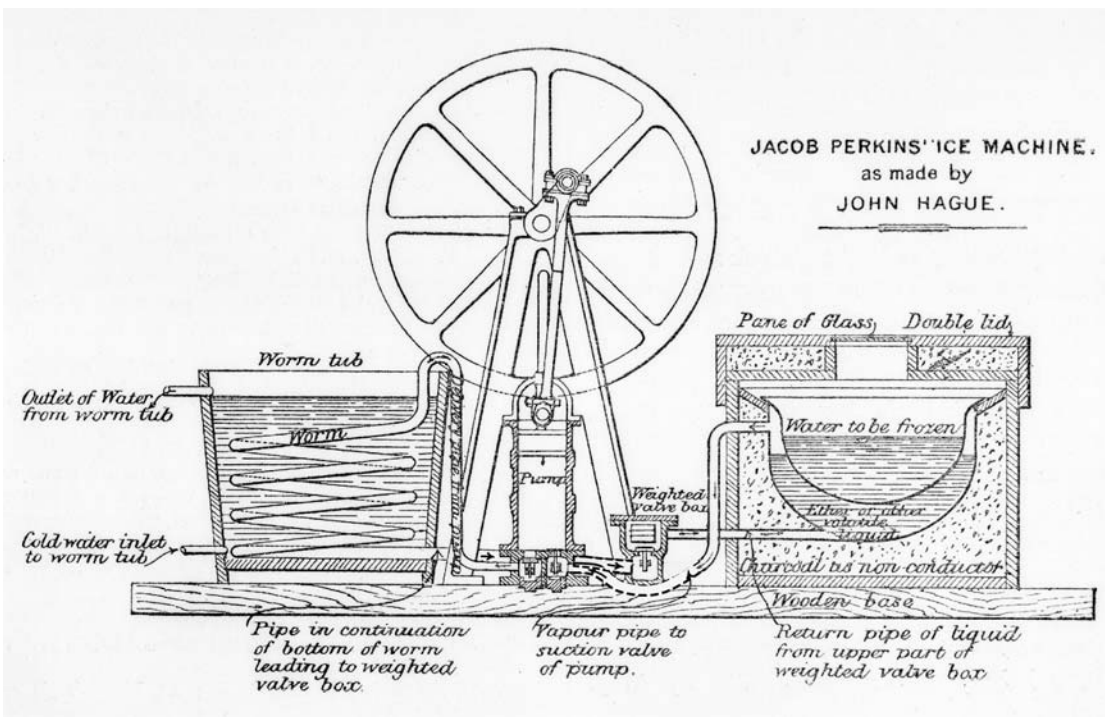

Figure 2. Drawing of the first vapor compression refrigerator by Perkins and made by Hague in 1934. Image courtesy of Science Museum/Science and Society Picture Library. (Minor drawing modification made by the author to clarify low-pressure return path to compressor.)

greatly influence the development of applications of these temperatures. As a result, this review of applications also examines the development of refrigeration techniques and cryocoolers to show how cryogenic applications are strongly dependent on improvements in refrigeration techniques.

THE BEGINNING OF CRYOGENICS

In examining low temperature developments over the past 150 years, we note that there is a convenient and interesting division into three 50-year time segments, where the developments in each time segment have their unique characteristics. Figure 3 summarizes the important developments in each time segment. Though this review focuses mostly on the last 50 years, it is instructive to briefly examine the developments in refrigeration and cryogenics that occurred in the two previous 50-year segments to understand how they contributed to the status of cryogenics at the time of the first Cryogenic Engineering Conference (CEC) in 1954. Also, by comparing developments in each 50-year segment, we may have a better idea how fast future developments might progress in the first half of the 21st century.

Figure 3 shows that between about 1850 and 1900 the development of thermodynamic fundamentals was the primary contributor to advances in cryogenics. Cryogenics in that half century was primarily of interest only to scientists, and there were almost no applications for temperatures below the ice point. At the beginning of that time period the first and second laws of thermodynamics were just being proposed. As part of those developments the
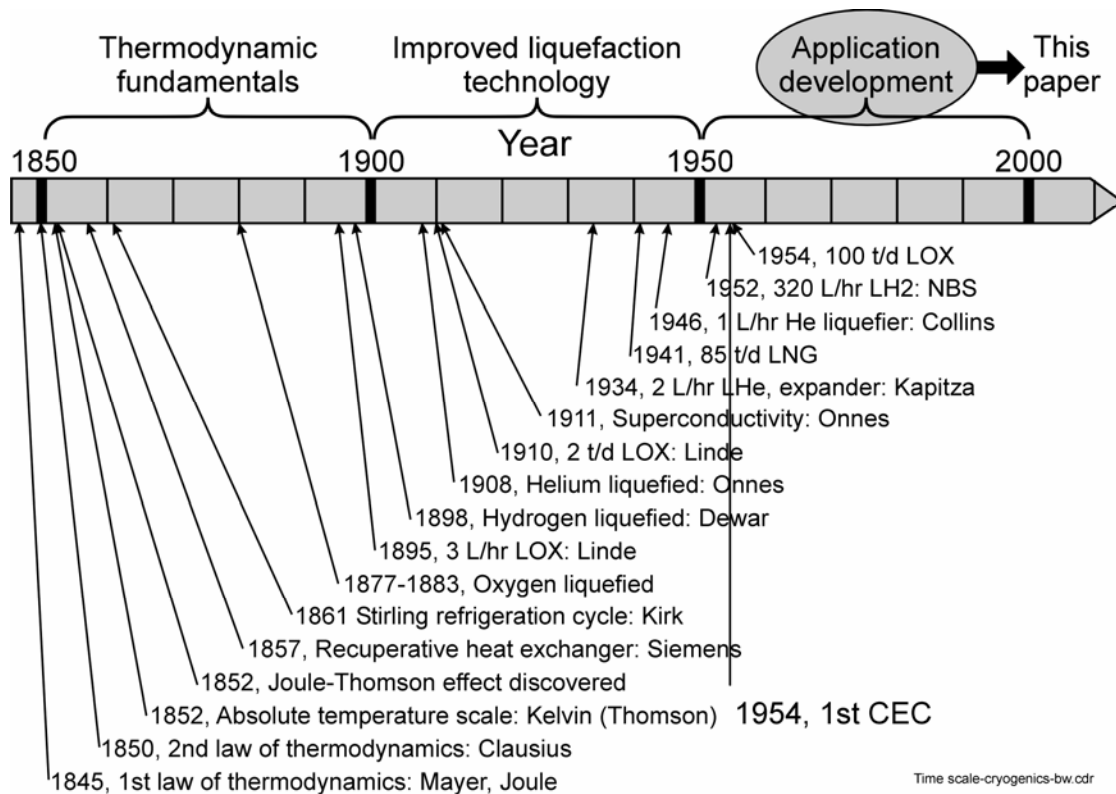
Figure 3. Time-line of significant cryogenic developments during the 100 years prior to 1954.

thermodynamic cycles required to liquefy the 'permanent' gases like oxygen, nitrogen, hydrogen, and helium were being invented. The critical temperatures of these 'permanent' gases are far below the ice point, and their very low normal boiling temperatures are now referred to as cryogenic temperatures. Cryogenics is usually defined as the science and technology dealing with temperatures less than about 120 K,[4, 5] although this review does not adhere to a strict 120 K definition. Kamerlingh Onnes first coined the adjective 'cryogenic' in 1894 by using it in a paper entitled, "On the cryogenic laboratory at Leiden and on the production of very low temperatures."[6] The techniques used to produce cryogenic temperatures differ significantly from those dealing with conventional refrigeration. One of the most important differences is the need to precool the compressed gas before it is expanded in order to reach cryogenic temperatures when starting from 0 °C or higher. Precooling can be accomplished with a cascade of refrigerant baths or with a heat exchanger. The concept for a recuperative counterflow heat exchanger was developed by Gorrie[7] in 1851 and refined by Siemens[8] in 1857. The Joule-Thomson (JT) effect discovered in 1852[9] was not sufficiently large to produce cryogenic temperatures when starting from the ice point without the precooling afforded by such a heat exchanger.

Oxygen was first liquefied (in the form of a mist) in 1877 by using the older techniques of Faraday and of Perkins, but with a cascade of precooling baths. Cailletet in Paris used a hand-operated screw jack with mercury to hydraulically pressurize oxygen (155 K critical temperature, T_{cr}) to 20 MPa in a thick-walled glass tube cooled to 169 K by a surrounding bath of liquid ethylene. The liquid ethylene (T_{cr} = 282 K) had been produced earlier using the Faraday technique with an ice bath for precooling. When the pressure on the oxygen was released via the screw jack handwheel, a fog appeared in the glass tube, but it quickly disappeared because of the heat input from the glass tube.[9, 10] On the same day, Pictet in Geneva produced a continuous mist of liquid oxygen from a JT valve by using a cascade of vapor-compression systems for precooling the oxygen. The cascade of precooling baths were operated continuously using piston compressors. The cascade consisted of sulfur dioxide (T_{cr} = 431 K, T_{NBP} = 263 K) and solid carbon dioxide (T_{cr} = 304 K, T_s = 195 K). The flowing high-pressure oxygen was cooled successively by the two baths before expanding through the JT valve to the atmosphere. A jet of liquid oxygen mist at 90 K sprayed out from the JT valve.[9, 10] The first to produce enough liquid oxygen and liquid nitrogen to study their properties were Wroblewski and Olszewski of Poland in 1883. They used the same cascade method as Cailletet, but the final stage was a pumped liquid ethylene bath at a temperature of 137 K.[11] Because the temperature of that bath was less than the 155 K critical temperature of oxygen, liquid formed inside the glass tube under a pressure of about 2.5 MPa. After releasing the pressure to atmosphere, a small quantity of liquid boiling at 90 K remained in the tube for a short period of time. Figure 4 shows the path in a temperature entropy (T-S) diagram followed by the various methods for liquefying oxygen.

Though the recuperative heat exchanger had been invented in 1857 by Siemens, little use was made of it until 1895 when Hampson replaced the cascade baths used previously for precooling oxygen with the recuperative heat exchanger. A JT valve at the cold end of the heat exchanger provided the cooling during expansion. Figure 5 is a schematic of the cycle used by Hampson to liquefy air,[12, 13] which is usually referred to today as simply the Joule-Thomson (JT) cycle. Figure 6 is a drawing of Hampson's air liquefier showing the closely packed copper tubing heat exchanger in the annular space between the tubes *D* and *F*. The JT valve *C* is controlled by the handle *E*. Glass wool surrounds the evaporator *G* and the heat exchanger. The liquefaction rate was 1 L/hr.[14] A very effective heat exchanger is necessary
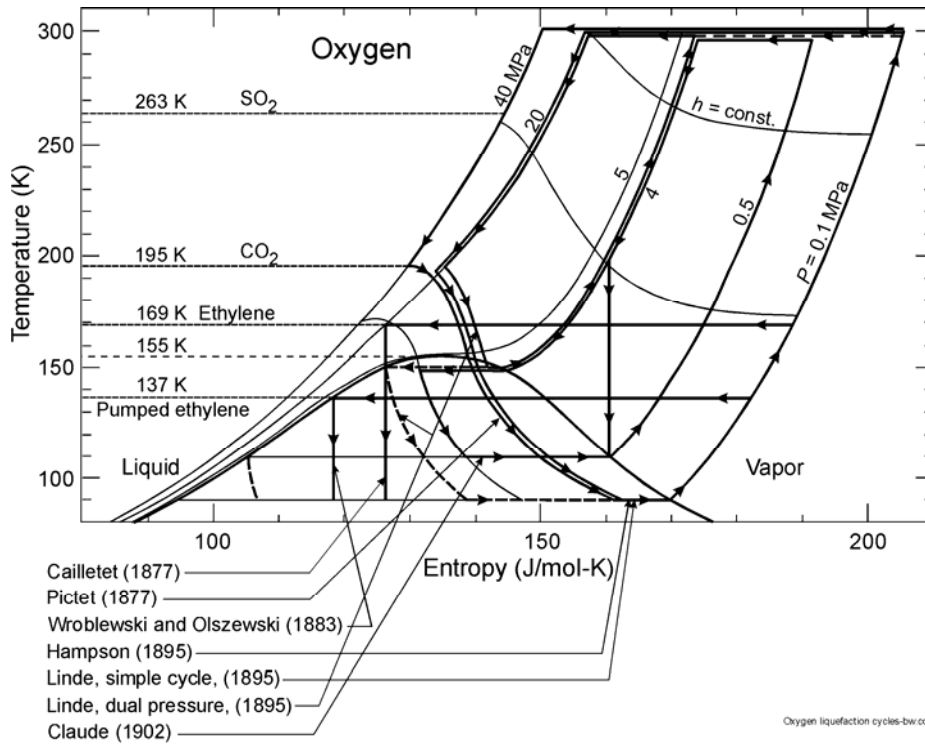
Figure 4. Paths of various cycles on a temperature entropy diagram.

to reach cryogenic temperatures with the warm end at 300 K. The requirement for such a heat exchanger is one feature that distinguishes cryogenic refrigeration from normal refrigeration. At the same time as Hampson's work, Linde in Germany also used the combination of a JT valve and a recuperative heat exchanger for the continuous liquefaction of air in 1895.[15, 16]
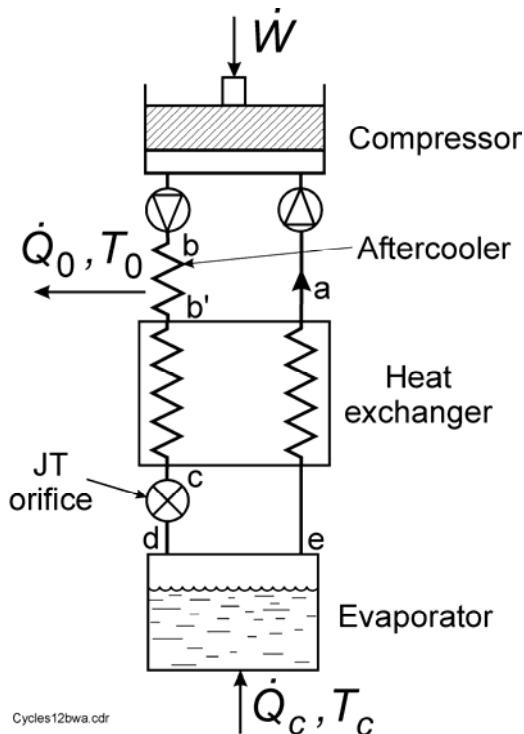

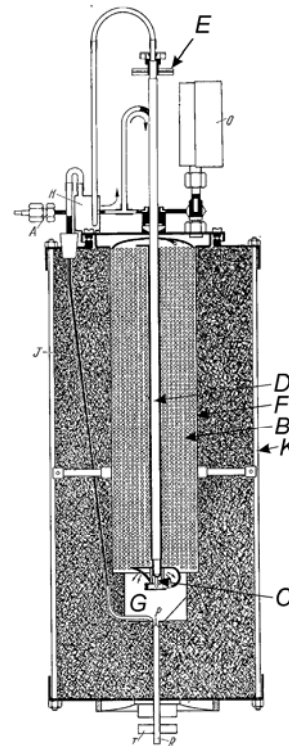**Figure 5.** Schematic of the Joule-Thomson cycle.

Figure 6. Hampson oxygen liquefier.[17]

The simple cycle first used by Linde is the same cycle Hampson used as shown in Figure 5. Linde also developed a dual-pressure cycle, as shown in Figure 7, which was more efficient than the simple cycle. About 80% of the gas was expanded from 20 MPa to 4 MPa and returned to the second-stage compressor. The remaining 20% (mostly liquid) was expanded from 4 MPa to 0.1 MPa (1 atm.) with the gas fraction being returned to the first-stage compressor.[17] Figure 4 shows the path of this cycle on a T-S diagram. With this cycle Linde was able to produce about 10 L/hr of liquid air. Linde quickly went on to commercialize the process and developed the technique of distilling liquid air into oxygen and nitrogen. By 1899 Linde was producing liquid air at the rate of 50 L/hr.[14] The early liquefiers of Hampson and Linde used glass wool for insulation even though James Dewar had invented the use of vacuum for thermal insulation in 1873 and the silvered glass vacuum container in 1892.[9] Such insulated containers are now known as a dewars.

The regenerative heat exchanger (regenerator) was invented by Robert Stirling in 1816 for use in an engine with oscillating flow. He called the device an economizer in which heat is stored for a half cycle in the heat capacity of the regenerator matrix. The Stirling engine, as patented by Robert Stirling in 1817 [18] was first used to pump water from a quarry and had the advantage of being much safer than steam engines of that time. The operating frequency was probably a few hertz. Stirling's patent drawing, given in Figure 8, shows the use of a displacer (#9 in the figure) to move the air working gas between the hot and ambient temperature regions. However, the drawing does not show an ambient temperature heat sink or the specific regenerator arrangement. In 1834 John Herschel proposed to reverse the cycle and use it as a refrigerator for producing ice.[19] However, it was not until about 1861 that
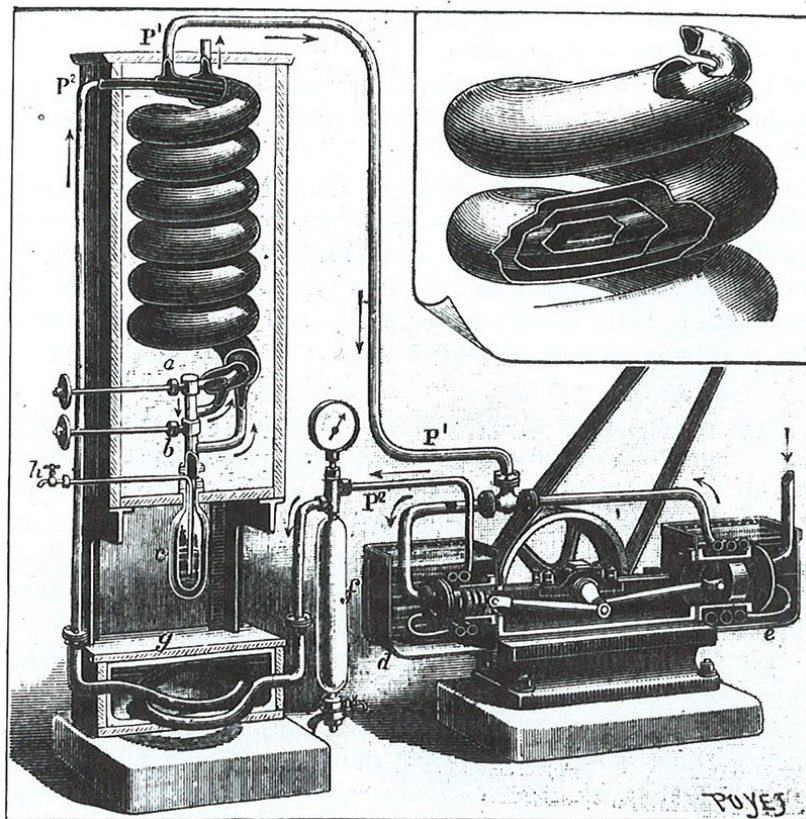

Figure 7. Linde dual-pressure cycle for air liquefaction. 10 L/hr liquefaction rate.[9]
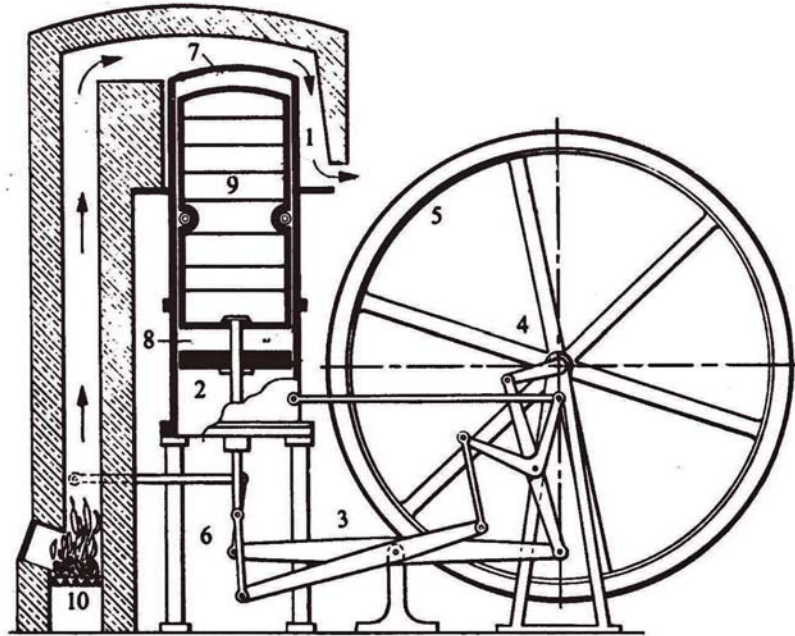
Figure 8. Drawing of Robert Stirling's first engine using air as the working fluid.

Alexander Kirk[20, 21] reduced the concept to practice. Figure 9 shows a drawing of the Kirk ice machine. The displacer filled with wire gauze O for the regenerator has conical end pieces connected to it with insulation N between them. Fresh water entering at C removes the heat of compression. Air was the working fluid in this early regenerative cooler. In spite of the high efficiency of the Stirling cooler, Kirk never made any attempt to reach temperatures below about -40 °C.[22] Schematics of two versions of the Stirling cooler are given in Figure 10. Kirk used the version with the internal regenerator. No further work was carried out on the Stirling cooler for about the next 80 years.
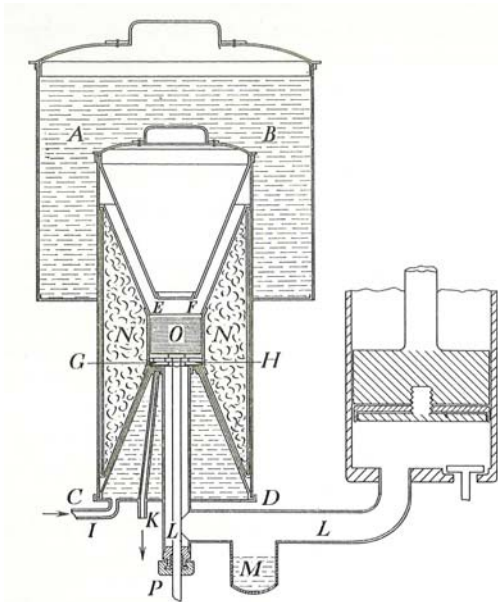
Figure 9. Drawing of the 1861 Stirling-cycle ice machine developed by Kirk.[22]

An air expansion engine for steady flow, similar to steam engines of that period, was first used by Gorrie in 1851 for an ice making machine.[7, 22] Several other air expansion engines for use in producing ice were developed in the latter half of 1800.[22] In 1896 Kamerlingh Onnes discussed in detail his concept to liquefy hydrogen with the aid of an expansion engine, but the technical difficulties forced him to abandon the idea.[23] The first successful use of an expansion engine to produce cryogenic temperatures was by Claude. Claude liquefied air in 1902 by allowing a portion of the high pressure air in a JT cycle to expand and cool in a reciprocating engine before returning it to the low-pressure side of the heat exchanger.[22, 24] This combined cycle, now called the Claude cycle and shown in Figure 11, increased the
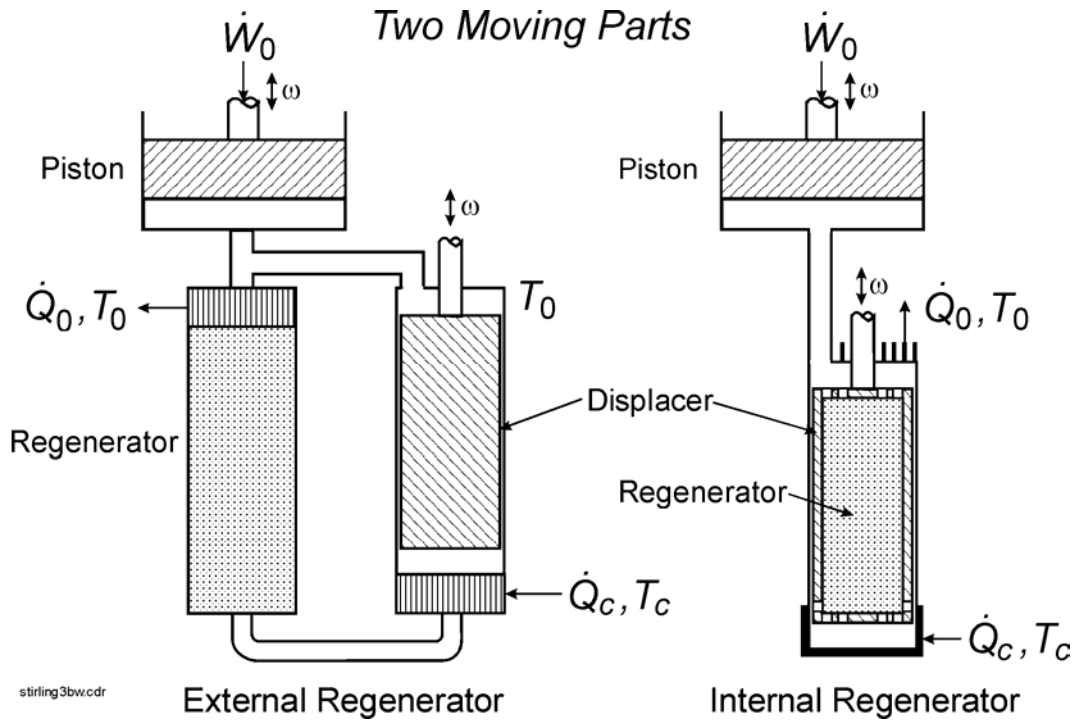
Figure 10. Schematic of the Stirling cryocooler with two versions of the regenerator.

efficiency of the liquefaction process and permitted the use of lower pressures. The arrangement used by Claude in 1902 did not have the third heat exchanger (HX3) shown in Figure 11. The path on a T-S diagram is shown in Figure 4. Claude initially used a high pressure of 2.5 MPa (increased to 4 MPa by 1906) compared to the 20 MPa used by Hamson and Linde for a JT expansion.[14]

A photograph of the original expansion engine used by Claude is shown in Figure 12. Its construction was very similar to steam engines and compressors of that period. Claude found that a leather cup work satisfactory as a flexible and dry sealing mechanism for the piston at low temperatures.[22] Within a few weeks of liquefying air, Claude formed the company L'Air Liquide to commercialize the production of oxygen using his air liquefaction technique and air separation through distillation. Oxygen could be produced by air separation much cheaper than by chemical means. Both Claude and Linde were marketing the oxygen to the rapidly growing demands of the welding industry for use in oxy-acetylene torches perfected by Picard in 1900.[14] Steel welding and cutting then became the first significant application of cryogenics and continues on to the present day.

Hydrogen was first liquefied at a temperature of 20 K in 1898 by James Dewar using the JT
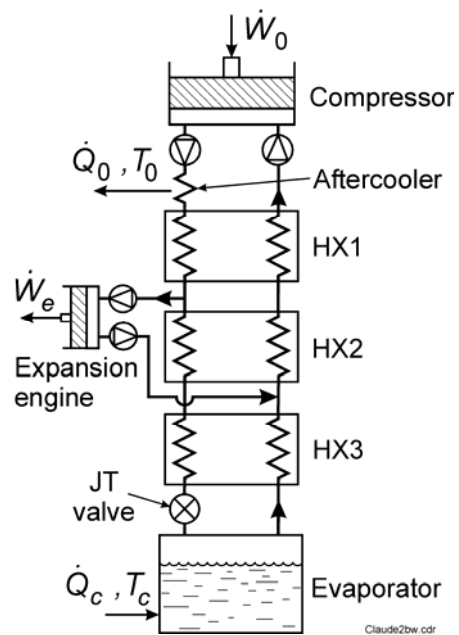
Figure 11. Schematic of the Claude cycle.

techniques of Linde and Hampson, but with a precooling bath of liquid air.[25] The liquefaction rate was about ¼ L/hr. Dewar made use of silvered, vacuum-insulated glass dewars he invented in 1892[9] to hold the liquid air and liquid hydrogen with low boiloff rates. After successfully liquefying hydrogen, Dewar became well known for his Friday evening lectures at the Royal Institution, London, on the properties of liquid and solid hydrogen and on properties of substances cooled using the liquid.

Helium was first discovered in the sun in 1868 and then found on Earth in the mineral cleveite in 1895. After hydrogen was liquefied in 1898, the attention of the cryogenic scientific community then turned helium because it was the only remaining 'permanent' gas that had not been liquefied. Around 1900 both Dewar of the Royal Institution in England and Kamerlingh Onnes of the University of Leiden in the Netherlands sought to obtain sufficient quantities of helium to liquefy it.

Figure 12. The first expansion engine of Claude. G. Claude (1913) *Liquid Air, Oxygen, and Nitrogen*

Contrary to common belief, their competition to be the first to liquefy helium remained rather cordial and each provided the other helpful suggestions.[26] In order to liquefy helium with the JT cycle, Onnes needed a sufficient quantity of liquid hydrogen for precooling the helium. Previously in 1894 Onnes had set up a cascade air liquefier using the vapor-compression cycle in four separate stages of methyl chloride (249 K), ethylene (169 K), oxygen (90 K), and air (82 K).[6] No recuperative heat exchangers are required in this cycle. This liquefier produced 14 L/hr of liquid air. To liquefy hydrogen Onnes would first liquefy a sufficiently large quantity of air (about 75 L) in the cascade liquefier. This liquid air was then siphoned into the hydrogen liquefier through an expansion valve where the liquid air at sub-atmospheric pressure would precool the high pressure hydrogen to about 64 K. The hydrogen was pressurized up to 20 MPa by a compressor that utilized a column of mercury to eliminate leakage of hydrogen by the piston. This type of compressor was invented by Cailletet for his use in liquefying oxygen and nitrogen. Counterflow heat exchangers between the high pressure hydrogen and the returning low pressure air and hydrogen were also incorporated into the apparatus to reduce the boiloff rate of the liquid air. After being cooled to 64 K the high pressure hydrogen passed into the recuperative heat exchanger and then expanded through the JT valve to form liquid hydrogen. Onnes completed this liquefier in 1906, which produced 4 L/hr of liquid hydrogen, much more than the 1 L/hr hydrogen liquefier of Dewar.[27]

Onnes then built a similar liquefier for helium, but with the liquid air being replaced by liquid hydrogen, which precooled the high pressure helium to 15 K before entering the recuperative heat exchanger and expanding in the JT valve to cool to the liquefaction point. The helium gas was pressurized to as high as 10 MPa by the same mercury-sealed compressor that had been used for the hydrogen liquefier. The unsilvered glass dewar for the liquid helium was surrounded by a liquid hydrogen bath and a liquid air bath, both of which were in silvered glass dewars with a slit in the silver to observe the liquid helium. Onnes succeeded to produce about 100 milliliters of liquid helium at a temperature of 4.2 K on July 10, 1908 [28]
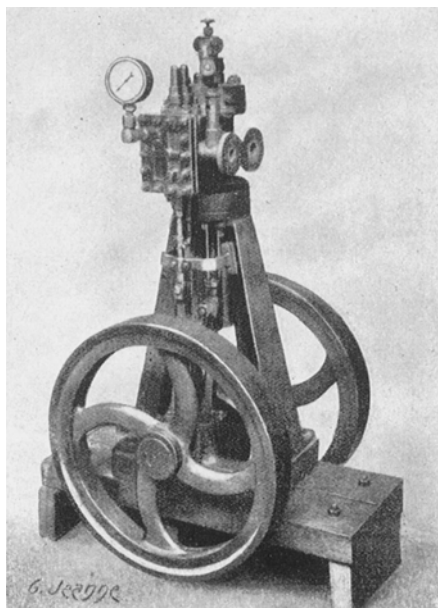
for which he received the Nobel Prize in 1913. With the capability to reach temperatures of 2 K, Onnes then discovered superconductivity in high-purity mercury in 1911 at a temperature of 4.2 K.[29]   No other laboratory was able to produce liquid helium until 1923 when McLennan at the University of Toronto built a helium liquefier similar to that of Onnes.[30] The first helium liquefier in the US was constructed by Brickwedde at NBS in 1931. It also used liquid air and liquid hydrogen baths for precooling a JT stage and produced 0.15 L/hr of liquid helium.[31, 32]

As summarized in Figure 3, the years between 1900 and about 1950 saw significant improvements in liquefaction technology, in which efficiency and reliability were greatly improved and liquefaction rates were increased by orders of magnitude.   In the case of liquid oxygen (LOX), the liquefaction rate for a typical plant was increased from about 3 L/hr in 1895 to 2 tonnes/day in 1910 and to 100 tonnes/day in 1954. (1 tonne = 1 metric ton = 1000 kg).   The fast growth in oxygen liquefaction capacity was driven by the first commercial application of cryogenics, which was the use of oxygen for oxygen-acetylene welding. Soon after Dewar liquefied hydrogen in 1898, he proposed an exhibit on liquid hydrogen for the British Pavilion at the 1904 St. Louis World's Fair. The hydrogen liquefier built for the Fair had a two-stage reciprocating hydrogen compressor capable of producing 20 MPa at the output with 0.6 MPa at the intermediate stage.[33] The flow rate was about 14 Nm^3/hr. The high-pressure hydrogen was precooled first to 203 K with liquid CO_2, then to 83 K with liquid air at atmospheric pressure, and then to 68 K with a pumped liquid air bath before expanding through a Joule-Thomson valve to form liquid at 20 K. The liquefaction rate was not given, but if we assume a liquid yield of 7 % (85 % heat exchanger effectiveness), then about 1 L/hr would have been produced. It performed well, but the leather piston rings had to be replaced during the night after each day's run. Thus, its mean-time-to-failure (MTTF) was probably not much more than one day.

At the close of the 1904 World's Fair the U. S. National Bureau of Standards (NBS), formed in 1901 (called the National Institute of Standards and Technology after 1988), purchased the hydrogen liquefier for research at low temperatures. It was not used for several years because of the daily maintenance required, but in the early 1920s it was overhauled by the British Oxygen Company with the compressor replaced by one using steel piston rings. The overhauled liquefier produced 2 L/hr of normal liquid hydrogen, which boiled rapidly because of the heat of conversion to parahydrogen.[33] Then in 1950 the U.S. Atomic Energy Commission funded NBS to design and construct a much larger hydrogen liquefier for the development of the hydrogen bomb. In 1952 the equipment fabricated in Washington was shipped to the new NBS facility in Boulder.[34] The plant first liquefied hydrogen on March 23, 1952 and a short time later was able to produce 320 L/hr of normal liquid hydrogen.[4, 35] After installing an ortho-para converter in the liquefier in 1953, the plant could produce 240 L/hr of liquid parahydrogen. The NBS liquefier used JT expansion of hydrogen compressed to 12 MPa and precooled with baths of liquid nitrogen at 77 K and 65 K. The liquid yield was 24.5 % compared with a theoretical value of 26.1 %,[4] which indicates a heat exchanger effectiveness of 98.4%.

In 1934 Kapitza, working at the Royal Society Mond Laboratory of Cambridge, described a 1.7 L/hr helium liquefier based on the Claude cycle.[36] The reciprocating expansion engine replaced the liquid hydrogen precooling bath of Onnes' JT process. A liquid nitrogen bath was still used. The lower operating pressure of 1.7 MPa also relaxed the requirements on the compressor. Kapitza developed a non-lubricated expansion engine using a clearance seal with labyrinth grooves on the piston. The expansion work was dissipated at room temperature in a

hydraulic mechanism. The connecting rod, in the form of a thin-walled tube had a room temperature gland to prevent the leakage of helium. The liquefier produced about 1.7 L/hr of liquid helium.[37]

Kapitza visited Moscow on vacation in 1934 and was detained there by government authorities until his death in 1984. Eventually he became the director of the Institute for Physical Sciences of the Academy of Sciences in Moscow. He built another helium liquefier in Moscow to study the properties of helium. In 1937 Kapitza[38] and Allen *et al*.[39-41] independently discovered superfluidity in liquid helium below 2.17 K. Kapitza received the Nobel Prize in 1978 for this work and for his work with helium liquefaction techniques.

The use of expansion turbines for gas liquefaction appears to have been first carried out in 1934 at the Linde facilities in Germany.[22, 42] In 1939 Kapitza described the design and construction of an air liquefier with an 80-mm diameter expansion turbine supported by ball bearings at room temperature and rotating at a speed of 40,000 rpm.[22, 43] The inlet pressure was 0.56 MPa, and the power output of the turbine was 4 kW. The turbine handled about 570 kg/hr of air and achieved an isentropic efficiency of 79 %.

In 1935 Collins also began work on a helium liquefier using the Claude cycle and reciprocating expansion engines. The work was interrupted by World War II, but in 1946 the liquefier was completed.[44] Collins used two reciprocating expansion engines to eliminate the need for both liquid nitrogen and liquid hydrogen precooling. He also used a clearance seal on the piston, as did Kapitza, but the expansion space was on top of the piston, so the connecting rod was always in tension. Thus, the connecting rod could be made with a thin flexible rod to minimize heat leaks. The liquefaction rate with no liquid nitrogen precooling was about 1 L/hr using a commercial compressor providing a pressure of 1.5 MPa and driven with a 10 hp (about 10 kW) motor. This efficient helium liquefier has become known as the Collins helium cryostat or liquefier.[22] This liquefier was then commercialized and allowed laboratories all over the world to produce liquid helium for low temperature research. The first commercial helium liquefier of about 1950, shown in Figure 13, produced about 4 L/hr with liquid nitrogen precooling. Between 1947 and 1970 , 365 units were marketed.[45]
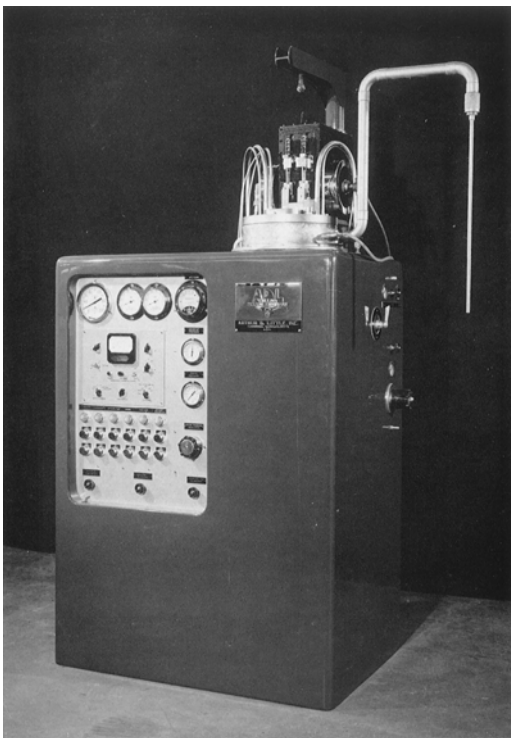
Figure 13. Early Collins helium liquefier. (Collins and Cannaday (1958))

After the liquefaction of [4]He at 4.2 K by Onnes there was no other gas with a lower boiling point, except for the rare isotope [3]He with a boiling point of 3.2 K. Temperatures of about 0.7 K could be achieved by pumping on liquid [4]He. An entirely new refrigeration method using adiabatic demagnetization of electron paramagnetic salts was proposed independently by Debye[46] and by Giauque[47] in 1926 to reach temperatures much lower than 1 K. For this technique the salt is magnetized at some high temperature around 1 K to align the magnetic spins with the field and reduce the entropy. The heat of magnetization is transferred to the surrounding bath. The salt is then thermally isolated from the bath and as the magnetic field is

removed the salt cools to some lower temperature. This is a one-shot process, and the salt warms up as it absorbs heat. The first successful experiment was carried out in Berkeley in 1933 by Giauque and MacDougall in which a magnetic field of 0.8 T was applied to the $Gd_2(SO_4)_3{\cdot}8H_2O$ paramagnetic salt at 1.29 K and then demagnetized to a final temperature of 0.242 K.[48]   Giauque received the Nobel Prize in 1949 for his work with adiabatic demagnetization and the third law of thermodynamics. Many researchers enter this field of adiabatic demagnetization of paramagnetic salts using higher magnetic fields and better salts to achieve lower temperatures.   In 1950 de Klerk *et al*.[49] at Leiden reached a low temperature of 1.4 mK using a mixed salt of chromium alum and aluminum alum.

In 1938 the Philips Research Laboratories in the Netherlands began research on the Stirling engine for use as electric generators to power radios in remote areas during World War II.[50] The effort was carried out in secret during the war and led to a rather efficient engine. When it was driven in reverse with an electric motor it acted as an effective refrigerator like the machine developed by Kirk in 1862 for production of ice. In 1946 the temperature of liquid air was achieved when low-pressure hydrogen was used as the working fluid and loose cotton wool was used as the regenerator.[51] The refrigeration capacity was low, but the results were encouraging enough that a small group was set up at the Philips Laboratories and headed by Kohler to study the Stirling cycle for use in liquefying air. After increasing the pressure of the hydrogen and using a dense metal screen, liquid air condensed on the outside of the cylinder at a rapid rate in 1950. An engineering model was demonstrated for the first time in 1953 at Grenoble for the International Institute of Refrigeration[52] and the first commercial machine (called the A-machine) was on the market in 1955.[51]   The operating principles and construction details were given by Kohler and Jonkers.[53, 54]   A cross-sectional drawing of the machine is shown in Figure 14. It is an integral machine with the piston and displacer in the same cylinder. The regenerator of fine metal screen is in the annular space outside the displacer. The helium or hydrogen working fluid was at an average
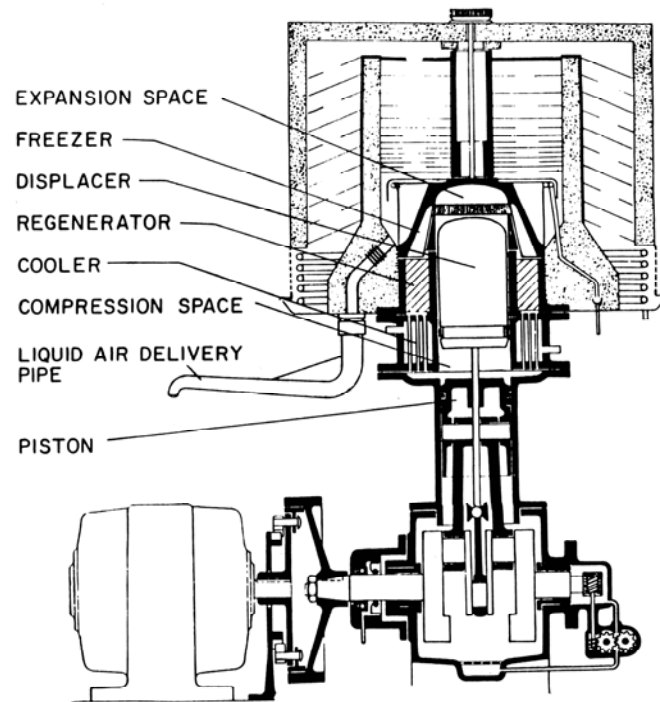
Figure 14. Early Philips air liquefier using the Stirling cycle.

pressure between 1.6 and 3.5 MPa and the operating speed was about 24 Hz. The high speed and the high pressure resulted in a small machine with high refrigeration capacity. It could produce 6.6 L/hr of liquid air with a yield of 1.14 L/kW-hr. A photograph of the first commercial machine (A-machine) is shown in Figure 15.

CRYOGENIC APPLICATIONS AROUND 1950

Around 1950 the only significant applications of cryogenics involved the use of cryogenic liquids. The liquefaction technology for these cryogens was developed primarily in the years between 1850 and 1900, and the transfer of the liquefaction technology to industry and the rapid scale up of liquefaction rates occurred primarily in the years from 1900 to 1950. As mentioned previously, the first application of cryogenics was for the production of oxygen from the distillation of liquid air to meet the needs of the welding industry for oxy-acetylene welding and cutting of steel. That application continues through today. The size of a typical oxygen production plant grew from about 2 t/d in 1910 to 35 t/d in 1925 to about 100 t/d in 1950. Figure 16 compares a 2 t/d plant from 1910 to a 100 t/d plant of the early 1950s. The largest plants in 1950 produced about 200 t/d of oxygen. In 1947 the U.S. production for oxygen was 0.541×10^6 metric tonnes (407×10^6 m^3 of gas). By 1954 the production had increased to 0.830×10^6 tonnes. The nitrogen production in 1947 was 0.0167×10^6 tonnes, which increased to 0.534×10^6 tonnes in 1960.[55] The delivery of oxygen or nitrogen from these plants to end users required the use of vacuum insulated tank trucks and rail cars, a relatively large industry in itself at this time. The nitrogen from these air separation plants was used some for inerting atmospheres in the steel and aluminum industries and was beginning to be used for the production of some chemicals, such as ammonia. Development of the basic oxygen furnace (BOF) for the production of steel was initiated in Switzerland by Robert Durrer in the late 1940s. The use of pure oxygen in these furnaces oxidizes impurities more efficiently, increases production rates and reduces the nitrogen content of the steel compared with the use of air. The first commercial 35-ton converter was set up in Austria in 1952. Similar furnaces soon were being used in the US to meet the rapidly growing steel demands of the automotive industry. This new application for oxygen was poised in the early 1950s to bring about a very rapid increase in the demand for oxygen. Other uses of oxygen in the 1950s were for medical and military breathing supplies.

The first use of liquid oxygen for rocket propulsion began with experiments by the American Robert Goddard. On March 16, 1926 he achieved the first successful flight with a rocket fueled by gasoline and liquid oxygen. Though the 12.5 m high flight was unimpressive, it led to much more development in this field of rocket science. The V-2 rocket (in Germany called the A-4) developed by Germany during World War II

Figure 15. First commercial Philips air liquefier. (A-machine) Kohler (1960).
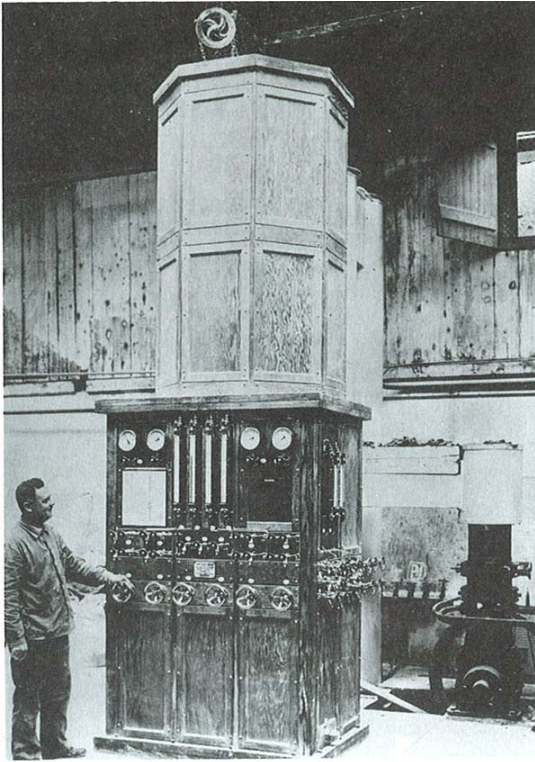
Figure 16a. Air separation plant from 1910. 2 t/d.[15]

Figure 16b. Air separation plant of the early 1950s. 100 t/d. Photo courtesy Praxair.

used alcohol (3800 kg) and liquid oxygen (4967 kg) for thrust.[56] Though small (14 m long by 1.7 m diameter, 249 kN thrust) compared with today's rockets it burned about one ton of the fuel-oxygen mixture every seven seconds. After the war, further developments of the V-2 rocket were carried out in the US, which led to the second generation V-2, the Redstone rocket (21 m long by 1.8 m diameter, 333 kN thrust). It was first launched on August 20, 1953 from Cape Canaveral, Florida.[57, 58]

In about 1945 the US Air Force at Wright Field began to look for aviation fuels with higher energy content.[59]   A 1945 Navy report showed that the hydrogen-oxygen combination offered the highest specific impulse.[60] Near to Wright field was the cryogenic laboratory of Ohio State University under the direction of Herrick Johnston, where a hydrogen liquefier of about 25 L/hr capacity had been built using the Joule-Thomson cycle precooled with liquid air, like that of James Dewar. The Air Force contracted with Johnson's laboratory to study hydrogen as a fuel and to study its properties. In 1948 some large scale experiments were conducted to investigate hydrogen as a fuel for ramjets. From 1947 to 1951 experiments with hydrogen-oxygen and hydrogen-fluorine in small rockets were carried out, including investigations of liquid hydrogen pumps similar to the V-2 liquid oxygen pumps. Similar research was being carried out on the west coast under Navy funding at the Jet Propulsion Laboratory and at Aerojet General. A hydrogen liquefier patterned after the Johnston liquefier was built there that produced 30 L/hr in 1948. The capacity was increased to 80 L/hr in 1949 by adding additional compressors. To produce enough liquid hydrogen the liquefier was run nearly continuously for three months with four days of lost time due to repairs. The rocket tests were mostly successful, but a change in emphasis in the Air Force and Navy led to these programs fading away.

In January of 1950 President Truman of the US gave the directive to begin development of the thermonuclear (hydrogen) bomb and conduct some critical tests. The Los Alamos Laboratory then intensified their study of thermonuclear fusion and determined liquid deuterium would be required. Hydrogen liquefiers were critical for this development. Los Alamos recommended a national laboratory for cryogenic engineering be established. The Atomic Energy Commission selected the National Bureau of Standards (NBS) to build such a laboratory because of its extensive experience with cryogenics originating with the purchase of the James Dewar hydrogen liquefier from the St. Louis World's Fair in 1904. A new site in Boulder, Colorado was selected, and in May 1951 construction of a research building and a liquefier building began. The buildings were completed in March 1952 and the hydrogen, helium, and nitrogen liquefiers were installed. As mentioned earlier the hydrogen liquefier constructed at NBS in Washington was shipped to Boulder and installed there. This effort was described at the first Cryogenic Engineering Conference, held at NBS-Boulder in 1954.[61] In March, 1952 the hydrogen liquefier was operating and producing 320 L/hr of normal liquid hydrogen or 240 L/hr of liquid parahydrogen by 1953.[4] Figure 17 shows this liquefier.

Large transportable dewars for liquid hydrogen were developed during that time, some of which included a small cryocooler to reliquefy the boiloff. A non-refrigerated 750 L dewar had a boiloff rate of 1 % per day and was designed for air transport.[62] A similar hydrogen liquefier was shipped to the Eniwetok Atoll in the Pacific Ocean for the liquefaction of deuterium for the first hydrogen bomb test on the nearby island of Elugelab. This first bomb was named Mike and was basically a large dewar of liquid deuterium 6 m high and about 2 m in diameter with a fission nuclear bomb at the top to trigger the system, as shown in Figure 18. Transportable dewars were used to bring liquid deuterium (23.3 K) from the liquefier to the Elugelab Island test site. On November 1, 1952 the bomb was detonated as shown in Figure 19 with a yield of 10.4 megatons of TNT that vaporized the island and left a crater about 1.6 km wide. Subsequent H-bombs used the solid lithium deuteride instead of the liquid deuterium. The end of the 'wet' bomb program reduced the need for liquid hydrogen after about 1954 but research on its properties continued at NBS-Boulder.

In about 1954 a super-secret program funded by the US Air Force returned to the study of liquid hydrogen for fuel, but this time for an air-breathing aircraft engine capable of flying at
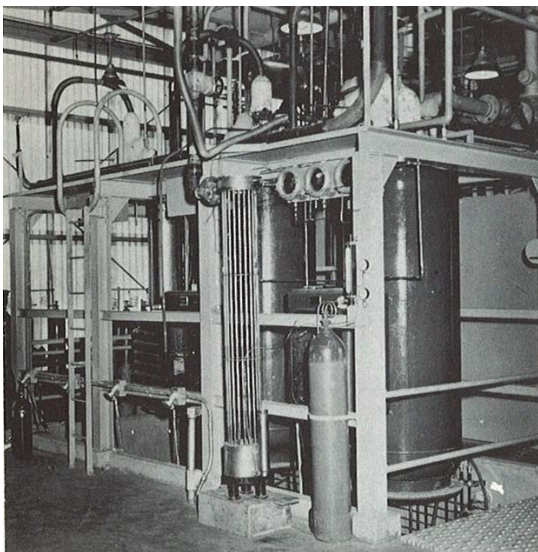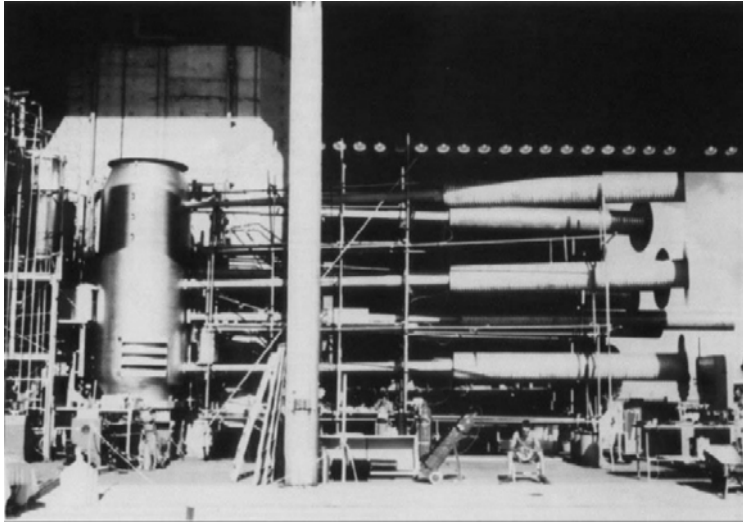

Figure 17a. NBS hydrogen liquefier of 1950s.
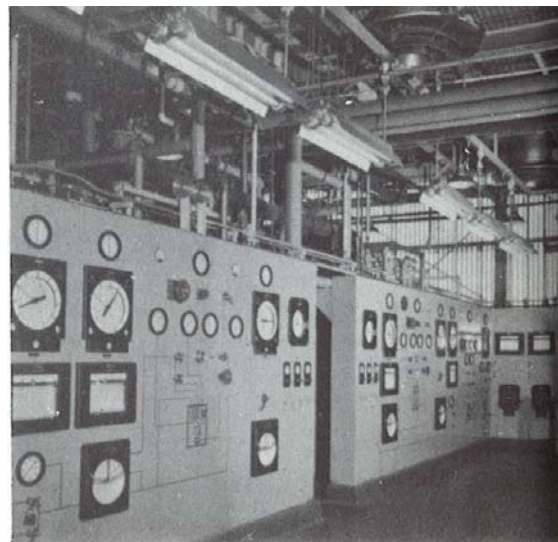
Figure 17b. Control panel for NBS hydrogen liquefier.

Figure 18. Preparing the first hydrogen bomb (Ivy-Mike) using liquid deuterium.

Figure 19. First hydrogen bomb (Ivy Mike). Wet bomb using liquid deuterium.

an altitude of about 30,000 m with a speed of Mach 2.5.[59] The purpose was for very high altitude reconnaissance to replace the U-2 spy plane. The plane to be built by Lockheed was designated the CL-400 but was better known as the Suntan. Large quantities of liquid parahydrogen would be needed, so a study and design of several sizes (up to 45 t/d) of parahydrogen liquefiers were completed. A 0.68 t/d liquefier was built in Painsville, Ohio, near a plant producing excess gaseous hydrogen. This liquefier was named 'Baby Bear' and became operational in May 1957. Another liquefier was built in Florida with a capacity of 4.5 t/d and was called the 'Mama Bear.' A third liquefier for 27 t/d was installed near 'Mama Bear' and was called 'Papa Bear.' It became operational in January 1959 and was the world's largest hydrogen liquefier. The last two liquefiers used expansion turbines and lower pressures and became the model for most subsequent hydrogen liquefiers.[59] However, before the CL-400 aircraft could be built and tested, various political and management problems led to the cancellation of the $100 million program in 1959. The liquefiers would not sit idle for very long as the US space program was about to begin.

The reliability of liquefaction systems in the 1950s was much improved over that of 50 years earlier, but was much inferior to what is expected today. Compressors required constant

maintenance. A typical maintenance schedule given by Croft[63] for hydrogen and helium compressors of that time period is as follows:

250 hours	Test for leaks in screwed unions, gaskets, etc..
	Tighten piston-rod glands (where applicable).
	Clean out oil pump to cylinders.
1000 hours	Re-lap valves or fit spare ones.
	Check belt tightness.
	Change crankcase oil.
2500 hours	Check, and if necessary, replace cylinder liners and piston rings.
	Take down bearings and adjustment shims if necessary.
	Check oil pump to bearings

Methane was first liquefied in small droplets by Cailletet in 1867 at a temperature of 112 K using his technique of compression and rapid expansion. The first large liquefaction plant for natural gas (mostly methane) was installed in Cleveland, Ohio, in 1941 with a capacity of 75 t/d (1.1×10^5 m^3/d gas, 177 m^3/d liquid). It used a cascade Joule-Thomson cycle with ammonia and ethylene stages for precooling. The total power input was 2.4 MW.[64, 65] It was used for a peak shaving application with three spherical storage tanks of 2700 m^3 liquid volume each. After a new cylindrical storage tank was added in 1944 it failed resulting in a fire and the loss of 200 lives. Interest in other LNG facilities was dampened at that time until 1952 when a barge mounted liquefier was put into operation near Lake Charles, Louisiana, on the Mississippi River in 1952. It produced 114 t/d of LNG, which was intended to be shipped via barge to Chicago.[65] However, the transport of the LNG along the Mississippi River was never approved because of a poor design of the LNG containers on the barges.

SUMMARY

To provide a background as to why applications in cryogenics did not begin to evolve until the last 50 years, it is helpful to understand the basic advances that were required even to achieve these temperatures. This historical summary has provided a progress report dating back to 1850, when thermodynamics concepts were just being introduced and high-pressure equipment was being developed fore steam power stations. Prior to that time laboratory techniques for reducing the temperature of a gas, liquid, or solid only a few degrees below ambient temperature required considerable skill and only attempted by a few scientists around the world. As practical schemes were visualized to achieve lower temperatures and supporting equipment was developed, the progress to achieve lower temperatures required between 50 to 100 years to obtain sufficient quantities of cryogenic fluids to provided the opportunities of using these fluids in applications that would benefit mankind. This opportunity has presented itself only over the past 50 years, and some of these applications are covered in this monograph.

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