Cryogenics at the end of the 19th and the first half of the 20th century (1880–1940)

2009 J. Phys.: Condens. Matter 21 164221

(http://iopscience.iop.org/0953-8984/21/16/164221)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **21** (2009) 164221 (8pp) doi:10.1088/0953-8984/21/16/164221

Cryogenics at the end of the 19th and the first half of the 20th century (1880–1940)

R de Bruyn Ouboter

Kamerlingh Onnes Laboratory, Leiden University, The Netherlands

Received 22 January 2009
Published 31 March 2009

Abstract

On the 10 July 1908 Heike Kamerlingh Onnes succeeded in the first liquefaction of helium. A very long preparation was necessary before Onnes succeeded. The underlying technological framework from his predecessors was mainly formed by the ingenious discoveries of Dewar. Onnes started with his cascade process of air liquefaction in 1892. In 1898 Dewar liquefied hydrogen for the first time and in 1906 the large hydrogen liquefier of Onnes was ready for use. The main part of this review concerns the first liquefaction of helium, for which the preparation of helium gas from monazite sand was needed, the construction of the liquefier and the mercury compressor of Cailletet, eventually rewarded with the first successful liquefaction. Subsequently, the later developments will be reviewed, i.e. Simon's expansion apparatus (1932), the helium liquefier of Kapitza (1934), and finally the Collins liquefier (1940–1947). This concludes the first half of the history of low temperature physics, after which a new area starts.

On 10 July, 100 years ago, Kamerlingh Onnes succeeded in the first liquefaction of helium [1], an event which we remember today. Three years later he had the first glimpse of the strange new world of superfluidity when he discovered superconductivity in mercury[1], one of the highlights of physics at low temperature. On that first day he found that the boiling point was 4.3 K, the critical temperature not much over 5 K and, when the bath pressure was reduced, a temperature of 1.7 K was reached. Thereby he opened up a whole new field of research. In figure 1 we see him proudly posing in front of his liquefier.

Here it is my intention to review cryogenics at the end of the 19th and the first half of the 20th century.

Kamerlingh Onnes was continually guided by theory in his work on cryogenics. Around 1870 Onnes became acquainted with the work of van der Waals. They became friends. van der Waals formulated in 1873 his equation of state by taking into account the actual space occupied by the gas molecules, along with the attractive forces they exert on one another and in 1880 he formulated the law of corresponding states. By studying this law at all possible points, this theory served as a guide for Onnes during his experiments and the construction of his liquefactors. The only way to test his ideas was to measure gaseous behaviour at extreme conditions, at low temperatures. The need for extremely cold conditions led Onnes to establish cryogenic facilities on a, for that time, large scale to create new environments to test theories and open a new field of research: physics at low temperatures.

A very long preparation was necessary before Onnes succeeded. The underlying technological framework inherited from his predecessors was mainly formed by the ingenious discoveries of Dewar (1842–1923): the use of silvered vacuum glasses (1892), the liquefaction of hydrogen (1898), and the absorption of gases in charcoal at low temperatures used to purify helium (1905).

In 1877 the French physicist L P Cailletet and the Swiss scientist R P Pictet independently succeeded in liquefying both oxygen and nitrogen; the quantities of liquid they could produce were extremely small. Onnes, however, needed large amounts to conduct his research. He started in 1882 when he was appointed at Leiden University and ten years later he succeeded in developing an apparatus for producing those large amounts: the cascade apparatus which could produce 14 l of liquid air per hour. In 1892, three years before Linde's invention, the *air liquefier* [3] based on the cascade process was ready. This is the only case in which this method was used to give large quantities of liquid air. The liquefier was so perfectly constructed and with such good efficiency that it was in use as a powerful instrument up to 1924. The cascade principle was invented by Pictet (1878).

A series of gases with ever lower critical condensation temperatures are compressed, cooled to their liquefaction point and then expanded into a separate low-pressure chamber, from which the vapour is pumped back to the compressor so that

---

[1] The author has elsewhere described the discovery of superconductivity [2].

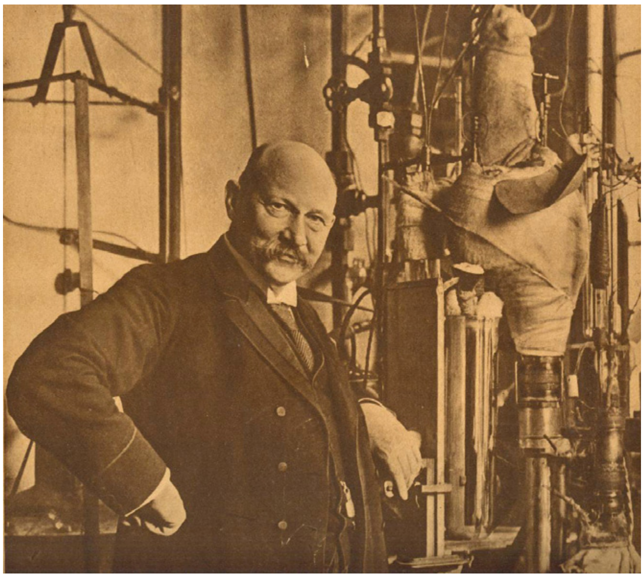


Figure 1. Kamerlingh Onnes (1853–1926), standing in front of the helium liquefier (reproduced with permission, archives Leiden Institute of Physics).

the gas circulates through the system. The vapour coming from the evaporated liquid cools the next compressed vapour in the series. Starting with methyl chloride, which condenses at +21 °C under 5 atm of pressure, ethylene (−87 °C at 3 atm), oxygen (−145 °C at 17 atm), and finally air (−193 °C at 1 atm) (figure 2) are sequentially condensed.

To get an idea of the requirements for the *liquefaction of hydrogen* one has to realize that its critical temperature is more than twice as low as the lowest temperature that can be produced with liquid air. In 1898 Dewar beat Onnes in liquefying hydrogen by taking advantage of the Joule–Thomson effect, the temperature of a gas goes down as it expands through a valve when the gas is below its inversion temperature (the maximum inversion temperature is for hydrogen gas 204 K). In May 1898 Dewar could telegraph to Leiden: Hydrogen liquefied. Onnes reported: ‘A new glorious triumph was won by him’. On 10 May 1898 Dewar had produced 20 cm^3 of liquid hydrogen boiling quietly in a vacuum glass. This announcement was made by Dewar at a meeting of the Royal Society [4], two days later. Neither at that meeting, on 12 May 1898, nor at any future occasion did Dewar give a description of his liquefier. Although Dewar drove hydrogen down to its liquefaction temperature of 20 K, his apparatus produced only small amounts of liquid hydrogen. It was not until 1906 that the hydrogen liquefier of Onnes, based on the Linde principle was ready for use, but it was a real liquefier designed to supply as much as needed for the experiments and more importantly for the production of liquid helium. As it turned out the availability of a steady supply of liquid hydrogen was the key to the attempt to liquefy helium.

One reason Onnes had to produce much larger amounts of liquid hydrogen than Dewar was that he needed this for the liquefaction of helium. Another factor in the delay was a frightened Leiden community. During the Napoleonic occupation of the Netherlands on 12 January, 1807 an ammunition ship exploded in a canal in the town destroying the area as large as two blocks of houses. The laboratory was built half a century later, on the ruins of the destroyed section of the town. In 1896, when the town council learnt that the laboratory housed considerable quantities of compressed hydrogen, a wildly combustible gas, the historical memory of the ship’s explosion drove them into panic. The authorities appointed a commission to study the matter, but even with the presence of van der Waals on that committee and a letter from Dewar imploring the council to permit the research to continue, Onnes’s hydrogen work was shut down for two years.

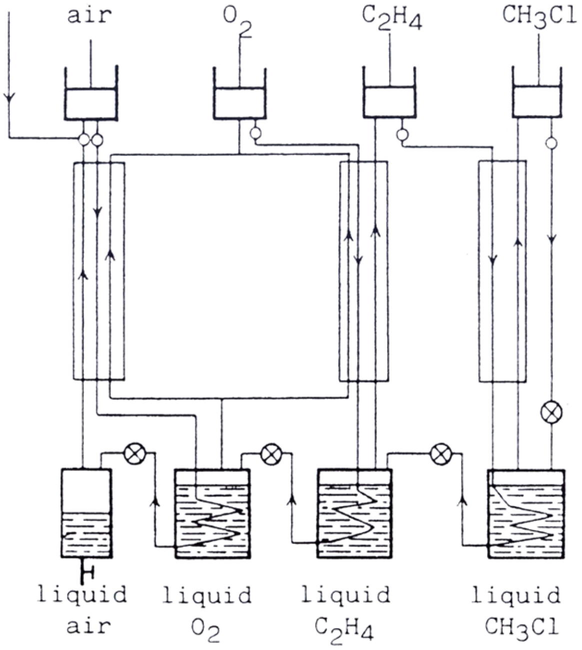


Figure 2. The principle of the cascade process of air liquefaction [3], with four stages (methylchloride, ethylene, oxygen and air). The liquefier operated roughly under the following conditions.

	Normal B. pt.	Condensed at		Evaporated at	
	°C	Temp. °C	Pressure	Temp. °C	Pressure
CH_3Cl	- 24	21	5 atm	- 87	20 cm Hg
C_2H_4	-104	- 87	3 atm	-145	2.7 cm Hg
O_2	-183	-145	17 atm	-193	20 cm Hg
Air	-193	-193	1 atm		

Each stage is of the simplest construction, comprising compression, cooling and throttle expansion leading to condensation. Incorporated are the essential heat exchangers. The vapour coming from the evaporated liquid is used to cool down the next compressed vapour before it enters the spiral immersed in the boiling liquid.

The compressed hydrogen gas entering at A (figure 3) is divided into two streams; one part through the regenerator coil B and the other part through regenerator B′. Both regenerator coils are connected again at C. In B the gas is cooled by the returning cold air vapour from the evaporated liquid and in B′ by the returning cold hydrogen vapour. Subsequently the hydrogen goes through the spirals D and E, the latter is situated in a liquid air bath at reduced vapour pressure, and finally through the principal regenerator F. Subsequently it goes through the expansion valve K. The liquid hydrogen is collected at G. The part of the hydrogen gas that did not liquefy passes around the regenerators and returns to the

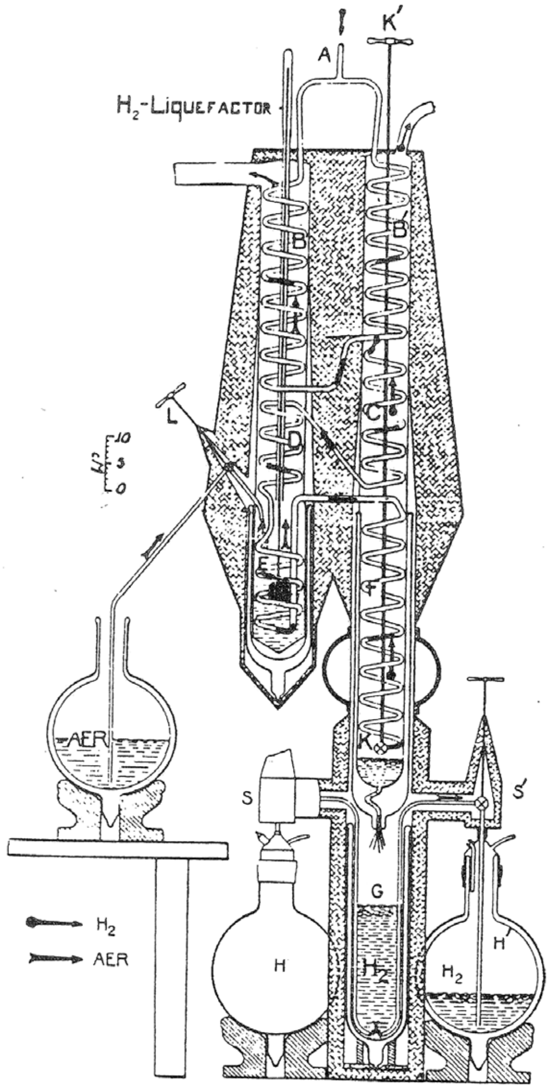


Figure 3. A schematic drawing of the hydrogen liquefier constructed by Kamerlingh Onnes in 1906 [5]. Production: 4 l liquid h^{-1}, in later years improved: 13 l liquid h^{-1}. (Reproduced with permission.)

compressor. The liquid can be syphoned over into a separate dewar.

When in 1906 his liquid hydrogen liquefactor [5] was ready he tells us in December 1907 that he remained convinced that only the determinations of the isotherms could decide how helium could be made liquid. The Boyle point was found to be between 20 and 23 K and he estimated the critical temperature as between 5 and 6 K.

The final project was to cool compressed helium by means of liquid hydrogen boiling under a pressure of 6 cm of mercury, quite near its melting point, and then lead it through a Hampson regenerator spiral which ended in an expansion valve.

The first step was to acquire a sufficient amount of the recently discovered helium gas. Helium was found to exist definitely on earth by Sir William Ramsey in 1895. Fortunately, one of Onnes's brother was director of the Office of Commercial Information in Amsterdam, and he was able to arrange for large amounts of monazite sand, which contains thorium and helium, to be purchased from North Carolina.

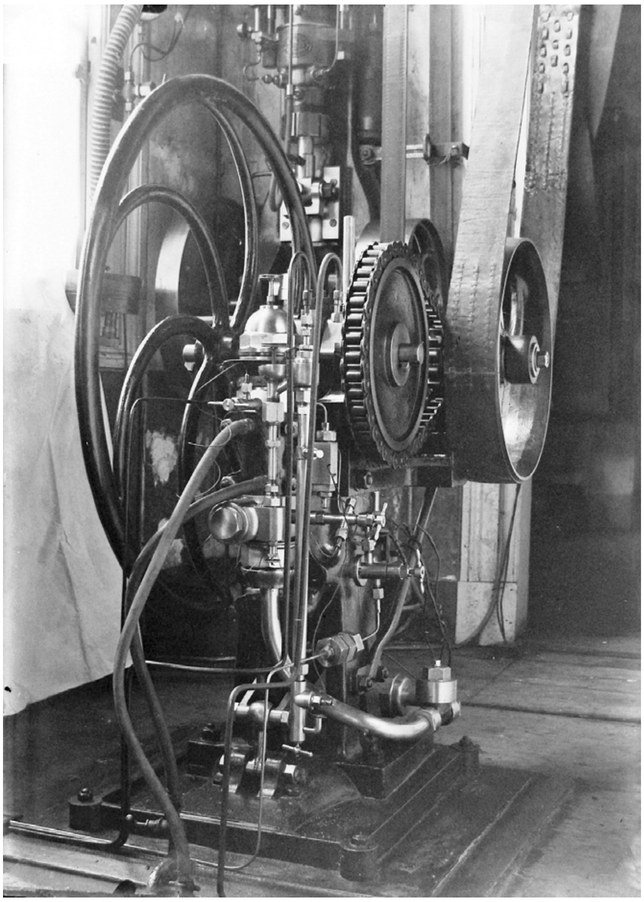
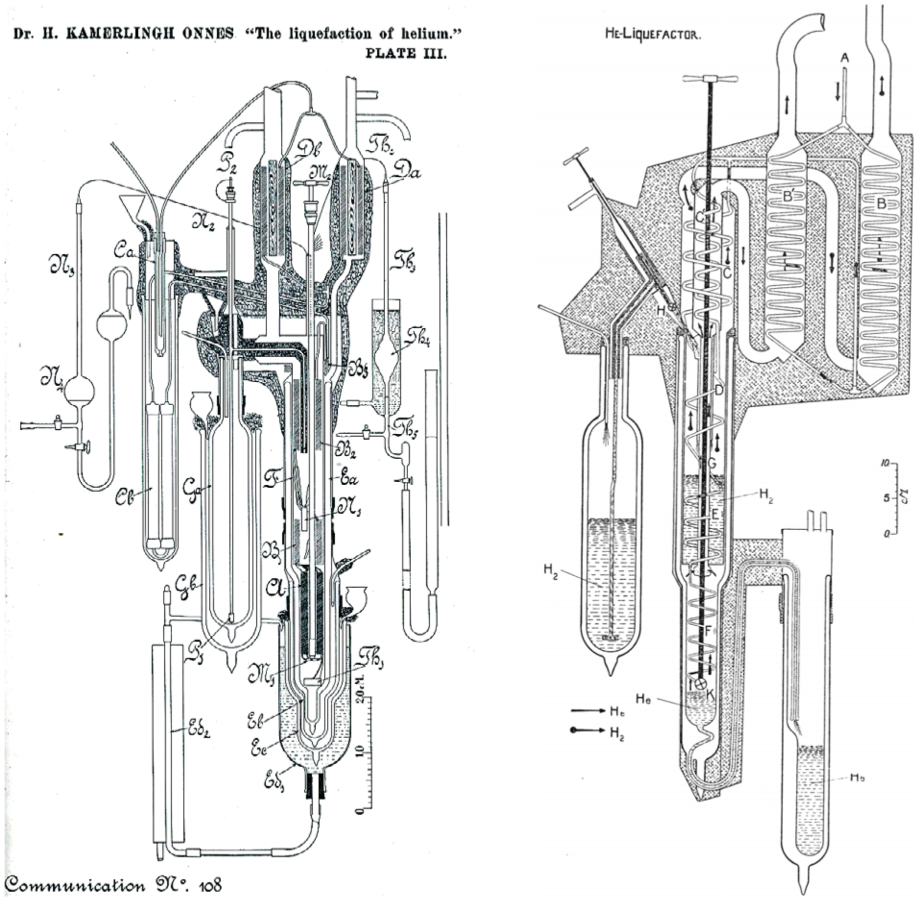


Figure 4. The Cailletet compressor, invented by L P Cailletet, who liquefied oxygen and nitrogen, was extremely useful to Onnes throughout his research. The compressor with mercury piston was modified (1894–1900). Because no gas is lost during compression or expansion, the device was suitable for working with pure and costly gases. It can be admired in the Boerhaave Museum in Leiden, and is described in Commun. no. 14 (Dec. 1894) and Commun. no. 54 (Jan. 1900). (Reproduced with permission.)

In Leiden *Communication no. 108* [1] the first *liquefaction of helium* is described with great precision, in full detail. p.5 'Even the quantity of 200 l (and 160 l of reserve) of the extreme purity required, though asking a great deal of labour was not out of reach'. p.16 'The gas was obtained from the monazite by means of heating, it was exploded with oxygen. Then it was burned over CuO and the oxygen and gases of the same volatility were removed by freezing them out in liquid hydrogen. Then it was compressed over charcoal at the temperature of liquid air, after which it was under pressure led over charcoal at the temperature of liquid hydrogen several times till the gas, which had been absorbed in the charcoal and then separately collected, no longer contained any appreciable admixtures'. 200 l of helium gas at normal temperature and pressure is a very small quantity. I have to emphasize this. Such an extremely small quantity of He-gas forces using heat exchangers/regenerators, tubes, etc of reduced inner diameters, no dead-volumes in the circuit and above all avoiding any gas loss. To realize this Onnes used his Cailletet compressor with a mercury piston in a U-shaped tube. The final result would be only 60 cm^3 of liquid helium. And we have to



(a) (b)

Figure 5. (a) A schematic drawing of the first helium liquefier (1908) [1]. For full details see Commun. no. 108. Production: 0.28 l liquid h^{-1} (1908), in the improved version (1912): 0.5 l liquid h^{-1}. See also figure 6 with a photograph of the actual liquefier. (b) Schematic drawing of the first helium liquefier (1908) with the helium cryostat (1911) attached to the liquefier [6]. (Reproduced with permission.)

realize that Onnes performed all his liquid helium experiments in the period between 1908 and 1918 with the above mentioned quantity of helium.

The purification of helium was done by chemistry students under the guidance of Mr H Filippo and Mr G J Flim. During the liquefaction process, p.9: 'Only Cailletet's modified compressor could be used, a compressor with mercury piston'. The compressor was working in 1890, five years before Ramsey discovered helium on Earth (figure 4). In his communication no.14 (Dec. 1894) he tells us: 'The idea on which Cailletet constructed this compressor is so exceedingly beautiful that I willingly spent a few years to work out the idea in an improved form'. There is no objection to raising the gas at once from a low pressure (normal or below 1 atm) to more than 100 atm. Because no gas is lost during compression or expansion this device was particular suitable during the liquefaction of helium. p.10: 'For a long time it was considered an insuperable difficulty that the compressor . . . could circulate at the utmost 1400 l of gas measured at ordinary temperature per hour, . . .' ('20–30 up and down movements of mercury per minute').

Again, a Joule–Thomson expansion would be tried to condense helium. Figure 5(a) shows the liquefier (W H Keesom's book on 'Helium', p. 154): 'Liquid hydrogen was to be syphoned over continuously from the glass Ga into the liquefier in order to keep the level of the hydrogen at the right height. This was checked with four gas thermometers $N_1 \ldots N_4$. The helium gas delivered by the compressor (with mercury piston) was driven along the following circuit: through a water and oil trap Ca, through two tubes Db and Da where it was preliminary cooled by the returning hydrogen gas and helium gas respectively, through a tube Cb filled with charcoal and immersed in liquid air, to retain the last traces of air, through three refrigerator tubes B_3, B_2 and B_1 cooled by liquid air, by hydrogen vapour, and by liquid hydrogen respectively, through a four fold wound Hampson regenerator spiral (A), to the expansion valve M_1, if liquid helium was formed it collected in the vacuum glass Ea. The helium that did not liquefy returned to the compressor. At some distance under the expansion cock a German silver reservoir of a helium gas thermometer (Th_1) had been mounted, it is soldered to a steel capillary which is connected with a manometer reservoir'.

In communication 108 [1] he writes: p.8 'The reduction of Hampson's regenerator coil to smaller dimensions does not diminish its action. . . . I could not, however, reduce below a certain limit without meeting with construction problems, ...

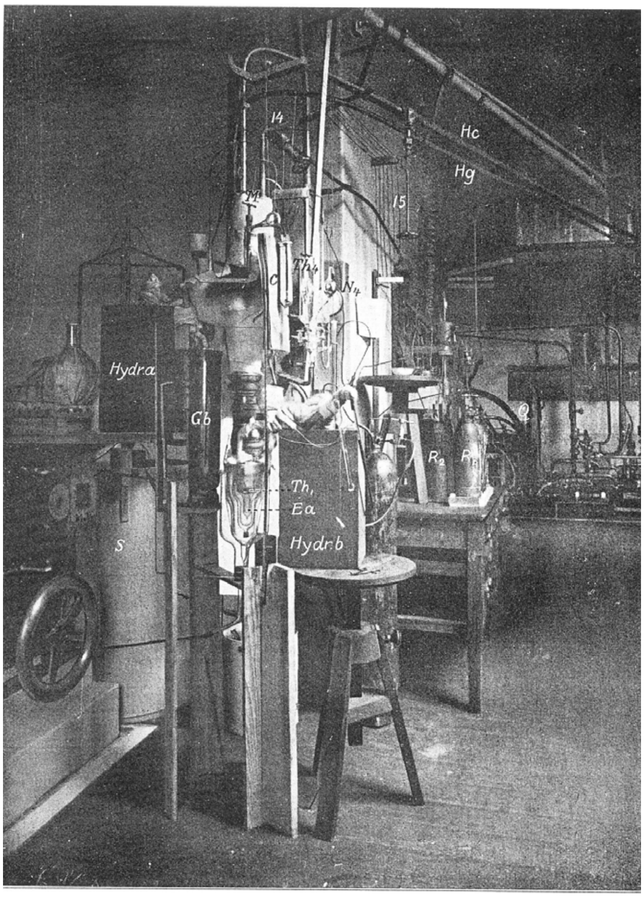


Figure 6. The helium liquefactor (1908) [1]. It has been arranged so that the liquid helium could be observed. Round the transparent bottom part of the vacuum glass Ea, a protection of liquid hydrogen (a second vacuum glass Eb, see figure 5(a)) has been applied. The hydrogen glass Eb is surrounded by a vacuum glass Ec with liquid air, which in its turn is surrounded by a glass Ed with alcohol (figure 5(a)). 'By these contrivances and the extreme purity of helium we succeeded in keeping the apparatus perfectly transparent to the end of the experiment'. In figure 5(a) is also drawn the German silver reservoir Th_1 of the helium gas thermometer. (Reproduced with permission.)

We had to be sure that the capillaries would not get stopped up, that the cocks would work perfectly, that the conduction of heat, viscosity etc would not become troublesome'.

'The utmost was demanded of the dimensions of the necessary vacuum glasses .... 'p.9: 'Besides the difficulties given by the helium liquefactor itself, the further arrangement of the cycle in which it was to be inserted, offered many more. The gas was to be placed under high pressure by the compressor, and was to be circulated with great rapidity. Every contamination was to be avoided, and the spaces which were to be filled with gas under high pressure were to have such a small capacity, that they only held part of the available naturally restricted quantity of helium'. p.10: 'with regard to the parts of the compressors, the auxiliary apparatus, and the conduits, which in the course of the experiment assume the same pressure as the regenerator coil, their joint capacity was small enough to enable us to make the experiment with a quantity of 200 l. '... the hydrogen circulation and the helium circulation could not be worked simultaneously with the available helpers to work them'. 'So on the same day that the helium experiment was to be made, a store of liquid hydrogen had to be previously prepared large enough to provide for the required cooling during the course of the helium experiment'.

So far the preparation. The system was up and running on 10 July, 1908, and word spread throughout the university. A small audience of scientists gathered to watch. By mid afternoon, helium gas flowed through the circuit, but no helium liquid was apparent by early evening, and the thermometer refused to go any lower than 4.2 K. A chemistry professor who happened to be present, F Schreinemakers, suggested that perhaps the thermometer reading had stopped declining because liquid helium was in fact already there, but was simply hard to see. Onnes proceeded to illuminate the double walled glass vessel from below. He later recounted that this was a wonderful moment, with the surface of liquid helium suddenly becoming clear against the glass wall like the edge of a knife, and that he was overjoyed to be able to show liquid helium to van der Waals.

Finally we read in Commun. No. 108 [1]: p.19: 'During the experiments and the preparations the utmost had been demanded from my assistants. In particular I wish to express my great indebtedness to Mr G J Flim, who not only assisted me as chief of the technical department of the cryogenic laboratory in leading the operations, but also superintended the construction of the apparatus according to my direction, and rendered me the utmost intelligent help in both respects'. p.15: 'In the preparation of the vacuum glasses Mr O Kesselring, glassblower of the laboratory, has met the high demands put to him, with untired zeal and devotion, for which I here gladly express my thanks to him'.

Over the next three years, Onnes devoted himself to developing better apparatus for using liquid helium in research. Merely moving the liquid from the liquefier vessel in which the small amount of helium condenses into a storage vessel presented great technical challenges. Finally, in 1911, a helium cryostat [6], which could maintain the liquid at constant temperature (figure 5(b)) was ready for investigating the behaviour of other substances at liquid helium temperatures.

A new field of research was now opened resulting immediately in the discovery of superconductivity in mercury (1911) [7], followed by the demonstration of persistent super currents in 1914 [8].

After the First World War in 1918 only 300 l of He gas were left. In 1919 the USA Government (Admiral Griffin, Bureau of Mines) presented Onnes 30 m^3 and in 1921 Professor McLennan from Toronto came personally to Leiden with a cylinder filled with He gas (2 m^3).

It was not until 1923 that helium was liquefied somewhere else. McLennan, in the Toronto cryogenic laboratory, had then built a hydrogen and a helium liquefier of the same type as Onnes's construction.

Cryogenics changed considerably after the First World War in several aspects: helium gas became available in large quantities and very important: new refrigeration techniques were developed. Of special interest are the Simon expansion method (1932, Breslau (Wroclaw)) later in Oxford and the

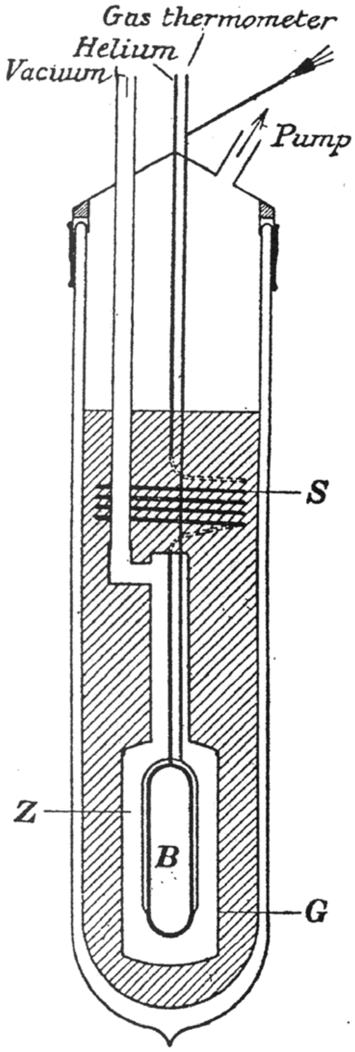


Figure 7. Simon's expansion apparatus (1932) [9].

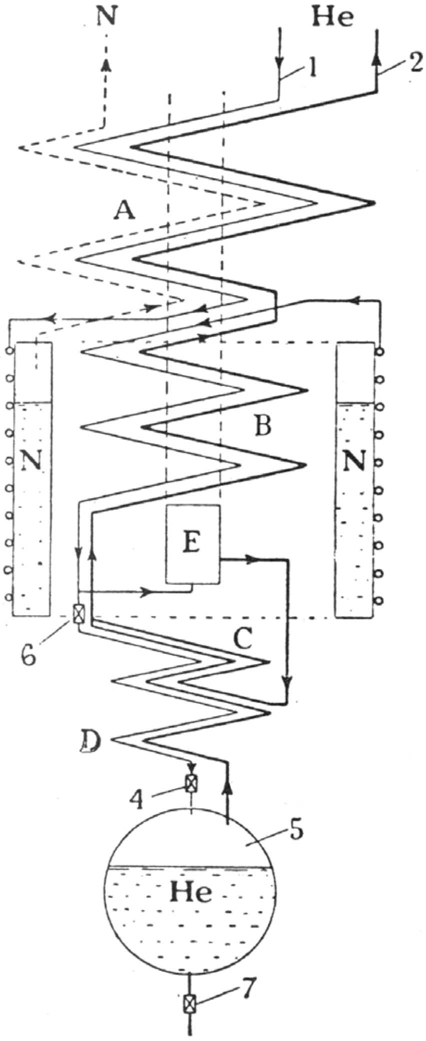


Figure 8. The heat exchangers and cooling stages in the Kapitza liquefier (1934) [16].

Kapitza expansion-engine liquefier (Cambridge (1934)) later in Moscow, which was followed by the closely related Collins liquefier (1940–1947, MIT).

In 1932 Simon [9] designed a new method for liquefying helium in a single shot isentropic expansion, shown schematically in figure 7. In a container B helium gas is compressed to a pressure of 100 atm and cooled to a temperature of about 12 K of liquid hydrogen under reduced pressure, the heat being transferred through a helium exchange gas in space Z. It is then thermally isolated by means of evacuating Z. The container B is connected with the outer space by means of a capillary that is closed with a valve. If this valve is opened the helium in the container performs work (external and against the van der Waals forces) during the expansion to a pressure of 1 atm, and after the expansion a substantial fraction of the space B is filled with liquid helium. In this temperature range this method is particular suited because of the small heat capacity of the metal vessel B. An experimental fact unknown during Onnes's first liquefaction.

In the same way, in this period the suggestion was made of adiabatic isentropic demagnetization of a paramagnetic salt in 1926 independently by Debye [10] and Giauque [11] and a few years later realized by Giauque and MacDougall [12] (1933); by De Haas *et al* [13] (1933) and by Kurti and Simon [14] (1935). A paramagnetic salt is magnetized in a strong magnetic field at a temperature of about 1 K, the heat of magnetization is transferred through helium exchange gas to the helium bath. After the exchange gas is pumped away, the magnetic field is slowly reduced to zero and the temperature of the salt drops very strongly down. Simon and Kurti even coupled the isentropic demagnetization to his single isentropic expansion of the helium.

In 1934 Kapitza (Cambridge, [15]) introduced a new type of helium liquefier, based on the same expansion-engine principles as the Claude–Heylandt liquefiers for air, without using liquid hydrogen for pre-cooling. Figure 8 shows the heat exchanger circuits. Helium gas at a pressure of 30 atm enters the liquefier at 1, passes through heat exchanger A, and is then cooled down to 75 K by passing round a ring shaped vessel N, containing liquid nitrogen at reduced pressure, then passes through the heat exchanger B to valve 6, which allows 8% of the gas to pass. The remaining 92% cools in the expansion

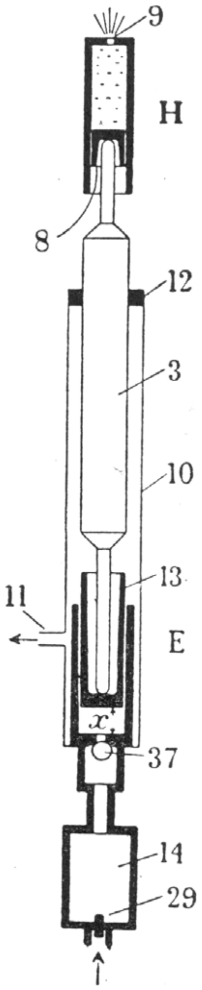


Figure 9. Schematic outline of the expansion engine [16].

machine E and flows through the heat exchangers C, B and A and finally leaves the liquefier at 2. The pressure of the 8% fraction is reduced by valve 6–18 atm, then passes through the heat exchangers C and D, and finally undergoes Joule–Thomson expansion through valve 4. The liquefied part is collected in 5 and the rest passes through D, C, B and A and leaves the liquefier at 2.

The expansion engine lowers the temperature of the gas from 20 to 10 K. An unlubricated expansion engine was used with a gap of 0.05 mm between piston 13 (figure 9) and cylinder, the small gas loss of about 4% passed the rapidly moving piston and acted as a lubricant as it escapes past the piston. The piston is connected by a universal joint and a thin copper–nickel tube 3 to the plunger in the hydraulic mechanism H. On the expansion stroke water is driven out through the hole 9, so that the expanding gas is forced to do external work. The piston is returned by readmission of the water. The piston makes about 100 strokes min^{-1}, thereby transporting about 28 m^3 of helium gas per hour through the expansion engine. This liquefier produced about 1.7 l liquid h^{-1}. Later on Kapitza build a whole series of this type, with improvements, in the Institute of Physical Problems in Moscow, both with expansion cylinders and turbines.

The closely related Collins liquefier (1940–1947, MIT) [17] has, differently from the Kapitza liquefier, two expansion engines, as is shown in the flow diagram of figure 10, the first is acting in place of the nitrogen cooling stage. For the expansion engines a very hard nitrited nitro-alloy steel was used allowing a very small gap (0.01 mm) between the piston and the cylinder wall so that the gas leakage was reduced considerably. Collins reports as early as 1940 a 50% efficiency for his expansion liquefier.

Later the Collins liquefiers were made by Arthur D Little Inc.. A tribute to their great success was that the history of low-temperature physics is divided into two eras: ‘before and after Collins’.

References

[1] Kamerlingh Onnes H 1908 The liquefaction of helium *Commun.* from the Physical Laboratory at Leiden University. 108

[2] de Bruyn Ouboter R 1987 Superconductivity: discoveries during the early years of low temperature research at Leiden 1908–1914 *IEEE Trans. Magn.* **23** 355–70

de Bruyn Ouboter R 1997 Heike Kamerlingh Onnes’s discovery of superconductivity *Sci. Am.* **273** 84

[3] Kamerlingh Onnes H 1894 *Commun.* 14

[4] Dewar J 1898 *Proc. R. Soc.* **63** 256

Dewar J 1899 *Proc. R. Inst. GB*

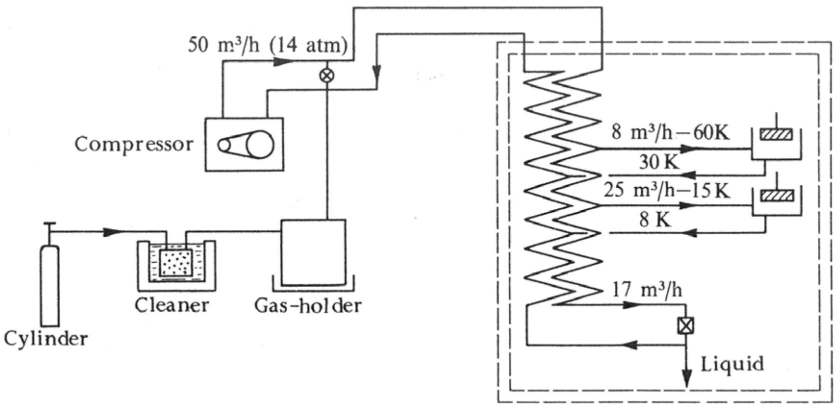


Figure 10. A simplified diagram of a Collins helium liquefier (earlier commercial models with flow rates) [18].

[5] Kamerlingh Onnes H 1906 *Commun.* 94f
[6] Kamerlingh Onnes H 1911 *Commun.* 123
[7] Kamerlingh Onnes H 1911 *Commun.* 120b, 122b, 124c
[8] Kamerlingh Onnes H 1914 *Commun.* 140b, 140c, 141b
[9] Simon F 1932 *Z.f.d. gesammte Kälte Industrie* **39** 89
Simon F 1933 *Z. Phys.* **34** 232
[10] Debey P 1926 *Ann. Phys.* **81** 1154
[11] Giauque W F 1927 *J. Am. Chem. Soc.* **49** 1864
[12] Giauque W F and MacDougall D P 1933 *Phys. Rev.* **43** 768
[13] de Haas W J, Wiersma E C and Kramers H A 1933 *Physica* **1** 1
[14] Kurti N and Simon F 1935 *Proc. R. Soc.* A **149** 152
[15] Kapitza P 1934 *Proc. R. Soc.* A **147** 189
Kapitza P 1934 *Nature* **133** 708
[16] Keesom W H 1942 *Helium* (Amsterdam: Elsevier) p 166
[17] Jacobs R B and Collins S C 1940 *Phys. Rev.* **57** 568
Collins S C 1947 *Rev. Sci. Instrum.* **18** 157
[18] White G K 1979 *Experimental Techniques in Low-Temperature Physics* 3rd edn (Oxford: Clarendon) p 23
[19] Dirk van Delft, 'Heike Kamerlingh Onnes, Een biografie', (2005), Uitgeverij Bert Bakker, Amsterdam, translated into English: 'Freezing Physics, Heike Kamerlingh Onnes and the quest for cold', Edita Amsterdam (2007).