

## Heike Kamerlingh Onnes and the first liquefaction of helium

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The liquefaction of air for the first time in 1877 – by the Frenchman Paul Louis Cailletet (1832-1913) and the Genevan Raoul Pictet (1846-1929), working independently of one another – set in motion a race towards absolute-zero temperature. A temperature of around 90 K (–183.15 °C) had been reached. The liquefaction of air for the first time marked the birth of a new science, the objective of which was to study low temperatures and their effects: *cryogenics*. In 1882, nitrogen would be liquefied by the Polish scientists Charles Olszewski (1846-1915) and Sigismund Wroblewski (1845-1888). It was not until 1898 that the Scotsman James Dewar (1842-1923) liquefied hydrogen at 19.85 K (–253.3 °C) before solidifying it at 15 K (–258.15 °C). In 1901, James Dewar turned his attention to the last atmospheric gas that had not been liquefied: helium. However, he failed in his attempts; indeed, it seemed that it was impossible to liquefy this gas.

### The kelvin

The kelvin is a unit of measure for temperature established by William Thompson (1824-1907), better known as Lord Kelvin, in the mid-19th century. The kelvin was quickly adopted by all physicists of the day. In 1702, having understood that temperature is the result of molecular movement, the French academician Guillaume Amontons (1663-1705) put forward the hypothesis of an absolute zero, corresponding to the total absence of movement. Lord Kelvin set the temperature 0 K at the calculated theoretical value of –273.15 °C, while at the same time maintaining the differential Celsius scale, which requires a difference of 100 degrees between the solidification of water and its boiling point at atmospheric pressure. To convert from degrees Celsius to the kelvin system, the following formula is used:

$$T_K = T_C + 273.15$$

Since 1954, the International Bureau of Weights and Measures has defined the kelvin as the fraction 1/273.16 of the thermodynamic temperature of the triple point of water (0.01 °C, i.e. 273.16 K).

Heike Kamerlingh Onnes began his race to the cold at the University of Leiden in the Netherlands in 1882. Although an experimenter, unlike his competitors he was also very attached to theory, and most particularly the electromagnetism of Hendrik Antoon Lorentz (who had made him chair of experimental physics at Leiden University) and the molecular theory of matter developed in 1873 by the Dutch scientist Johannes Diderik van der Waals (1837-1923), to whom he was close. Indeed, he opens his paper to the Academy of Science by emphasising the importance of this theory in obtaining liquid helium:

*The first step towards the liquefaction of helium, according to Mr van der Waal's theory, has been the determination of isotherms ...*

Van der Waals made changes to the equation of state for ideal gases hitherto used to link the pressure, temperature, volume and quantity of matter of a gas. He added two new terms that made it possible to report the different intermolecular forces in gases, called van der Waals forces. These famous isotherms are the curves linking pressure to volume at a constant temperature. By tracing these curves experimentally, it is possible to deduce the critical temperature and pressure of an element using the van der Waals equation of state. Onnes had therefore estimated the critical temperature of helium to be between 5 K and 6 K in a previous communiqué of 1907,<sup>1</sup> which is correct.

### **Critical point (thermodynamics)**

The different phases (gas, liquid and solid) of an element vary depending on its pressure and temperature. The gas/liquid distinction is possible only below a certain (critical) pressure and temperature. To liquefy a gas, it is therefore essential to go below the critical temperature and pressure.

The critical points of helium and water are as follows:

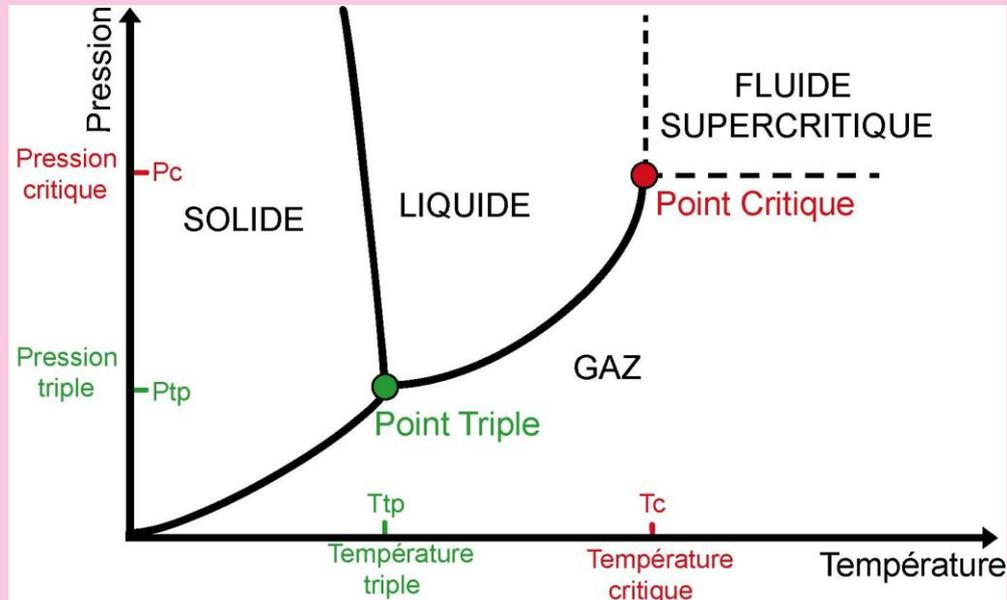
Helium:  $T_c = 5.2 \text{ K}$  and  $P_c = 2.23 \text{ bar}$

Water:  $T_c = 647.15 \text{ K}$  and  $P_c = 218 \text{ bar}$

The distinction between two phases is possible only if there is an exchange of energy at constant pressure and temperature during the change of phase. For example, energy is needed to vaporise a liquid (i.e. for it to turn from a liquid state to a gaseous state), whereas energy must be removed from a gas in order to liquefy it (for it to go from a gaseous state to a liquid state). The quantity of energy

1. Kamerlingh Onnes, H., "Isotherms of monatomic gases and their binary mixtures. I. Isotherms of helium between +100°C and -217°C", *Proceedings of the Royal Netherlands Academy of Arts and Sciences*, 10 II, 1907-1908, Amsterdam, 1908, pp. 445-450.

associated with the change of phase is known as *latent heat*. Beyond the critical point, there is no more latent heat and there is thus no longer any difference between the liquid state and the gaseous state. This is called a *supercritical fluid*.



**Figure 1: Phase diagram of a pure element**

There is also another remarkable point, the *triple point*, which is the thermodynamic state at which the three phases coexist. The triple point of water lies at a temperature of 273.16 K and a pressure of 0.006 bar.

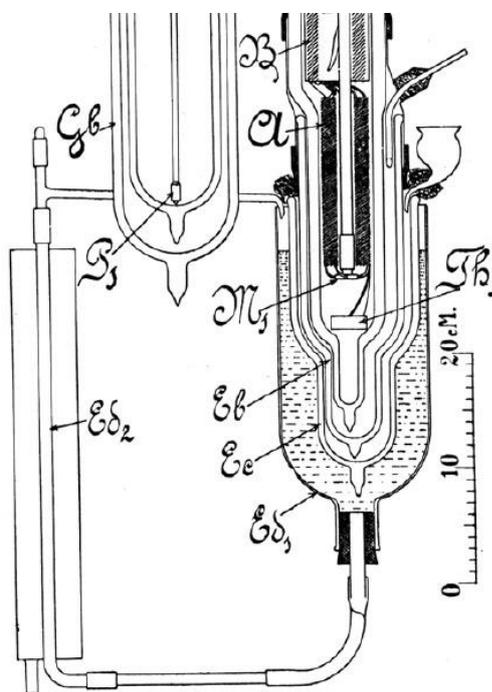
Onnes continues by stressing the importance of the relationship between theory and technology to liquefy helium:

*[...] alongside the theory of Mr van der Waals, I have also indicated the importance of the means that Mr Dewar has made available to physicists to this success.*

Among other things, he alludes to the famous eponymous flask invented by James Dewar. A Dewar flask is a cryostat (an insulating storage vessel that makes it possible to conserve cryogenic fluids at very low temperature, thereby minimising thermal losses). These losses come in three types: *conduction* losses, due to the transfer of heat in a material; *convection* losses, due to the exchange of heat via the movement of fluids; and *radiation* losses, due to the fact that any body with a temperature that is not zero emits thermal radiation (black-body radiation shift). A Dewar flask is formed by two thin flasks (made out of glass or metal), with one slotted inside the other and separated by a near-vacuum space

that reduces convection losses. There are as few contact points between the two flasks as possible in order to minimise the convection losses, while the walls are lined with silver to reduce radiation losses, because silver has very low thermal emissivity. Onnes went even further to reduce the thermal losses while still making it possible for him to observe the liquid in his experiment:

*The liquid helium collects at the bottom of the vacuum-glass of the liquefier, where its accumulation can be seen: the bottom part of the liquefier glass was unsilvered; the surrounding vacuum glasses, the first one containing liquid hydrogen, the second one liquid air, were also transparent. The glass with liquid air was protected against condensation of moisture from the air by a glass in which alcohol, kept at atmospheric temperature, circulated.*<sup>2</sup>



**Figure 2: Diagram of the terminal section of Kamerlingh Onnes' helium liquefier.**

*In the centre, four vacuum-glasses are inserted one inside another. The liquid helium collected in the centre is surrounded by liquid hydrogen, which is surrounded by liquid air, which is itself surrounded by circulating alcohol to extract the heat and prevent the liquid helium from evaporating.*

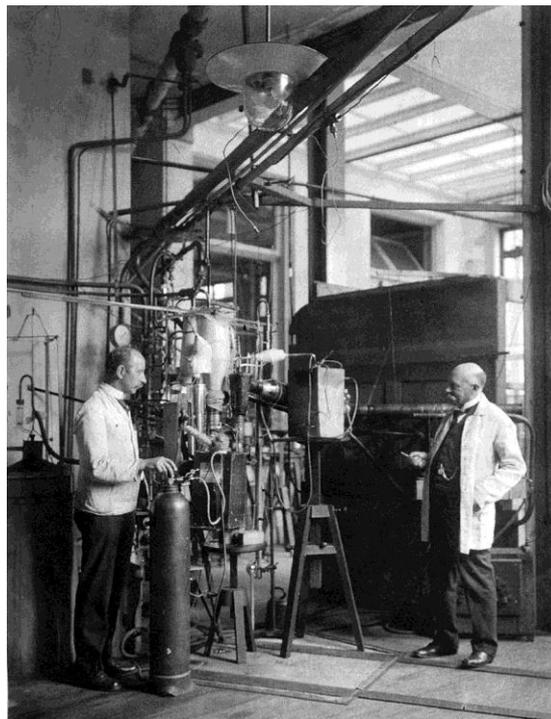
Onnes had thus established a kind of "thermal screening". This was essential to prevent the liquid helium from immediately evaporating, because for oxygen, nitrogen and hydrogen, the latent heat of vaporisation (the energy required for a given quantity of liquid to evaporate) is far greater than that of helium: 447

2. *Through Measurement to Knowledge: The Selected Papers of Heike Kamerlingh Onnes 1853–1926*, available on archive.org: [https://archive.org/stream/springer\\_10.1007-978-94-009-2079-8/10.1007-978-94-009-2079-8\\_djvu.txt](https://archive.org/stream/springer_10.1007-978-94-009-2079-8/10.1007-978-94-009-2079-8_djvu.txt)

joules are needed to evaporate 1 gram of hydrogen, whereas it takes only 21 joules to evaporate 1 gram of helium at atmospheric pressure. The Stefan-Boltzmann law states that the power radiated by a body is proportional to the fourth power of the body's temperature. The use of a series of heat shields thus drastically reduces the helium's losses through radiation: the power lost by radiation between 4 K and 80 K is 256 times greater than the power lost between 4 K and 20 K. The circulation of the water, meanwhile, evacuates heat outwards (see Figure 2).

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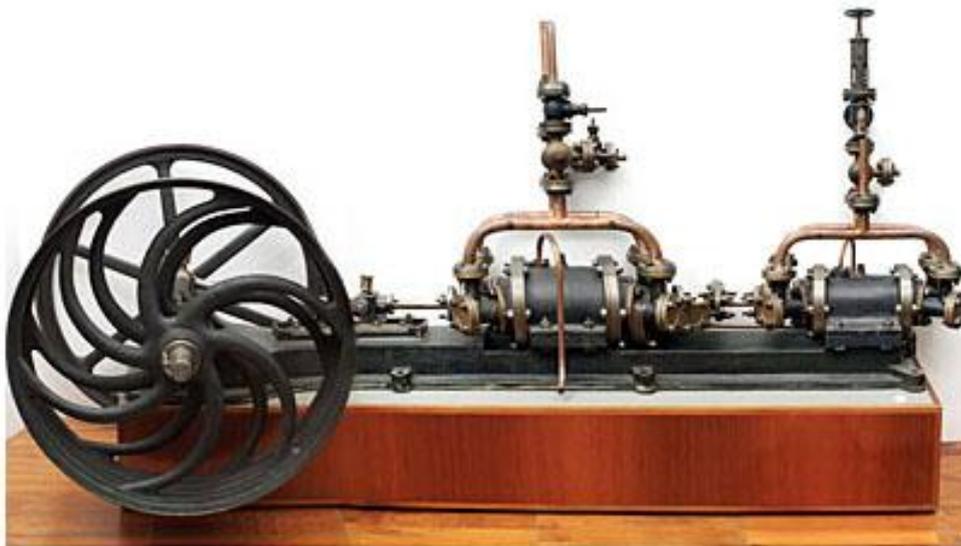
In the early 20th century, most scientific experimenters worked in small laboratories with few resources. Kamerlingh Onnes was the first to build a quasi-industrial academic laboratory dedicated to cryogenics, one that brought together physicists, chemists and mechanics to conduct its experiments. He even went as far as founding a school for glass blowers at Leiden, this being essential to the fabrication of the various glass walls used in the liquefier.



**Figure 3:** *H. K. Onnes (right) and G. J. Flim (left), head of the cryogenics laboratory, standing before the helium liquefier at the University of Leiden in 1908.*

To liquefy helium, Onnes used the Joule-Thomson (or Joule-Kelvin) principle, which consists in subjecting a gas to significant adiabatic expansion, i.e. a rapid change of pressure without any loss of heat to the environment. This

can easily be achieved by forcing the gas through a small orifice such as a valve. If this expansion is effected below a certain temperature, known as the *inversion temperature*, the temperature drops significantly, and, if the temperature before the expansion is sufficiently close to the critical point, the gas can be liquefied. To compress the helium, Onnes used a Cailletet compressor that he himself had adapted, so as to achieve pressures of around 100 bar (See Figure 4). The high-pressure helium then undergoes a series of drops in temperature: it is first cooled by the liquid air, then by the liquid hydrogen to around 15 K (the temperature at which hydrogen solidifies). It was very important to monitor the temperature of the hydrogen because, were the hydrogen to freeze, its solid form would have prevented the liquid helium from being observed. Lastly, a Joule-Thompson expansion was effected using the small valve labelled  $M_1$  in Figure 2.



**Figure 4:** *The Cailletet mercury compressor used by Kamerlingh Onnes to compress helium to 100 bar. It is exhibited at the Museum Boerhaave, near to Leiden, in the room devoted to the liquefaction of helium (photo: Museum Boerhaave, Leiden, Netherlands).*

After fourteen hours of intense efforts, the liquid helium was glimpsed for the first time. Onnes was impressed by the appearance of this new liquid:

*The experiment began on 10 July at 5.45 am ... At 4.20 am, the helium began to circulate. At 7.30 am, the liquid helium was observed for the first time.*

*Looking through the three glasses, we could see, simultaneously, the menisci of the liquid air, the liquid hydrogen and the liquid helium. The*

*difference between this latter exceptional liquid and the others was plain to see. The capillarity of helium is extremely low; the surface of the liquid helium attaches to the walls like the blade of a knife.*

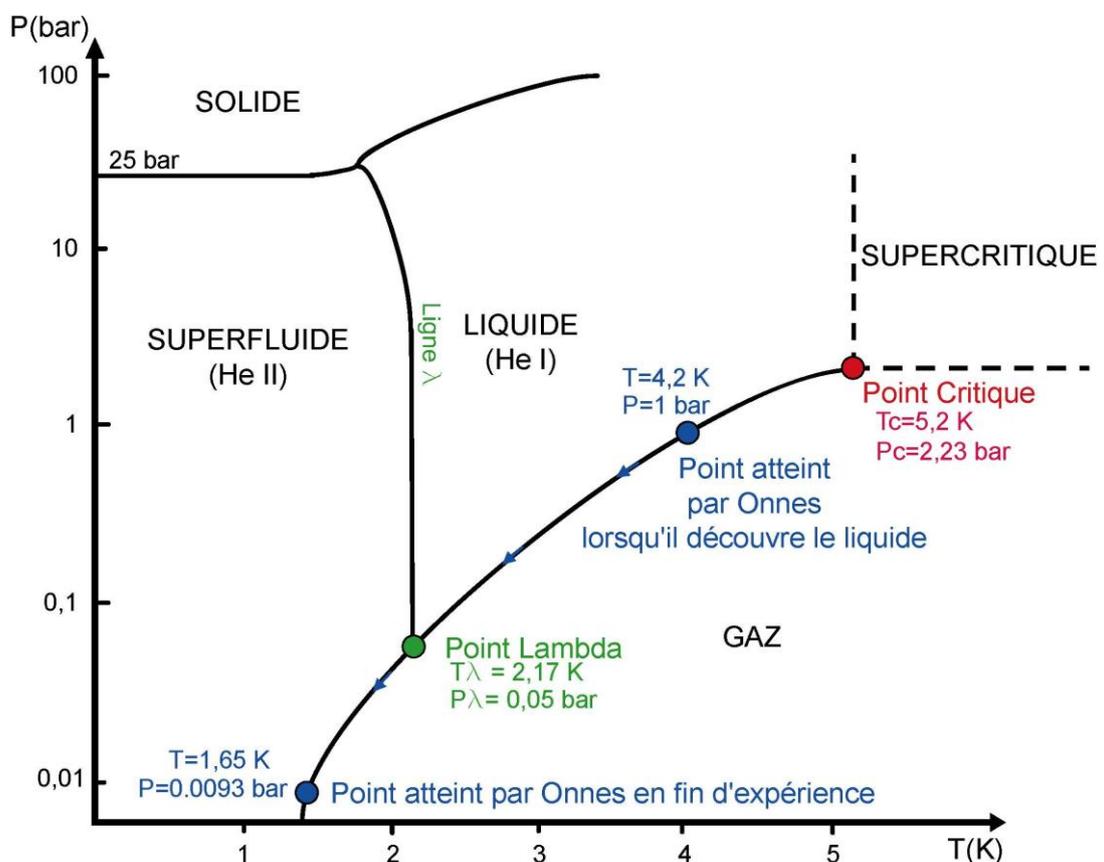
Onnes was quite right to be surprised, for liquid helium possesses unique thermodynamic and mechanical properties such that its extremely low viscosity. The measures taken were extremely precise for the time: Onnes estimated the density of the precious liquid to be  $0.154\text{g/cm}^3$  and the boiling temperature to be  $4.5\text{ K}$  (the real values are  $0.125\text{ g/cm}^3$  and  $4.2\text{ K}$  at atmospheric pressure). Once the liquid has been obtained, the liquid and the gas coexist within the same space: they are in thermodynamic equilibrium. This mix is positioned at the saturated vapour/liquid line in the phase diagram (see Figure 1). If no heat is exchanged with the environment, this equilibrium is maintained. Thus, if the pressure inside drops, the gas/liquid mixture will “follow” the saturation line, which entails a drop in temperature. If the pressure drops low enough, we reach the triple point, or the point at which the three phases (liquid, gas and solid) coexist. Onnes is surprised not to have reached the triple point for helium, but he assumes it is simply lower than previously thought:

*The helium did not solidify when the vapour pressure fell. The connection with the large vacuum pump was not adequate on this occasion, but there is no doubt that I went to 1 cm, perhaps even 7 mm. At this temperature, the liquid was still extremely mobile. If it behaved like pentane, it would become solid only at  $1^\circ\text{K}$ .*

Onnes states that by using a vacuum pump the experiment had obtained a pressure of 10 mm, or even 7 mm (millimetre of mercury). This corresponds to pressures of 13.3 mbar and 9.3 mbar, i.e. equivalent temperatures for a vapour-liquid equilibrium of  $1.74\text{ K}$  and  $1.65\text{ K}$ . Quite reasonably, he thought that it would be possible to reach the triple point of helium by reducing the temperature further. However, he did not know that helium does not have a triple point, due to a fourth phase known as *superfluidity*, which was discovered in 1937 (solid helium does indeed exist, but at pressures in the order of 25 bar for temperatures lower than  $3.5\text{ K}$  (see Figure 5). In fact, Onnes must have unknowingly obtained superfluid helium from 50 mbar (i.e.  $2.17\text{ K}$ ) onwards, but this phase change – which was difficult to detect in experiments at this time – understandably escaped his notice. Nevertheless, in measurements taken in the following years, he noticed a peak in the density of the liquid at around  $2.2\text{ K}$  and

an anomaly in the specific heat around this point. Yet he did not publish these observations, assuming they were due to experimental errors, which was not in fact the case! The liquid was in effect very mobile since superfluid helium has zero viscosity. Onnes' optimism and vision for the future are plain to see in the final paragraph:

*Naturally, it will be more difficult to conduct research with liquid helium than with liquid hydrogen. But the extent of the difficulty should not be gauged from that pertaining to the first liquefaction. Once the conditions for obtaining liquid helium are well known, the greatest difficulty will be removed, and one will be able to concentrate one's efforts on the utilisation of the new liquefied gas.*



**Figure 5: Helium phase diagram.** Helium is distinctive in that it has two liquid phases: a normal liquid phase (He I) and a superfluid liquid phase (He II). Helium therefore does not have a triple point, but rather what is known as a "lambda" point where the gaseous, liquid and superfluid phases intersect.

Kamerlingh Onnes was different from other cryogenics experimenters of his day in that, for him, the liquefaction of helium was not an end in itself. Liquid helium was a means to further reduce the temperature of samples in order to attain better knowledge of physical phenomena (thermodynamics, mechanical

and electrical phenomena, etc.) at low temperature. The physicists of the day were already encountering the need to use cryogenics in their experiments, a need of which Onnes was perfectly aware. Indeed, he cites the work of Jean Becquerel, the son of Henri Becquerel, with whom Kamerlingh Onnes had worked at Leiden, on the subject of what Jean Becquerel called "positive electrons"<sup>3</sup>: Becquerel needed to conduct his experiments at very low temperatures, and in this respect Onnes' laboratory was the most advanced of the day. Later on, experimental quantum physics would be very dependent on liquid helium cryogenics to study particles and atoms at ultra low temperatures.

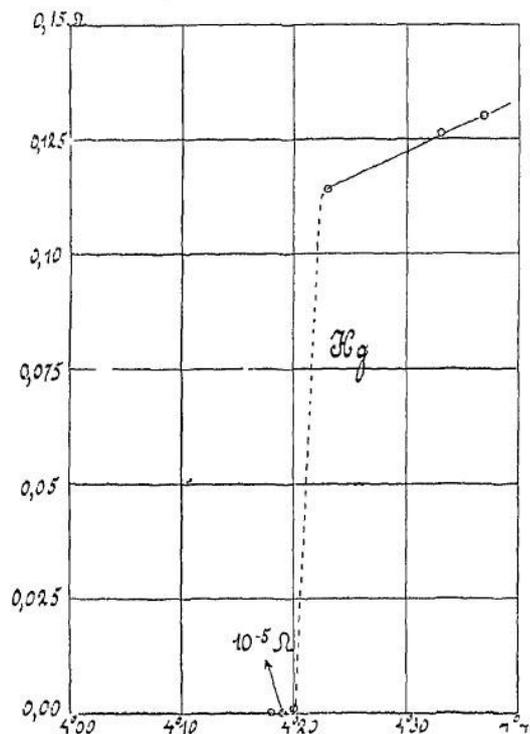
In the space of a few years, Onnes would master the liquefaction of helium, focusing all his research on electrical resistivity at low temperatures. Starting with platinum and then gold, he strove to prove his theory: the harder the metal, the more its resistivity falls as the temperature drops. He then decided to use mercury, which is liquid at room temperature and therefore easy to purify. Thus in 1911, during experimental tests on the resistivity of mercury in liquid helium, Kamerlingh Onnes' student Gilles Holst observed for the first time what Onnes would, two years later, in a paper delivered to the Netherlands Academy of Sciences, call *superconductivity*.<sup>4</sup> Yet this observation did not correspond to the fundamental theory formulated by Onnes, since the resistivity dropped abruptly to zero, falling below the detection threshold of the equipment (see Figure 6). This phenomenon was later reproduced with other metals, yet Onnes was never able to explain the new phenomenon. It was not until 1956 and the advent of BCS theory<sup>5</sup>, which is based on the formation of pairs of electrons in superconductors, that the first quantum explanations of superconductivity were developed.

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3. Jean Becquerel, "Sur les électrons positifs", *Radium* (Paris) 5, 1908, pp. 193–200 ([online](#), in French).

4. Kamerlingh Onnes, H., "Further experiments with liquid helium. H. On the electrical resistance of pure metals etc. VII. The potential difference necessary for the electric current through mercury below 4°19K", *Proceedings of the Royal Netherlands Academy of Arts and Sciences*, 15 II, 1912–1913, Amsterdam, 1913, pp. 1406–1430.

5. BCS stands for the names of the physicists who formulated this theory: John Bardeen, Leon Cooper and John Robert Schrieffer. John Bardeen (1908–1991) received the Nobel Prize for Physics on two occasions: in 1956 for his transistor, and in 1972 for his work on superconductivity. Leon Cooper (born in 1930) and John Schrieffer (born in 1931) were awarded the Nobel Prize with Bardeen in 1972 for their work on superconductivity.



**Figure 6:** Plan of the resistivity of mercury as a function of temperature, produced in 1911 at the laboratory in Leiden.<sup>6</sup> It shows that resistivity completely disappears at 4.2 K. This observation was made possible by the liquefaction of helium three years earlier in the same laboratory.

## Superconductivity and superfluidity

*Superconductivity* is the phenomenon in which electricity flows without any resistance to the current (zero resistance). *Superfluidity* is the phenomenon of a fluid flowing without any mechanical resistance (zero viscosity). These two phenomena, both directly issuing from the liquefaction of helium by Onnes in 1908, were explained only fifty years later by quantum physics. They are the only two macroscopic quantum phenomena that can be observed directly.

Superconductivity now has various scientific and industrial uses in various fields such as particle physics or medical imaging, which use superconducting magnets generally cooled with liquid helium.

A superconducting magnet is an electromagnet – a conducting coil through which an electrical current passes, thereby generating a magnetic field – which uses a superconducting material cooled to

6. Kamerlingh Onnes, H., "Further experiments with liquid helium. G. On the electrical resistance of pure metals etc. VI. On the Sudden Change in the Rate at which the Resistance of Mercury Disappears", *Proceedings of the Royal Netherlands Academy of Arts and Sciences*, 14 II, 1911–1912, Amsterdam, 1912, pp. 818–821.

below its critical temperature (the temperature below which the material is superconducting). This type of magnet takes up little space and generates powerful magnetic fields, making it possible, for example, to curve clusters of charged particles so that they maintain a circular trajectory enabling them to pass into accelerating rectilinear cavities several times.

Exactly one hundred years after the liquefaction of helium by Onnes, the European Organization for Nuclear Research (CERN) in Geneva started up its new particle accelerator, the LHC (Large Hadron Collider), which is the largest superconducting and cryogenic installation in the world. The LHC is made up of 27 kilometres of superconducting niobium-titanium magnets, which generate magnetic fields of 8 teslas. This required the development of huge cryogenic helium installations. All the magnets are immersed in static pressurised superfluid helium at 1.9 K and heat is extracted through the circulation of superfluid helium saturated at 1.8 K. In total, 60 tonnes of liquid helium (normal and superfluid) are used to cool down the 36 800-tonne machine.



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