

# Chapter 1

## Introduction

**Abstract** The study of matter at very low temperature is fascinating because the phonon activity dies down at very low temperatures and one can look into the electronic behaviour minutely. Cryogenic baths of liquefied gases provide excellent medium to cool down samples. Liquefaction of a gas is a combination of an isothermal compression followed by an adiabatic expansion. Cascade process were adopted in liquefying oxygen by Cailletet and Pictet independently in 1877. The final cooling stage has always been a Joule-Thomson (J-T) valve. Another important breakthrough came in 1898 when James Dewar succeeded in liquefying hydrogen making a temperature range of 20–14 K accessible. The moment of triumph came in July, 1908 when years of hard work by Kamerlingh Onnes at Leiden ultimately resulted in the liquefaction of helium. A temperature range of 4.2–0.8 K thus became accessible in the laboratory. A cascade process using  $\text{La}_2$ ,  $\text{LO}_2$ ,  $\text{LN}_2$  and  $\text{LH}_2$  and the J-T expansion valve was employed. Within 3 years of this discovery came the defining moment of the discovery of superconductivity in April, 1911 in pure Hg at just below 4.2 K.

### 1.1 Why Low Temperature Is So Exciting?

Temperature is one of the most important variable parameter like pressure and magnetic field which can be manipulated to change the phase of the material and thus its mechanical, thermodynamical, chemical, electronic and phonon properties. To carry out studies at low temperatures is particularly interesting. At ambient temperatures lattice vibrations (which are quantized and are called phonons) in any material are dominant and usually mask its fine properties. As the temperature is lowered the amplitude of these vibrations is reduced and at very low temperature (close to absolute zero) die down completely. In other words the dominant phonon contribution almost disappears and one can observe the quantum behaviour of matter. Normal laws valid at ordinary temperatures may not hold any more. Some of the properties in fact violates all our norms about the matter as to how it ought to behave. Superconductivity and Superfluidity are perhaps the most striking

phenomena observed at low temperature which display the quantum behaviour at a macroscopic scale. An electric current can flow persistently in a superconductor (without dissipation) without a voltage and similarly a superfluid can flow effortlessly (no viscosity) through fine pores, impervious to normal liquid, without a pressure head.

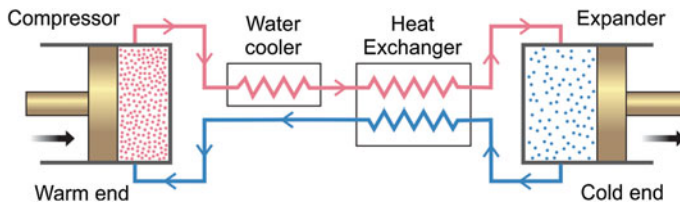
## 1.2 How to Conduct Experiment at Low Temperatures?

The best way to carry out studies at low temperature is to have a suitable cryogenic bath which can cover the temperature range of interest. A cryogenic bath is best provided by a liquefied gas. One can pump over the liquid surface to reduce vapour pressure and obtain still lower temperature until it freezes. Thus for example, nitrogen ( $N_2$ ) gas boils at 77 K (Kelvin) and can be pumped down to 65 K, hydrogen ( $H_2$ ) boils at 20 K and be pumped down to 14 K. Helium (He) is the only stable gas which boils at the lowest temperature, that is, 4.2 K. One can pump liquid helium and can achieve a temperature of 0.8 K. There is a rare isotope of helium with a mass number of 3 called  $^3\text{He}$ . It boils at a temperature of 3.2 K and can be pumped down to 0.3 K. Most interesting thing about these two liquids is that they refuse to freeze even at zero absolute. Both can be solidified only at very high pressure. For their unique and very peculiar properties they are referred to as Quantum Liquids.

To go to temperature lower than 0.3 K, one can use what we call as  $^3\text{He}/^4\text{He}$  dilution refrigerator (DR) and is based upon the finite solubility of  $^3\text{He}$  (6.4 %) into  $^4\text{He}$  down to absolute zero.  $^4\text{He}$  at 1 K is used as a pre-cooling agent. We can use a DR to produce a temperature of a few milli Kelvin (mK). To go to still lower temperatures this DR is used as a pre-cooling stage to an adiabatic nuclear demagnetization system and temperature of a few micro Kelvin ( $\mu\text{K}$ ) is achieved. By using a cascade of demagnetization stages one can go down to nano Kelvin (nK) and pico Kelvin (pK). A world record of ultra low temperature  $\sim 100$  pK is held by the Low Temperature Laboratory of the Helsinki University of Technology, Finland. Whenever the scientific community entered a new regime of low temperature, some discovery or the other of very fundamental importance took place.

## 1.3 Gas Liquefaction

Broadly speaking, a gas liquefaction is a combination of two thermodynamic processes, an isothermal compression followed by an adiabatic expansion. In the first step a gas is compressed at high pressure at constant temperature. This is achieved by removing the heat of compression by a suitable cooling mechanism. In the second stage the compressed gas is allowed to expand under adiabatic conditions wherein heat is neither allowed to enter nor escape from the system.



**Fig. 1.1** Principle of gas liquefaction

The temperature therefore drops. The process goes on till the gas liquefies. This is schematically shown in Fig. 1.1. The expansion could be of either isenthalpic or isentropic type.

### 1.3.1 Isenthalpic Process

In isenthalpic expansion one uses an expansion valve or a Joule-Thomson valve through which the high pressure gas throttles and gets cooled. There is no change in the enthalpy (zero heat transfer and zero work transfer) in this expansion process. This process is sometimes also referred to as the internal-work method as it does not remove the energy from the gas. It only moves the molecules apart against the inter-atomic forces. This process is irreversible and therefore not an efficient thermodynamical cycle. Further, the isenthalpic expansion does not always lower the temperature. If the temperature of the gas is above the maximum inversion temperature, it will heat up the gas. The temperature of the compressed gas before expansion should therefore be below its inversion temperature. It is for this reason that gases like helium (45 K), hydrogen (205 K) and neon (250 K) cannot be liquefied using a J-T valve expansion, their inversion temperatures being below the ambient temperature ( $\sim 300$  K). These gases have to be pre-cooled to below their inversion temperature before they suffer J-T expansion. A J-T valve is however integral to any liquefier and always forms the last stage of cooling since the liquid formation in the expander cannot be sustained. Table 1.1 lists the maximum inversion temperatures (at  $P = 0$ ) of a few permanent gases. The gases therefore have to be pre-cooled to below their respective inversion temperature before entering the J-T valve.

### 1.3.2 Isentropic Process

In the isentropic process the energy is extracted as external work and always produces cold in contrast to the isenthalpic process. This is also referred to as the external work method. Gas expands in an expander which can be of reciprocating engine type or can be a turbine. The process is reversible and thus

**Table 1.1** Maximum inversion temperature of some gases

S. no.	Gas	Max. inversion temperature (K)
1	<sup>4</sup> Helium	45
2	Hydrogen	205
3	Neon	250
4	Air	603
5	Nitrogen	621
6	Oxygen	761
7	Argon	794
8	Carbon dioxide	1,500

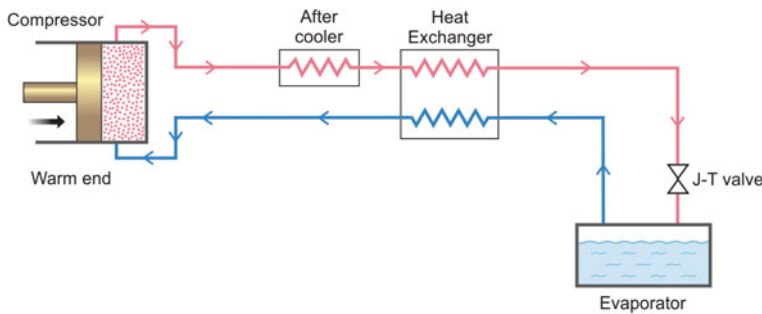
thermodynamically more efficient. With the same initial temperature of the gas this process always leads to lower temperature than obtainable with the isenthalpic process. As stated above, the operational problem associated with the expansion of the two phase mixture (liquid and gas) in an expander makes it mandatory to use a J-T expander as the last stage of the cooling cycle.

### 1.3.3 The Linde-Hampson Process

Oxygen was first time liquefied by Louis Cailletet of France and Raoul Pictet of Switzerland independently within days of each other in the year 1877. Pictet used a cascade process wherein a precooling stage is cooled by another precooling stage. He used liquid SO<sub>2</sub> and then dry ice (−80 °C, solid CO<sub>2</sub>) for precooling. Cailletet used liquid SO<sub>2</sub> for precooling oxygen before it throttles through a J-T valve. A good historical account of the liquefaction processes can be found in “Cryogenic Engineering” [1]. Carl von Linde [2] and Hampson [3] perfected the oxygen liquefaction technology by using more reliable ammonia cycle for precooling compressed oxygen and the counter current heat exchangers before the gas expands through a J-T valve. Linde founded Linde Eismaschinen AG in 1879 and later obtained a German Patent in 1895. Basic principle in this process is that air/oxygen is alternatively compressed, pre-cooled and expanded in a J-T valve. This results each time in reducing the temperature till the gas gets liquefied. The pressure used in Linde process is rather high. For example, for air at 300 K the optimized pressure is about 40 MPa (~5,880 psi) but the actual machines use a pressure of about 20 MPa. A typical Linde-Hampson cycle is shown in Fig. 1.2.

### 1.3.4 The Claude Process

Claude Process [4] is an isentropic process which is adiabatic and thermodynamically reversible and therefore more efficient than the isenthalpic process to produce cold.

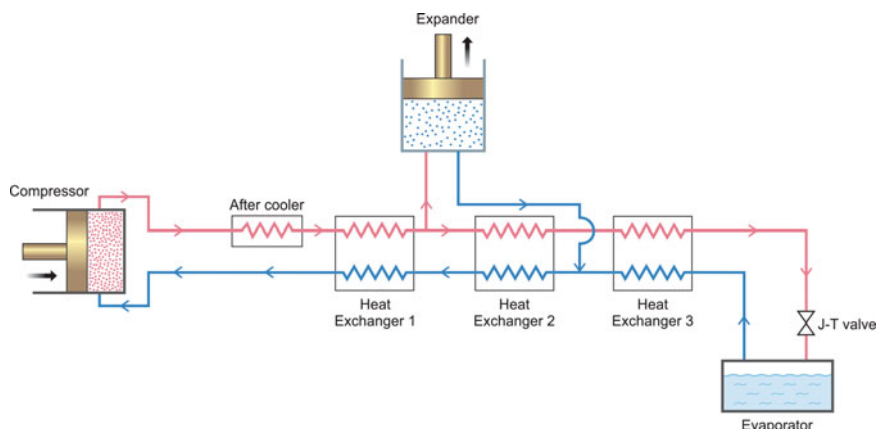


**Fig. 1.2** Linde-Hampson liquefaction cycle consisting of a compressor, a counter current heat exchanger and a J-T valve at the final stage

Another added advantage is the lower operating pressure needed for this cycle  $\sim 1.7$  MPa ( $\sim 250$  psi). In this process the gas does an external work in an expansion engine. The engine can either be of reciprocating piston type or of a rotating type. As shown in Fig. 1.3 the gas is compressed to the required pressure and passes through the first heat exchanger. A portion of the gas (60–80 %) is then sent to an expander and the rest continues to move along the main stream path. The expanded low pressure cold gas is fed back to the returning gas just after the second heat exchange. The return gas cools down the high pressure incoming gas via the two heat exchangers. Thus the cold high pressure gas proceeds via the third heat exchanger and expands in a J-T expander and gets liquefied. The cold vapours from the liquid reservoir return to the compressor via the heat exchangers giving out cold to the incoming high pressure gas. A J-T expansion valve is still necessary because liquid formation in the cylinder of the expansion engine is not desirable. The stresses caused by the low compressibility of the liquid can damage the cylinder. Rotary turbine expander can, however, tolerate almost 15 wt% liquid without causing damage to the turbine.

Two great inventions which took place in the history of gas liquefaction need to be mentioned here. First in 1892 when James Dewar developed a double walled vacuum-insulated cryogenic-fluid storage vessel (popularly known as Dewar Flask). This made it possible to store, transport or pour cryogenic-fluid from one vessel to another. Experiments with cryogenic-fluids for long duration became possible. Second invention [5, 6] by Dewar was the first time liquefaction of hydrogen in 1898, lowering the temperature range for studies to 20 K and to 14 K under reduced pressure. Dewar used the Linde cycle (that is, high pressure and J-T expansion) with liquid nitrogen as the pre-cooling stage.

A masterpiece treatise on the liquefaction cycles has been written by Randall F. Barron [7]. Readers are advised to consult this book for greater details on gas liquefaction and most of the cryogenics topics.



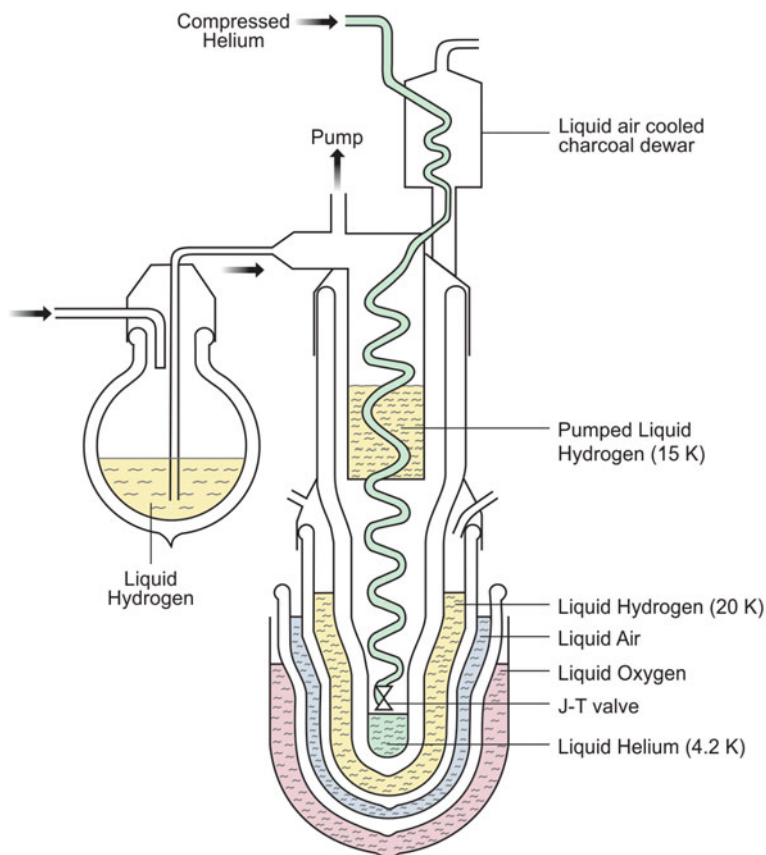
**Fig. 1.3** The Claude cycle consisting of a compressor, a series of heat exchangers, an expansion engine and a J-T valve in the final stage

### 1.3.5 Liquefaction of Helium (1908)

Heike Kamerlingh Onnes at Leiden Institute, The Netherlands had great fascination for the study of Van der Waals equation of corresponding states down to lowest ever temperatures. Nernst heat theorem and Planck's zero point energy theory further added to his curiosity to achieve lowest possible temperature. His passion to liquefy helium became all the more stronger. He made use of the Linde technique, that is, pre-cooling compressed helium to the freezing point of hydrogen (14 K) and subjecting it to J-T expansion. He succeeded in liquefying helium on July 10, 1908. This turned out to be a turning point for the entire condensed matter physics community. This opened the flood gate for getting to lower and lower temperatures. Discoveries one after another followed in quick succession. The first one was, of course the discovery of superconductivity in 1911 by Kamerlingh Onnes himself. Kamerlingh Onnes got Noble Prize in 1913 for this work. The Noble Prize citation dated Dec. 10, 1913 states "*For his investigations on the properties of matter at low temperature which led inter alia, to the production of liquid helium*". Figure 1.4 shows the schematic diagram of the apparatus used by him for helium liquefaction [8].

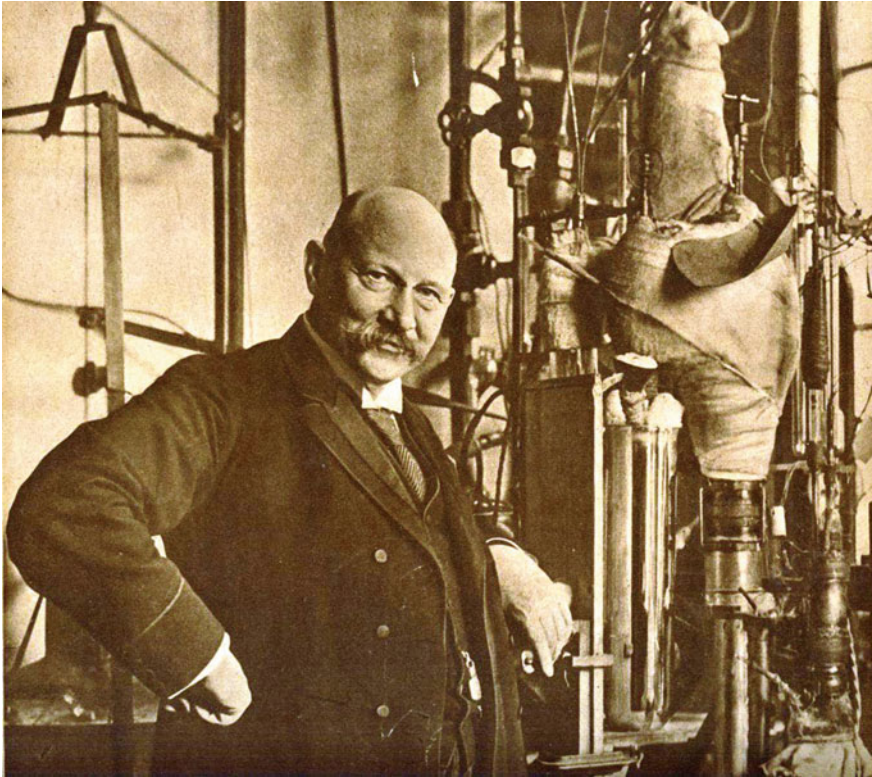
As seen in Fig. 1.4, compressed helium gas flows through the liquid air cooled charcoal dewar to get rid of moisture, gets cooled through a spiral immersed in pumped hydrogen (15 K) and expands in the inner most dewar through a J-T expansion valve and gets liquefied. Kamerlingh Onnes with his original liquefier is seen in Fig. 1.5. The boiling temperature of helium is 4.2 K at atmospheric pressure. For the next 20 years the Leiden Laboratory remained a most sought after place for research by the condensed matter physics community from Europe and USA and Kamerlingh Onnes enjoyed complete monopoly.

John Cunningham McInnan built the second helium liquefier at the Toronto University in 1923. The design of this machine was borrowed from Kamerlingh



**Fig. 1.4** A schematic diagram of the apparatus used by Kamerlingh Onnes for the liquefaction of helium first time (Courtesy Peter Kes, Kamerlingh Onnes Laboratorium, Leiden University)

Onnes but looked little more elegant. In reality low temperature research started flourishing around 1934–35. Four German scientists, namely, Franz Simon, Heinrich Kuhn, Nicolas Kurti and Kurt Mendelssohn joined Clarendon Laboratory at Oxford University at the invitation of Lindemann. Low temperature research started at Oxford when Simon built a mini He-liquefier. Around the same time Pjotr Kapitza too built a He-liquefier [9] at the Cambridge University. This machine was based upon a rotating expansion engine or the so called ‘turbine’. He made a similar liquefier at the Institute for Physical Problems, Moscow during 1935. The commercial machine [10] built by Samuel Collins (MIT) and marketed by M/S Arthur D Little of the USA was the beginning of the spread of low temperature studies using liquid helium the world over. Many countries around the globe bought this machine and the low temperature research now flourished all around. My earlier place National Physical Laboratory, Delhi too acquired Collin’s helium liquefier in 1952 and started low temperature under the leadership of David Shoenberg.

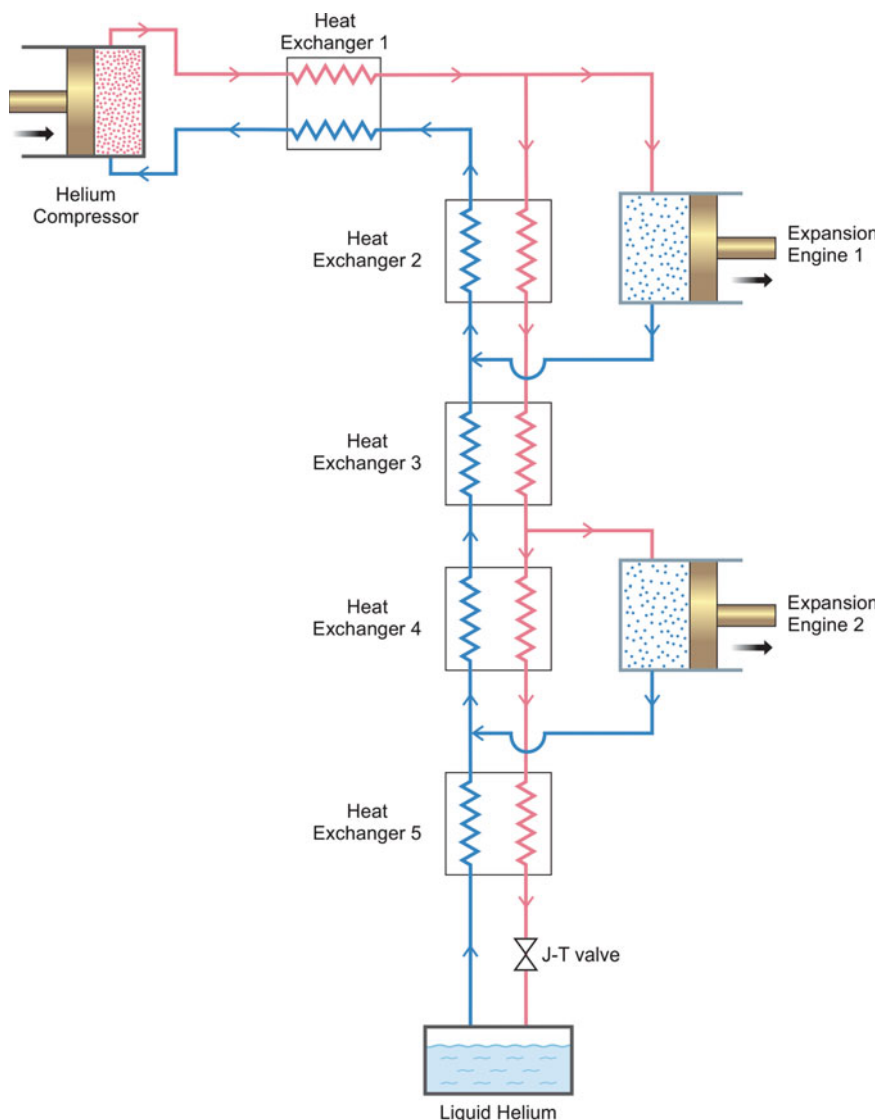


**Fig. 1.5** Kamerlingh Onnes in his Low Temperature Laboratory (Courtesy Peter Kes, Kamerlingh Onnes Laboratorium, Leiden University)

### ***1.3.6 Collins Liquefaction Cycle***

The liquefaction cycle used by Collins and shown in Fig. 1.6 is an extension of the Claude cycle (Fig. 1.3). The machine uses three stages of cooling for helium liquefaction, two expansion engines of the reciprocating piston type followed by the J-T expansion valve. Pure helium gas is compressed to about 225 psi pressure, precooled to 77 K and passes through the first heat exchanger. Thereafter, part of this cold gas expands in the first expander cooling the gas further to about 60 K. This low pressure gas goes back to the compressor via the second and first heat exchangers cooling in-turn the incoming high pressure gas. Rest of the gas continue to proceed through yet another (third) heat exchanger and again a fraction of the gas expands in the second expander bringing down the temperature of the gas to about 20 K. This temperature is well below the inversion temperature of helium gas. Low pressure gas again returns to the compressor via the series of the heat exchangers transferring its cold to the incoming high pressure gas. The cold gas now at 6 K



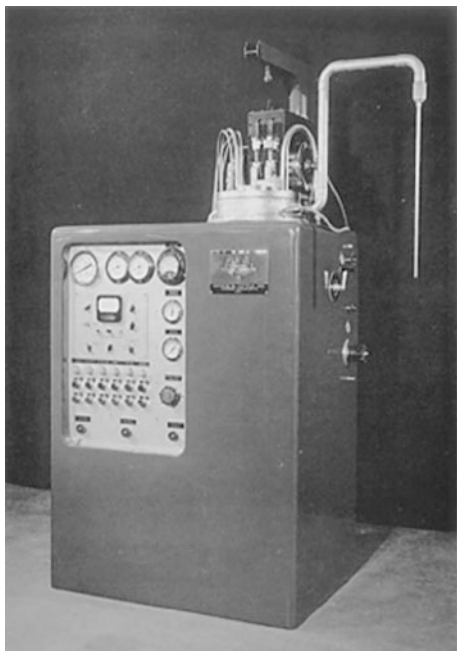


**Fig. 1.6** The flow diagram of the Collins helium liquefaction cycle

finally throttles through the J-T valve, liquefies and gets collected in the vessel. The liquid helium can be siphoned out of the container for use. The evaporated gas from this container continues to travel to the compressor via the heat exchangers for a continuous operation.

Precooling helium gas with liquid nitrogen though not essential, nevertheless increases the yield of liquid helium, by almost a factor of two. Figure 1.7 is the photograph of this first generation Collins liquefier of the ADL make. This machine

**Fig. 1.7** First generation commercial Collin's helium liquefier ADL make with 4 l/h LHe capacity



used to produce 4 l/h liquid with a single compressor. In recent years reciprocating engines have been replaced by the turbo-expanders which rotate at speeds varying between 250,000 and 300,000 rpm. These machines can produce several hundred litres of liquid helium per hour. Figure 1.8 is a photograph of a modern turbo-cooled helium liquefier custom manufactured and installed by Linde Kryotechnik AG with a refrigeration capacity of 900 W ( $\sim 300$  l/h) at our Centre, IUAC in 2012.

## 1.4 Discovery of Superconductivity—A Fall Out of Helium Liquefaction

The liquefaction of helium gas in 1908, and just discussed above, was the culmination of a well designed programme of Kamerlingh Onnes of studying properties of materials at lower and lower temperatures achieved by the successive liquefaction of permanent gases, viz; oxygen, air, hydrogen and finally helium. Till this time, there were only conjectures that the electrical resistance of metals will drop to zero as the temperature approached absolute zero or will show a minimum and rise again and so on. Kamerlingh carried out electrical resistivity measurements on pure platinum and gold and found that the resistivity attains a temperature independent constant value below about 10 K. Purer the material smaller is the value of this residual resistivity. He then took up pure mercury for his studies as it was possible to obtain mercury in ultra-pure form through multiple distillations. What he found



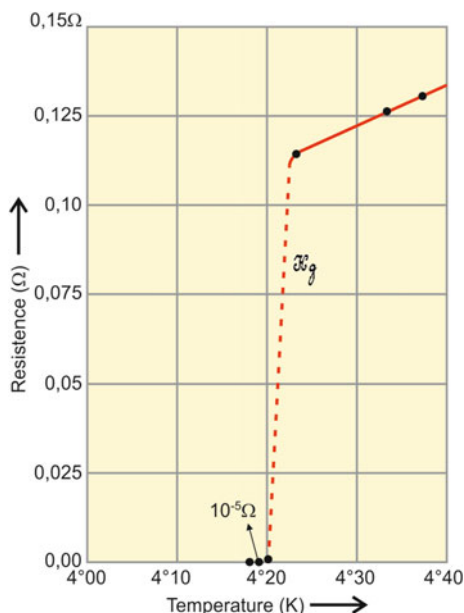
**Fig. 1.8** A modern day turbine based helium liquefier with a refrigeration capacity of 900 W ( $\sim 300$  l/h) manufactured by Linde Kryotechnik AG installed at IUAC in 2012 (Photo courtesy IUAC Delhi)

was quite startling and unexpected. The resistance in mercury just close to 4.2 K ‘abruptly’ dropped to zero (one thousand-millionth part of the normal temperature value) with no potential difference. He thus proclaimed that mercury just below 4.2 K has entered a new state which he named ‘suprageleider’ and when translated from Dutch to English became ‘superconductivity’ and finally changed to superconductivity [11]. His original resistance versus temperature plot for mercury is shown in Fig. 1.9. Lead and Tin were next metals from the periodic table to have shown superconductive transition at 7.2 and 3.7 K respectively.

Kamerlingh Onnes also realized soon that this zero potential difference lasts only up to a threshold current in the sample beyond which it rises sharply. Lead, for example, stood superconducting up to a threshold current density of  $4.2 \text{ A/mm}^2$  only.

He also observed that superconductivity stays in lead up to a threshold magnetic field of 600 Gauss without a sign of magneto-resistance. Beyond this field, the resistance appears and rises fast with magnetic field. Notwithstanding these limitations, Kamerlingh Onnes did realize that superconducting coils can be used to produce fields in excess of 10,000 Gauss without Joule heating. His dream did come true and it is all for us to see the great revolution these materials have brought about. How this phenomenon unfolded, understood, different classes of superconductors

**Fig. 1.9** First observation of superconductivity in pure Mercury by Kamerlingh Onnes (Courtesy Peter Kes, Kamerlingh Onnes Laboratorium, Leiden University)



discovered and put to use in producing high magnetic fields, in accelerators, in fusion reactors and such other applications (NMR, MRI, SMES, levitation etc.) is discussed in the following chapters.

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