Mankind has been interested in quantifying the difference between hot and cold since very old times. The original apparatus, called thermoscopes, served merely to show the changes in the temperature of its surroundings. Eventually the need arose for quantifying these observations and the different thermometers began to be developed. Astronomers built most of these instruments, particularly for measuring low temperatures. Development of thermometric scales such as those of Réaumur, Fahrenheit and Celsius, led in a natural way to the question whether there was a lower limit to temperature, and correspondingly, to the behaviour of materials under those circumstances.

While studying the proper way to calibrate an air thermometer Guillaume Amontons (1663-1705) noticed that when the temperature was changed between the boiling point of water and ambient temperature, equal drops in temperature resulted in equal decreases in the pressure of the air. From these results he concluded that on further cooling the air pressure would become zero at a finite temperature, which he estimated at -240°C. Since the pressure of the gas could not become negative, it followed that there must exist a lowest temperature beyond which air, or any other substance could not be cooled. Amontons also considered that air might be a body of high volatility, capable of liquefaction or even solidification by sufficiently strong cooling.

In 1815 Joseph-Louis Gay-Lussac (1778-1850) made a large number of observations of the cooling effect produced by the evaporation of liquids and remarked that under certain conditions the heat of vapourization would be equal to the heat transferred through the walls of the vessel. However, if the liquid evaporated into a vacuum surrounded by a freezing mixture the cooling effect could be increased indefinitely as long as the liquid exerted an appreciable vapour pressure. John Leslie (1766-1832) not only had been able to freeze water by absorbing its vapour at the same rate it was produced; he had also been able to reach a temperature almost as low as the melting point of mercury (234 K) by evaporation of ether. Gay-Lussac reported that he had succeeded in freezing mercury by evaporating water in a vessel surrounded by a freezing mixture. Gay-Lussac had no doubt that with a volatile liquid it would be possible to obtain even lower temperatures.

According to Gay-Lussac, if the liquid evaporated in a perfectly dry gas instead of a vacuum the cooling would not be so great because the gas pressing the liquid would retard the evaporation process. The cold achievable had a maximum value corresponding to the equilibrium between the caloric (heat) absorbed by the vapour and the caloric lost by the air. Gay-Lussac then proceeded to develop the following formula describing the degree of cold (degree de froid) produced by evaporation:

$$P^0 \delta H = [P - P^0(T)](t_{g} - t)c$$  \hspace{1cm} (1)

where, $\delta$, $\Delta H$, and $c$ are the density, heat of vapourization, and heat capacity of the vapour at the temperature $t$ in question, and $P^0$ and $P$ the vapour pressure and the pressure, both in atmospheres.

In the case of water the above equation became

$$P^0(T) = 0.76(10^{0.015457x-0.00006585x^2})$$  \hspace{1cm} (2)
Gay-Lussac also prepared a table comparing the experimental results obtained by wetting the bulb of the thermometer with a cloth (wet bulb temperature) with those predicted by Eq. 2 for the case of air at atmospheric pressure.

In a later publication Gay-Lussac analyzed the production of cold by the expansion of a gas. He realized that cooling by evaporation was limited and pointed out that the minimum temperature achieved was only \(-80^\circ\text{C}\). He believed that it was possible to achieve lower temperatures by using the equivalence between cooling caused by the expansion of a gas and heating caused by compression. It was known that compressing the air to one-fifth of its original volume increased the temperature to 300°C and Gay-Lussac thought that the temperature might be increased to 1000°C or even 2000°C, if the process was rapid. If air was first compressed to five atmospheres, then allowed to cool to atmospheric temperature, and finally allowed to expand, it should absorb as much heat as was given out in its compression and its temperature should be lowered by 300°C. From these results he believed that “en prenant une masse d’air comprimée par cinquante, cent, etc., atmosphères, le froid produit par sa dilatation instantanée n’aura point de limite” (if we take a mass of compressed air to 50, 100, etc., atmospheres, the cold produced by its instantaneous expansion will have no limit). In other words, it would be possible to achieve unlimited cold by the expansion of gases.

Gay-Lussac concluded his paper stating: “S’il est incontestable que, par la dilatation des gaz, on peut produire un froid illimité, la détermination du zéro absolu de chaleur doit paraître une question tout-à-fait chimérique” (If it is undisputable that expansion of a gas can produce an unlimited amount of cold, then the determination of the absolute zero of heat must seem a complete fantasy).

Later on, Charles-Bernard Desormes (1777-1862) and Nicolás Clément (1779-1842) argued that there was an absolute zero and that Gay-Lussac had shown what this temperature was. According to Gay-Lussac the coefficient of expansion of gases was \(1/266.66\) per degree Celsius, hence, Clément and Desormes argued that there was a limit of contraction at \(-266.66^\circ\text{C}\), which was the absolute zero.\(^5\)

**Early works on the liquefaction of gases**

The possible effect of the low temperatures yet to be achieved, were described in a prophetic way by Antoine Laurent de Lavoisier (1743-1794) in his book *Elements of Chemistry*, published in 1789. Lavoisier wrote: “If the earth were suddenly transported into a very cold region, the water which at present composes our seas, rivers, and springs, and probably the greater number of fluids we are acquainted with, would be converted into solid mountains and hard rocks at first diaphanous and homogeneous, like rock crystal, but which, in time, becoming mixed with foreign and heterogeneous substances would become opaque stones of various colours. In this case, the air, or at least part of the aerviform fluids which now compose the mass of our atmosphere, would doubtless lose its elasticity for want of a temperature to retain it in that state: it would return to the liquid state of existence, and new liquids would be formed, of whose properties we cannot, at present, form the most distant idea. Solidity, liquidity, and aerviform elasticity are only three different states of existence of the same matter, or three particular modifications which almost all substances are susceptible of assuming successively, and which solely depend upon the degree of temperature to which they are exposed, or, in other words, upon the amount of caloric with which they are penetrated”.

Starting in the late 1700’s many scientists looked for ways of reaching lower and lower temperatures and liquefying gases. In 1799 Martinus Van Marum (1750-1837) and van Trovstwyk performed experiments trying to determine if the Boyle-Mariotte’s law was applicable only to air or for all gases.\(^6\) For this purpose he chose ammonia and proceeded to compress it in a system piston-cylinder. When the pressure reached about seven atmospheres he noted that although the volume of the gas continued to decrease, the pressure did not change. Van Marum understood that he had liquefied ammonia by a simple compression process without resorting to cooling. He also observed that reduction of the gas volume was accompanied by an increase of the liquid volume. In the same year, Louis-Bernard Guyton de Morveau (1737-1816) liquefied ammonia by simple cooling to about \(-50^\circ\text{C}\) with a freezing mixture of calcium chloride and ice\(^6\) while Antoine-François Foureroy (1750-1809) and Louis Nicolas Vauquelin (1763-1829) failed to liquefy hydrogen chloride, hydrogen sulphide, and sulphur dioxide.\(^9\) In 1801 Gaspar Monge (1746-1818) and Jean François Cloutet (1751-1801) succeeded in liquefying sulphur dioxide by passing a stream of SO\(_2\) through an U-tube submerged in a refrigerant mixture of ice and salt; they noticed that the
tube filled up little by little with a colourless and high mobile liquid, similar to water.

Thereafter, many scientists tried to liquefy gases by a compression process. The next important step were the results obtained in 1823 by Michael Faraday (1791-1867), while investigating the influence of heat on chlorine hydrate. He introduced hydrate crystals in one of the extremes of an inverted V-tube closed on both ends and proceeded to heat them with a water bath at 100°C. Faraday noticed that the crystals first melted and then released a yellow gas that on cooling yielded a heavy bright yellow fluid floating on top of a solid phase. Faraday understood that chlorine gas had separated from the hydrate and condensed under its own pressure.

Faraday's experiment in fact, presented an alternative method for liquefying gases, instead of generating them in a separate apparatus, followed by their compression with the help of pumps, of complicated design, operation, and nonflexible, the gas was now produced in an enclosed space, in increasing amounts by a chemical reaction that served to generate the necessary pressure in a cooled closed tube.

In the course of the same year (1823), Faraday's procedure was used to liquefy hydrogen sulphide produced by the reaction between hydrogen chloride and iron sulphide; SO₂ produced by the reaction between mercury and sulphuric acid; nitrous oxide from the decomposition of ammonium nitrate; cyanogen, and CO₂.

Faraday's equipment was limited to the production of a very small amounts of liquefied gas; in 1834 a very smart modification by Charles Sainte-Ange Thilorier allowed increasing substantially the amount of liquefied gas, particularly liquid CO₂. Thilorier's apparatus was composed of two large vessels connected by a tube. The first vessel, built of copper lined with lead, was used as the reactor. This vessel hung from two pivots so that it could be oscillated to increase the mixing of the reagents (for example, sulphuric acid and sodium bicarbonate). The reaction produced large amounts of gas, with the corresponding increase of the pressure inside the vessel. No liquefaction took place on account of the temperature increase, which took place due to the heat of reaction. A valve was now opened on the top of the vessel and the gas was allowed to flow into the second vessel, held at room temperature, where liquefaction now took place. Opening of a valve located on top of the second vessel released the pressure and resulted in a violent evaporation of the liquid with the corresponding intense cooling and solidification of the remaining liquid into a white snow.

Thilorier studied also the properties of liquid CO₂ and found that it had a very large coefficient of expansion, from 0 to 30°C its volume increase from 20 to 29, which was four times larger that the expansion of air in the same temperature range. Similarly, in the same temperature range the vapour pressure of the liquid increased from 36 to 73 atmospheres, that is, one atmosphere for each degree. Liquefied CO₂ was soluble in all proportions in alcohol, ether, naphtha, turpentine, and carbon disulphide, and insoluble in water.

Afterwards, it was found that a mixture of solid CO₂ and volatile liquids such as ether (Thilorier's mixtures) were capable of producing very low temperatures (below -80°C). In 1845, Faraday combined the two liquefying methods (cooling and compression) into one by taking advantage of Thilorier's mixtures to produce low temperatures. He now used a regular U-tube submerged in a Thilorier mixture that allowed reducing the temperature to -110°C, and connected to two pumps operating in series that allowed increasing the pressure up to 50 atmospheres. With this new apparatus it was possible not only to liquefy gases such as HCl, HBr, SiF₄, PH₃, AsH₃, and ethylene but also to solidify others such as H₂S, N₂O, and HClO. He was unsuccessful to liquefy hydrogen, nitrogen, oxygen, carbon monoxide, and, methane at 50 atmospheres and -110°C.

By mid-nineteenth century, all but six of the known gases had been liquefied, and temperatures below 170 K had been achieved by evaporating a Thilorier mixture of solid CO₂ and diethyl ether. The six remaining gases (oxygen, nitrogen, carbon monoxide, nitrous oxide, methane, and hydrogen) were called permanent gases and believed to be non-condensable. Helium was not considered then because this gas was discovered only in 1869 while observing the sun and identified by a bright yellow line in a spectrum analysis of the sun's corona. Ramsay discovered the first deposits in the earth in a sample of pitchblende, a dark rock containing radium and uranium.

George Aimé (1810-1846) tried, without success, to liquefy oxygen and nitrogen by immersing recipients containing air in the sea, to a depth corresponding to more than 200 atmospheres. In 1844 Johann August Natterer (1821-1900) succeeded in producing large quantities of liquid nitrous oxides but later on he
failed to liquefy air by compressing it to pressures between 1300 to 2800 atmospheres\(^\text{18}\).

In 1850 Victor Regnault (1810-1878)\(^\text{18}\) made extensive measurements of the velocity of sound in different gases and of the heat absorbed during the expansion of the gas through an orifice in a vessel, through capillaries, and when the gas was suddenly stopped. In some of his experiments on the discharge of a gas through a capillary tube he observed a small cooling effect but dismissed them as experimental errors. Two years later, James Prescott Joule (1818-1889) and William Thomson (1824-1907, Lord Kelvin)\(^\text{19}\) would report the same result and understand its significance (the Joule-Thomson effect).

Based on his findings on the behaviour of the compressibility of gases Regnault predicted\(^\text{18}\), as was later demonstrated, that application of insufficient pressure was the only obstacle for the liquefaction of oxygen and nitrogen. Also, that if hydrogen was cooled, it would show enough compressibility to be liquefied. On December 24, 1877, Regnault sat for the last time in a session of the Académie, he was already very ill and would die a few weeks later. On that opportunity Dumas read Cailletet’s communication on the liquefaction of oxygen (mentioned below). A week later, Cailletet announced that he had also succeeded in liquefying nitrogen.

Joule and Thomson performed a series of experiments of throttling air at pressures up to 4,11 atm and temperatures up to 171°F through a pipe blocked at one end by a piece of calf-skin leather and found “there is a final cooling effect produced by air rushing through a small aperture at any temperature up 170°F, and that the amount of this thermal effect decreases as the temperature is increased”. Not only that, their results indicated that in the case of saturated steam the density values used by Regnault were lower by a factor 1.019 from the real ones\(^\text{19}\).

It was found empirically\(^\text{13}\) that the Joule-Thomson cooling effect \(\Delta T\) was proportional to the pressure drop \(\Delta P\) and inversely proportional to the square of the absolute temperature \(T\), according to following equation,

\[
\Delta T = n \Delta P \left( \frac{273}{T} \right)^2
\]

... (3)

where \(n\) is a constant characteristic for each gas (for air \(n = 0.276\)), \(T\) is in kelvins, and \(P\) is in atmospheres.

It took the experiments of Andrews to understand the reason of the failure\(^\text{21,22}\).

Thomas Andrews (1813-1885) studied the behaviour of gases under high pressures and different temperatures and was able to formulate the concept of coexistence of the vapour-liquid equilibrium and the constancy of temperature during a phase change (Andrew’s isotherms). Andrews demonstrated that for every gas there exists a temperature (called the *critical temperature*) above which it was impossible to condense the gas, no matter how high a pressure was applied. For this purpose he used \(\text{CO}_2\) partly because of the facility with which it can be produced in a pure state (by the action of boiling sulphuric acid over marble, and dried by passing through sulphuric acid) and its critical temperature being 31°C. Previous experimenters\(^\text{18}\) had shown that \(\text{CO}_2\) deviated sensibly from Boyle’s law, even at temperatures well above the critical one.

Andrews found that on partly liquefying \(\text{CO}_2\) by pressure alone, and raising simultaneously the temperature to 88°F, the surface of demarcation between the liquid and gas phases disappeared gradually. At temperature above 88°F there was no apparent liquefaction of the gas, only one phase was visible, even at pressures as high as 400 atmospheres\(^\text{23}\). He used the concept of critical temperature to distinguish between a vapour and a gas, a distinction that was based previously on the boiling point, a clearly arbitrary definition. Andrews proposed calling vapour any gas that was at a temperature below the critical one, and gas if it was above this temperature. According to his definition a vapour could be changed into a liquid by a simple increase in pressure and the two phases could coexist in equilibrium.

Another important experimental result was that the gaseous and liquid forms of matter could be transformed into one another by a series of continuous and unbroken changes\(^\text{21}\). In 1873 the continuity of the gas and liquid state would be the subject of Johannes Diderik van der Waals’ (1837-1923) doctoral thesis (Over de continuïteit van de gas-en vloeistofstaat)\(^\text{25}\).

In what follows we describe the life and works of Louis Paul Cailletet (1832-1931), the first to show that permanent gases could be liquefied, and the events that accompanied this achievement.

**Louis Paul Cailletet**

Louis Paul Cailletet (Fig. 1) was born in Châtillon-sur-Seine, Côte-d’Or, France, on September 21, 1832,
into a well-to-do family engaged in metallurgy. He did his first studies at the college of Châtillon-sur-Seine, completed his secondary studies at the Lycée Henri IV in Paris, and then enrolled for two years as an auditeur libre at the École des Mines in Paris. While in Paris he used to visit the chemistry laboratory of the École Normale Supérieure, directed by the Henri Saint-Claire Deville (1818-1881) who had invented the industrial process for the production of aluminum in 1855, and with whom he became a close friend. After finishing his studies Cailliet returned to Châtillon and at the age of twenty-eight took over the management of his father's metal working mills, Forges de Saint-Marce. He became particularly interested in the operation of the blast furnaces, interest that led to his first investigations in metallurgy. He studied the operation of forges, the process of cementation, the mechanism of iron purification, the permeability of hydrogen in iron, and developed procedures for improving the combustion process in blast furnaces. He did also extensive work on the behaviour of gases at high pressures and their liquefaction. For some unknown reasons, he also had a short interest in plant physiology.

Other of Cailliet's accomplishments includes the installation of a 300-meter manometer on the Eiffel Tower. It was built of a 4.5-mm internal diameter tube connected every three meters to a projecting pipe with a cock and glass tube, permitting pressure readings at different heights. The apparatus allowed reaching a pressure of almost 400 atmospheres. He also used the Eiffel Tower to study the effect of air resistance on the fall of bodies. Cailliet worked on the construction of devices, such as automatic cameras and air sample collectors, for the study of upper atmosphere by weather balloons, as well as the design of a liquid-oxygen respiratory apparatus designed for high-altitude ascents. These investigations led to Cailliet being chosen president of the Aéro Club de France.

Cailliet was elected correspondant of the Académie des Sciences on December 17, 1877 and became académicien libre on December 27, 1884.

Louis Paul Cailliet died in Paris, on January 5, 1913, at the age of 81.

Scientific activities

Plant physiology

Cailliet published several works related to plant physiology\(^27\). It was then known that the green parts of a plant decomposed carbon dioxide when exposed to sunlight and released an equivalent quantity of oxygen when in darkness. Cailliet decided to study the influence of rays of different colours (radiation of different wavelength) on the decomposition of CO\(_2\) by plants and for this purpose he enclosed several varieties of plants in a box built of a coloured glass that could be submitted to the direct action of sunlight and did not allow an increase in temperature, a side phenomena important in the case of a red glass. His results indicated that similar to the chemical rays, the heat rays did not affect the decomposition of carbon dioxide, which seems to be the most under the influence of yellow rays. In addition, he observed that green light exerted a totally unexpected action; instead of helping assimilate CO\(_2\) it acted like total darkness. Plants illuminated by green light cracked and oxidized, while losing carbon dioxide\(^24\). Cailliet results where later confirmed by Paul Bert's (1833-1886) experiments\(^8\).

Another phenomenon studied by Cailliet was the possibility that leaves could absorb liquid water\(^23\). For this purpose he constructed an apparatus that allowed introducing a leaved branch of a plant into a glass probe full of water and provided with a manometer. His results indicated that a plant growing in a humid soil would not absorb water though its leaves. When soil humidity was insufficient the leaves would absorb a large amount of water to maintain the plant viable (these results are known today to be wrong).

Another work was related to the origin of the carbon fixed by a green plant\(^26\). The prevalent idea was that plants growing in an almost dry soil that did not contain the elements of ash (potassium carbonate), obtained all their carbon from the air. It had not been proved if part of the carbon originated from carbon dioxide dissolved in water that was then assimilated by the roots. Cailliet studied the behaviour of different well-developed plants (colza, lentil, and passiflora) under an atmosphere devoid of carbon dioxide. He found that in this situation plants ceased their development; the lower leaves became yellow and fell and the upper part of the trunk dried and eventually died. When the plant was almost dead, passing air through water charged with carbon dioxide reanimated the plant and reinitiated its development. From these experiments Cailliet inferred that atmospheric carbon dioxide was indispensable for the life of green plants.

In another study\(^27\) Cailliet found that there were substantial differences between the ashes of mush-
rooms and chlorophyll plants. He analyzed the ashes of a piece of tree on which mushrooms grew and found that the largest majority of the minerals had been absorbed by the latter. To him, this fact explained why a tree subject to the action of cryptogams deteriorated seriously. In addition he found that silicon that constituted about 70% of the weight of ferns and graminae, was not present in mushrooms. The ashes of the latter were poor in calcium oxide and magnesium oxide, but very rich in alkali and phosphoric acid.

Metallurgy

Operators of blast furnaces were aware that they had to do their work carefully to avoid explosions. Similarly, it was known that mechanical work of cast iron might result in its catching fire. A series of accidents of this nature in his factory moved Cailliet to study their origin.

Jacques Joseph Ebelmen (1814-1852) and other chemists had occupied themselves with the analysis of the gases produced in the blast furnace, by aspirating them with a long iron tube containing an internal porcelain tube, and under conditions that resulted in their cooling. Cailliet rejected their results because on cooling the dissociating compounds recombined again, as predicted by the dissociation phenomena discovered by Saint-Claire Deville. In order to avoid this problem Cailliet designed his equipment to sample the gases from the midst of the furnace (operating at a temperature well above the fusion point of platinum) followed by sudden cooling (quenching). His results indicated that the gas composition was substantially different from that reported by Ebelmen and others: Carbon dioxide and other flammable gases such as hydrogen, carbon monoxide were present in very small amounts. The gas mixture was opaque because it carried a large amount of finely divided carbon in suspension that required a long time to settle.

It was a well-known fact that when using cast iron for fabricating molded pieces the melt released combustible gases while it solidified. The large amounts of gas released required special precautions to avoid an explosion. Many theories had been proposed to try to explain the origin of the gases dissolved in the cast and in molten steels. In foundries it was believed that the gases originated from the decomposition of the water occluded in the molding earth by the metal at high temperature. Cailliet believed that the gases were actually furnace gases that had dissolved in the liquid metal, before it’s being discharged from the furnace. To prove his point he cast the liquid melt in water-jacketed molds made of metal to avoid the presence of humidity. Analysis of the gases released indicated that instead of water it was a mixture of hydrogen, nitrogen, and carbon dioxide.

Cailliet did also work on the permeability of different gases, particularly hydrogen, oxygen, and carbon monoxide, and use his results to explain the failures that occurred during the tempering of incompletely forged pieces of iron of large dimensions and also during cementation. In the latter case, he found that the puffs contained hydrogen and carbon monoxide and that they accumulated in those areas where the metal sponge was incompletely forged.

It was known that metals like iron, platinum and aluminum hardly amalgamated with mercury. Although the same phenomenon was observed if mercury was replaced by a dry amalgam of sodium or ammonia, addition of water resulted in amalgamation and release of hydrogen gas. Cailliet performed an ingenious experiment to demonstrate that amalgamation took place together with hydrogen release: He used an electrolytic cell that had a sheet of iron, platinum, or aluminum as the negative electrode and a layer of mercury under an electrolytic bath made of acid or basic water. Dropping the metal sheet into the mercury resulted in the immediate apparition of hydrogen bubbles and this was enough to obtain amalgamation. When a few drops of a lead or copper salt were added to the electrolyte hydrogen generation stopped and the metal used as negative pole was unable to amalgamate.

Cailliet used this procedure to produce amalgams of the metals known to amalgamate with difficulty and to study their properties. He remarked that the amalgam of mercury and aluminum was unusual in its ability to decompose pure water.

Liquefaction of gases

The most important researches of Cailliet are related to the behaviour of gases under pressure and their liquefaction, particularly oxygen. Between the end of 1877 and the beginning of 1878 Cailliet liquefied all the gases considered permanent.

In his first work he studied the validity of Mariotte’s law (ideal gas) at high pressures, using a piece of equipment which was a prototype of the one he would use later to liquefy gases. His first results indicated that at high pressure hydrogen and air did not behave ideally, the compressibility of hydrogen decreased regularly with increased pressure, while that
of air first increased to a maximum value at about 80 atm and then it decreased more rapidly than that of hydrogen. Further work with nitrogen indicated that this gas did also not behave ideally and that its compressibility presented a maximum value at 15°C and about 92 atm.

He then used his equipment to liquefy carbon dioxide under temperature and pressure conditions not reported by other investigators. Cailletet found that liquid CO₂ was colourless and very mobile, did not conduct electricity, and that electricity produced a burst of brilliant induction sparks, in the midst of a very volatile liquid. Liquid CO₂ was not attacked by sodium, did not dissolve sulphur or phosphorus but mixed with ether in all proportions. Iodine gave it a violet tint. Cailletet thought that since CO₂ and water had a similar structure they would dissolve the same salts. Contrary to his expectations liquid CO₂ did not dissolve NaCl, Na₂SO₄, or CaCl₂. Liquid CO₂ dissolved partially in water; the less dense layer being CO₂.

Next, Cailletet studied then the compressibility of acetylene at high pressures and found that the gas behaved according to the law of Mariotte (ideal gas). Cailletet built his equipment essentially along the same lines as those used by Andrews for his experiments with CO₂ (Fig. 1). The central piece was an inverted probe (TT), opened at its bottom and connected to a hydraulic pump through a layer of mercury (tube TU). The upper part of the probe was fused to a thick capillary tube containing the gas to be studied. The capillary was inside a liquid bath (P) containing water or a refrigerating mixture, as desired. The bath was made of glass and was surrounded by a bell jar (C) that offered protection in case of a burst. The capillary was subjected on the outside to atmospheric pressure and on the inside to an internal pressure that determined liquefaction. The probe was subjected to the same pressure, inside and out. The glass construction permitted observation of what was happening inside the capillary.

Previous to building his equipment, Cailletet had developed the necessary ancillary elements. For example, he studied the resistance of glass tubes to rupture and the building of manometers for the measurement of high pressures.

Acetylene was chosen first because it had been suggested that at room temperature a pressure of about 600 atm might be sufficient to liquefy it. In October 1877, during a routine verification of acetylene, an incident took place: Before the liquefaction pressure could be reached the apparatus sprang a leak and the compressed gas escaped. The sudden release of the gas resulted in a considerable drop in temperature and appearance of a thick mist (brouillard épais). At first, Cailletet thought that his gas was impure and what he had seen was condensation of humidity. Cailletet had now the brilliant idea of repeating his experiment using a sample of very pure acetylene provided by Marcelin Berthelot (1827-1907) and again observed the formation of mist. Cailletet understood that the liquefaction had been achieved by the intense cooling produced by the sudden release of pressure and that he had now in his hands a new technique for gas liquefaction.

Cailletet observed that compression of acetylene, initially at 18°C, to a pressure of 83 atm, resulted in the formation of many droplets dripping on the walls of the vessel. Reduction of the pressure by several atmospheres resulted in vaporization of the vessel and the tube being filled with a fine mist.

The liquid acetylene obtained was colourless, highly mobile, and apparently very refringent. It was lighter than the water and dissolved in a large proportion into it. It dissolved paraffin and greases. Cooling the liquid to 0°C in the presence of water and linseed oil produced a white snowy substance, which decomposed rapidly on slight heating or lowering of the pressure, generating a large amount of gas bubbles.
Cailletet determined the following pressures and temperatures at which acetylene was liquefied:

<table>
<thead>
<tr>
<th>T°C</th>
<th>atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>48</td>
</tr>
<tr>
<td>2.5</td>
<td>50</td>
</tr>
<tr>
<td>10</td>
<td>63</td>
</tr>
<tr>
<td>18</td>
<td>83</td>
</tr>
<tr>
<td>25</td>
<td>94</td>
</tr>
<tr>
<td>31</td>
<td>103</td>
</tr>
</tbody>
</table>

Comparison of the above values with those reported by Din for the liquid-vapour saturation dome of acetylene shows that Cailletet reported the conditions upstream the throttling process and not those of the vapour-liquid equilibrium.

Cailletet used the same equipment to liquefy ethane, and found that at 4°C the required pressure was about 46 atm, that is, slightly larger than that required for acetylene.

Cailletet closed his paper with the remark that his liquefaction equipment was very simple and easy to operate and that he intended to test it with other gases.

In Cailletet's experiment the discharge (expansion) of the gas may be considered adiabatic, hence, assuming as a first approximation ideal behaviour, it is possible to calculate the final temperature with the relation

\[ T_f = T_i \left( \frac{P_i}{P_f} \right)^{\frac{y-1}{y}} \]

where i and f indicate the initial and final condition, respectively. According to Eq. (4) the final temperature depends on the value of \( y \), that is, on the gas in question. \( y \) is about 1.67 for monatomic gases and about 1.40 for diatomic gases like \( \text{H}_2, \text{O}_2, \text{N}_2, \text{CO}, \text{and NO} \).

Assuming 103 atm and 304.15 K as initial conditions, a drop to atmospheric pressure corresponds to a final temperature of about 81 K. The cooling effect is due to the external work done by the gas in expanding against the downstream pressure. The actual cooling will be less because of the cooling effect of the walls of the vessel, and heat losses to the environment.

In a following publication Cailletet reported that he had used his equipment to liquefy nitrogen dioxide at 104 atm and -11°C. At 8°C \( \text{NO}_2 \) remained in the gaseous state at pressures up 270 atm, He also observed that when methane was compressed to 180 atm at 7°C, a sudden release of the pressure produced a mist similar to the one observed with carbon dioxide; for this reason he believed he would be able to liquefy methane. This publication carried a comment by Berthelot about the importance of Cailletet's findings because so far it had been impossible to liquefy gases that behaved according to Mariotte's law. Berthelot mentioned that in the last years Andrews had shown that the reason for the failure was that every vapour had a critical temperature, above which the vapour could not be transformed into liquid, no matter how much a pressure was applied to it.

According to Berthelot, Cailletet's experiences showed that the critical point of nitrogen dioxide was between 8 and -11°C. He also believed that Cailletet's procedure would soon lead to the liquefactation of oxygen and carbon monoxide.

**Liquefactation of oxygen**

Liquefactation of oxygen represents a sensational scientific accomplishment that was achieved in 1877 almost simultaneously by Cailletet and Raoul Pictet (1846-1929) using completely different experimental techniques. This achievement was also accompanied (and continuous to be) by much discussion regarding priority to the discovery.

Cailletet and Pictet's results were communicated to the Académie des Sciences by the Permanent Secretary, Jean Baptiste André Dumas (1800-1884) during the session held on December 24, 1877, and appear in Compt. Rendu, 85, 1212, 1877.

It is important to give a detailed account of this particular session in order to understand the reasons of the priority polemic that followed the announcement.

Dumas opened the session reading the prophetic words of Lavoisier, written almost one-hundred years before, regarding the new liquids that could be produced by liquefactation (see above).

Cailletet's note "De la Condensation de l'Oxygène et de l'Oxyde de Carbone" was read immediately thereafter. In it Cailletet reported that if oxygen or carbon monoxide were put in his apparatus (bioxide, REF) at 300 atm and cooled to -29°C with boiling sulphur dioxide, both gases remained as such. If the gases were then released suddenly they would cool, according to Poisson's formula, to a temperature 200° below the initial, and immediately an intense mist (brouillard intense) would be seen, caused by the liquefaction and perhaps the solidification of oxygen or
Wisniak: Louis Paul Caillet—The liquefaction of the permanent gases

Carbon monoxide. The same phenomenon was observed when the gas was carbon dioxide, nitrous oxide, and nitrogen dioxide. This mist was produced when compressed oxygen was released after it had cooled to room temperature. Caillet indicated that he had demonstrated this fact during experiences he had performed on Sunday, December 16, in the chemistry laboratory of the École Normal Supérieure, in the presence of various investigators and professors, some of them members of the Académie.

Caillet added that to authenticate that oxygen or carbon monoxide were in the liquid or solid state it was enough to perform an optical test, which unfortunately was easier to say than to do because of the shape and thickness of the tubes in his apparatus. Several certain chemical reactions had allowed him to bear out that oxygen had not transformed into ozone during the compression.

Caillet finished his report indicating that he had applied the same operating conditions to hydrogen without observing the presence of mist and that he intended to apply them to try to liquefy nitrogen.

Afterwards, Mr. de Loyens, the Paris representative of the firm Raoul Pictet & Co., read the telegram sent by Pictet and received on December 22 at 8 PM, reporting the liquefaction of oxygen in the following words: “Oxygène liquéfié aujourd’hui sous 320 atmosphères et -140 de froid par acide sulphureux et carbonique accumulés”. The telegram had been followed by a document describing in detail the equipment and procedure utilized for achieving the condensation (Fig. 2).

Q and R are double-effect aspiration pumps. R operates on liquid anhydrous sulphur dioxide contained in tube C at -65°C. The gaseous SO₂ generated in C is directed to the condenser D, operating with refrigerated water, where it liquefies at -25°C and about 2.75 atmospheres. The diameter of pipe k is small enough to produce the required backpressure to condense SO₂.

Similarly, pumps R operated on liquid CO₂ contained in the annular space H, held at the proper pressure to evaporate the liquid at -140°C. The gaseous CO₂ produced is directed to the condenser K surrounded by a tube containing liquid SO₂ at -65°C and 5 atmospheres. The diameter of pipe d is small enough to produce the required backpressure to condense CO₂. The liquid CO₂ returns to H through the connector k.

Fig. 2—Scheme of Caillet’s equipment

L is a flask made of forged iron, capable of sustaining a pressure of 500 atmospheres, used to generate pure oxygen by heating potassium chlorate with a heat source. The quantity of salt added to the flask determines the oxygen pressure achieved. The gas thus produced accumulates in the internal tube of H, maintained at -140°C. After several hours of operation oxygen achieves the conditions of 320 atmospheres and -140°C.

Opening the cock at N results in a strong expansion of the compressed and cold oxygen and a large part of it liquefies and fills the tube M.

After de Loyens’ words, Dumas read a letter sent on December 2 by Caillet to Sainte-Claire Deville that the latter had deposited the next day in the hands of the Secretary of the Académie, in a sealed envelope, which he now proceeded to open and read: “I hasten to inform you, and you first without losing a moment that I have liquefied this day both carbonic oxide and oxygen. I am perhaps wrong in saying liquefied, because the temperature I obtained by evaporating sulphurous acid, is at -29°C and under 200 atmospheres pressure, I did not see any liquid, but a fog so dense that I was able to infer the presence of a vapour very close to its point of liquefaction. I have
written today to Mr. Deleuil to ask him for some protoxide of nitrogen, by means of which I shall doubtlessly be able to see carbonic and oxygen flow.

P.S. I have just carried an experiment, which satisfies me completely. I have compressed hydrogen to 300 atmospheres, and after cooling it down to \(-28^\circ\text{C}\). I expanded it suddenly. There was no trace of mist in the tube. My gases (CO and O) are, therefore, certainly at the point of liquefaction, as this mist is only produced by vapours close to liquefaction. The forecasts of M. Berthelot are completely verified”.

After Dumas finished reading Cailletet’s letter Sainte-Claire Deville rose to add more details. He said that on Sunday December 16, Cailletet had repeated his experiences on the condensation of oxygen at the laboratory of the École Normale and that they had successfully duplicated the results he had reported in his previous note. Cailletet had not wish to publish them because he was a candidate to the position of Correspondant of the Académie, position that he was awarded on the session of December 17, and he did not want that the discussion of his merits for the position included a piece of work that its results and not been repeated in front of appropriate judges. He did not want to publish such an important achievement exactly on the day of his election. Fortunately, on December 3, Sainte-Claire Deville had put the letter, properly sealed, in the hands of the Permanent Secretary. For these reasons Sainte-Claire Deville believed that the priority of the discovery belonged to Cailletet. He also added that the remarkable work of Pictet had hardly been quoted; his operating procedure being completely different from that of Cailletet.

Afterwards, several members expressed their views that both methods were proof that oxygen had been liquefied or solidified. Jules Jamin (1818-1886) indicated that the real confirmation of the actual state would be the ability to maintain liquid oxygen at its boiling temperature, as had been done with liquid nitrous oxide; or at the solid state, as had been done with carbon dioxide.

For their investigations on the liquefaction of oxygen Cailletet and Pictet received the Davy Medal from the Royal Society of London (November 1878) and the Prix Lacaze from the Académie des Sciences (1883). The selection committee members were Berthelot, Auguste Cahours (1813-1891), Michel Eugène Chevreul (1786-1889), Henri Debray (1827-1888), Jean Baptiste André Dumas (1800-1884), Edmond Frémy (1814-1894), Charles Friedel (1832-1899), Louis Pasteur (1822-1895), and Charles-Adolphe Wurtz (1817-1884).

A year later after the presentation at the Académie, Pictet published an extensive memoir giving many details about his equipment and the results of the numerous experiences he had done.

**The polemic about priority**

Although the proceedings of the session of the Académie des Sciences indicate that Cailletet reported the liquefaction of oxygen ahead of Pictet, there has been much argument about how well do they present the facts as they really took occurred.

Kurti did a thorough study of all the documents related to the proceedings of the Académie and found several discrepancies. For example, Dumas omitted part of the letter that de Loynes had sent to justify his employer claims. In the paragraphs omitted, de Loynes indicated that Pictet’s was well-known for manufacturing $SO_2$ anhydrous, a critical element for achieving the liquefaction of oxygen in both Cailletet’s and Pictet’s procedures. In addition, Sainte-Claire Deville had explained that the reason why he had not reported before to the Académie the results achieved by Cailletet was that the latter was a candidate to membership and did not want that this important achievement be part of the argument, before it had been endorsed by competent judges. According to
of the Academy, located the original letter and on reading it found that when reading it to the Académie Dumas had cut three paragraphs from the original. In the missing material it is clearly stated that Cailliet thought that his preliminary results would help him achieve membership.

Kurt raises the question: “Why did Sainte-Claire Deville insist on Cailliet’s priority over Pictet. Was it chauvinism—France versus Switzerland?”

Benaroche raises other arguments based on photocopies of the critical documents present in the archives of the Académie: (a) According to Sainte-Claire-Deville he deposited Cailliet’s letter of December 2, on December 3, in a sealed envelope, in the hands of the Secretary of the Académie. There is no record in the Académie (as existed for other similar letters) that this letter was delivered, (b) Sainte-Claire-Deville claimed that Cailliet was candidate as correspondent for the election held on December 17. Cailliet’s name does not appear in the list of candidates that was posted in the session held on December 10, as was the usual procedure, (c) the most curious fact is that the letter that was supposed to be received on December 3, was actually received on December 2, (d) the post-script in Cailliet’s letter to Sainte-Claire-Deville (delivered on December 23), was dated December 2, and hence it was not possible that the post-script was delivered on December 3, and finally (e) it is clear that in the letter from Sainte-Claire-Deville to Dumas the date has been corrected.

Benaroche is not sure if all these inconsistencies represent a chain of clerical errors or other motives.

In this context we can mention the accusations of plagiarism that Karl Dühring (1833–1921) made against Paul de Mondon in his book Neue Grundsätze zur Rationellen Physik und Chemie (“Fundamental Laws of Physics and Chemistry”), published in two volumes. The second volume closes with a two-page statement entitled “About Plagiarism of the first volume of Fundamental Laws of Physics and Chemistry”. In it Dühring makes a bitter attack on several people he accuses of copying his ideas about the corresponding temperatures of boiling liquids. In particular he singles out Winkelmann for the papers he published in Annalen der Physik and de Modesir for the paper he published in Comptes Rendu. In the middle of the second volume there is also a copy of the letter sent on December 5, 1880, by Ulrich Dühring to the Permanent Secretary (Dumas) of the Académie des Science, requesting that the Academy publish an attached document entitled Réclamation de la loi des températures d’ébullition correspondents (Claim regarding the law of corresponding boiling points). Ulrich pointed out that on the session held by the Académie February 23, 1880, Sainte-Claire Deville had read a communication by Paul de Modesir regarding a comparison between the temperatures at which pure components exerted the same vapour pressure. De Modesir’s communication was published in Comptes Rendu, 1880, 90, 360-367. Ulrich Dühring pointed out that his father had already published the law “discovered” by de Modesir in essentially the same terms and using the same vapour pressure measurements made by Regnault. More than that, his father had not only published the law and explained it theoretically, he had also suggested its practical applications and its relation to the chemical structure of the molecules. Dühring’s book reports that the Académie published only an extract of Ulrich’s letter (Comptes Rendu, volume 91) under the title Réclamation de priorité au sujet de la loi des températures d’ébullition correspondents. Extrait d’une lettre de M. U. Dühring. The way that the original letter was reduced in length caused another blast of Dühring against the scientific establishment and its journals.

Liquefaction of other gases

In the same year that he liquefied oxygen (1877) Cailliet reported that he had been able to liquefy nitrogen, and air, and probably hydrogen. To liquefy nitrogen he first compressed the dry gas to about 200 atm at 13°C; after a sudden release of the pressure the formation of large liquid drops was observed, which disappeared in contact with the walls of the vessel, forming a sort of liquid column along the axis of the tube. The total phenomenon lasted for about three seconds. On December 30, 1877, he repeated the experience at −29°C, in the presence of several members of the Académie, among them Jean-Baptiste Boussingault (1802-1887).

Cailliet used the same technique to liquefy air, absolutely dry and free of CO₂ and commented that thus Lavoisier’s prophetic words had been confirmed: production of substances with new and unknown properties. He also remarked that hydrogen had always being considered the most non-condensable gas because
of its low density and mechanical properties almost identical to those of ideal gases. Anyhow, he performed his experiments of sudden expansion from 280 atm, in the presence of Berthelot, Sainte-Claire-Deville, and Éleuthère Mascart (1837-1908), and all had had the experience of observing a very fine and light mist, suspended in all the mass of the gas, that disappeared very fast.

In a following work, Caillelet was able to liquefy ethylene under various pressure and temperature conditions. For example, at 10°C the pressure required was 60 atm while at 1°C it was 45 atm. From his many measurements he estimated the critical temperature of ethylene to be about 13°C (actually 282.4 K) in comparison with 31°C for carbon dioxide. In a footnote he indicated that determination of the critical temperature was difficult because it varied strongly with small amounts of impurities.

The low value of ethylene’s critical temperature suggested Caillelet the possibility of using boiling ethylene instead of boiling nitrous oxide (N₂O, Tₑ = 309.6 K) to achieve lower temperatures. He repeated his experiments on the liquefaction of oxygen using this time liquid ethylene at −105°C as the coldest source, instead of liquid N₂O at −88°C and found that there were substantial differences between the two liquids. With N₂O, the free expansion produced only a thin mist of very short life while with liquid ethylene a definite amount of liquid oxygen was produced that boiled vigorously for a long period of time. Caillelet remarked that liquid ethylene was not only capable of producing lower temperatures, it also had the advantage of being transparent, in contrast with liquid CO₂ and liquid N₂O, which were opaque.

Caillelet and Hautefeuille discovered the possibility of using boiling ethylene instead of boiling nitrous oxide (N₂O, Tₑ = 309.6 K) to achieve lower temperatures. He repeated his experiments on the liquefaction of oxygen using this time liquid ethylene at −105°C as the coldest source, instead of liquid N₂O at −88°C and found that there were substantial differences between the two liquids. With N₂O, the free expansion produced only a thin mist of very short life while with liquid ethylene a definite amount of liquid oxygen was produced that boiled vigorously for a long period of time. Caillelet remarked that liquid ethylene was not only capable of producing lower temperatures, it also had the advantage of being transparent, in contrast with liquid CO₂ and liquid N₂O, which were opaque.

Caillelet and Hautefeuille discovered that when phosphine was compressed in the presence of water it would liquefy and float on top of the water layer. If the pressure was suddenly released a white crystalline body would form that would disappear if the pressure was reduced further. The formation and decomposition of the crystal occurred at fixed pressures and temperatures; for example at 2.2°C and 2.8 atmospheres, and 20.0°C and 15.1 atmospheres. The critical temperature of formation (congruent and critical point) was 28°C. Caillelet and Bordet believed that the crystals were composed of phosphine hydrate, although they were unable to determine its composition.

They repeated the experience with other wet gases and found similar results. For example, the compression of equal volumes of wet CO₂ and phosphine regenerated a white crystalline solid, without leaving a gaseous residue that was assumed to be a mixture of the hydrates of the two gases. Hydrogen sulphide also combined with water yielding a hydrate having a critical temperature of 29°C.

Caillelet and Mathias designed a very simple apparatus made out of glass to measure the density of the vapour and liquid phases of a pure compound as it approaches its critical point. A plot of their experimental results of the density for N₂O, ethylene, and CO₂, showed that the mean density of both phases decreased linearly with the temperature and that the straight line drawn through the middle point of the chords went through the critical point. They suggested employing this fact to determine the critical temperature and density of a gas, using measurements below the critical point.

This finding is known today as the Caillelet-Mathias rule.

Mathematically

\[ \rho_{\text{average}} = 0.5 (\rho_L + \rho_G) = a - bT \]  \hspace{1cm} \text{... (5)}

where \( \rho_L \) and \( \rho_G \) are the densities of the liquid and gas phase, respectively. Applying Eq. (5) to the values \( T = 0 \) and \( T = T_c \) we get \( a = 0.5 \rho_s \) and \( \rho_L = \rho_G = \rho_c \), where \( \rho_s \) is the density of the solid phase at 0 K and \( \rho_c \) the density at the critical point. Hence,
\[ \rho_L + \rho_G = \rho_s - (\rho_s - 2\rho_L) T^{-T_c} \quad \ldots \quad (6) \]

**Epilogue**

The existence of liquid oxygen have a picturesque angle in Jonathan Swift’s book “Gulliver’s Travels” and in Jules Verne’s book “Le Docteur Ox” (REF). In chapter V of “A Voyage to Balnibarbi”, Lemuel Gulliver describes his visit to the Grand Academy of Lagado and the projects its scientists are engaged: “I had hitherto seen only one side of the Academy, the other being appropriated to the advancement of speculative learning, of whom I shall say something when I have mentioned one illustrious person more, who is called among them the ‘universal artist’. He told us ‘he had been thirty years employing his thoughts for the improvement of human life’. He had two large rooms full of wonderful curiosities, and fifty men at work. Some were condensing air into a dry tangible substance, by extracting the nitre, and letting the aqueous or fluid particles percolate...”

In “Le Docteur Ox” Doctor Ox and his assistant Ygene come to the small quiet community of Quiquendone located in Flanders. He promises to light this town with a network of oxyhydric gas pipes. During the construction of this network, the quiet community becomes quite excitable, to the point where they are ready to go to war against a neighboring community. But what is the cause of this change in the nature of the good people of Quiquendone? Perhaps it is something in the air, but only Doctor Ox and his assistant Ygene know for sure.

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Notes
1. Galbanum is a resinous oil that was imported from the Middle East and used for medicinal purposes and incense offerings. It also mentioned in the Bible, Exodus 30:34 under the name of chelbanoh.