In 1877 Louis Paul Cailletet in France and Raoul Pictet in Switzerland liquefied oxygen in the form of a mist. The liquefaction of the first of the so-called permanent gases heralded the birth of low-temperature research and is often described in the literature as having started a ‘race’ for attaining progressively lower temperatures. In fact, between 1877 and 1908, when helium, the last of the permanent gases, was liquefied, there were many priority disputes—something quite characteristic of the emergence of a new research field. This paper examines Cailletet’s path to the liquefaction of oxygen, as well as a debate between him and the Polish physicist Zygmunt Wróblewski over the latter’s contribution to the liquefaction of gases.

**Keywords:** Louis Paul Cailletet; liquefaction of oxygen; nineteenth-century low-temperature research; Zygmunt Wróblewski; priority controversies
In 1877, however, and for a few years thereafter, Cailletet was the dominant figure in the area of low-temperature research, a major contributor to the construction of more sophisticated experimental apparatus, the liquefaction of other gases, and attempts to study their properties. Raoul Pictet, in contrast, was more interested in examining the effect of low temperatures on a variety of physical and chemical phenomena, although he was involved at the same time in activities related to the fast-growing large-scale refrigeration industry. Although both Cailletet and Pictet had liquefied oxygen within a few days of each other, there was no priority dispute between them. Both achievements received equal recognition, and the evidence that Cailletet had indeed liquefied oxygen a few days before Pictet was never disputed.

Nevertheless, Cailletet’s career in low-temperature research was not without tensions. In 1883, and much to Cailletet’s dismay, Zygmunt Wróblewski (1845–88) and Karol Olszewski (1846–1915), working at the Jagiellonian University in Cracow, succeeded in producing small quantities of liquid oxygen in stable form. A year later, in 1884, an exposé of the history of the liquefaction of air by the French physicist Jules Jamin (1818–86) undermined the contribution of the two Poles to the liquefaction of gases, and this got Cailletet involved in a rather heated debate with Wróblewski. The debate started in a non-scientific journal, the Revue des Deux Mondes, although signs of it are evident in several notes that Cailletet published in Comptes Rendus of the Académie des Sciences from 1884 onwards. This is a little-known debate and is one of several that took place between 1877 and 1908. Such debates are indicative of the history of the emergence of new research fields—in this case cryogenics—in which many new experimental results are decisive in determining the boundaries of the new field. Although it is meaningless to attribute the emergence of low-temperature research to a single person, it seems that Cailletet wanted to be acknowledged as the ‘founder of high-pressure chemistry’—because one of the key elements in the liquefaction processes was the need to subject gases to high pressures before they could be liquefied. The bitter dispute with Wróblewski raised issues of scientific authorship, the paternity of the methods used, and the results attained. Interestingly, Wróblewski’s account of his own work gives us further insights into Cailletet’s methods and career that could not be deduced from the latter’s publications alone.

In this paper I examine Cailletet’s path to the liquefaction of oxygen, placing special emphasis on the industrial environment in which he was reared, his dexterity in the design and construction of experimental apparatus, his close links within the Parisian scientific community, especially with the chemist Henri Sainte-Claire Deville (1818–81), and his ambition to become a pioneer in high-pressure chemistry. Cailletet was a rare case of someone who gained prominence and respect in the French scientific community without having completed any professional training or having followed the typical career path of the French ‘ingénieurs savants’, physicists or chemists during the second half of the nineteenth century. By focusing on the debate between Cailletet and Wróblewski I highlight some aspects of the emerging field of low-temperature research and use the example to bring out certain characteristics of French science at the time.
returned to his home town to work in his father’s ironworks at Chenecières and Villote-sur-Ource. Although little is known about the exact nature of his work at these sites, Cailletet seems to have been interested not only in improving the quality of the steel and iron goods that the factory produced but also in applying the knowledge he had gained in Paris.

From 1856 Cailletet published studies on phenomena he observed in the ironworks and on procedures that enhanced the quality of the products. Most of his accounts were published in *Comptes Rendus*, where they were presented by the chemist Henri Étienne Sainte-Claire Deville. At that time, Deville taught chemistry at the École Normale Supérieure, as well as giving lectures for the ageing Jean-Baptiste Dumas at the Sorbonne. He was also in charge of the first industrial production of aluminium at the chemical works in Javel and the Glacie`re factory in central Paris, and later at a factory in Nanterre. Cailletet probably met Deville during his stay in Paris. A personal letter to him from Deville in 1864, in which Deville calls him almost colloquially ‘dear friend’, suggests that their relationship was not characterized by the forms of courtesy typical in the formal environment of the Parisian scientific elite. Deville’s support was also evident through comments that he wrote to accompany Cailletet’s notes. Reciprocally, Cailletet’s work endorsed and extended previous work conducted by Deville himself.

Cailletet’s research was centred on chemical metallurgy. Most of what he did focused on phenomena that had been observed in ironworks but never properly explained, such as the blistering of pieces of cast iron or the disengagement of combustible gases when molten iron was poured into moulds. In 1866, Cailletet published a lengthy note on the phenomenon of dissociation based on the investigations of Deville. In a series of experiments Deville had established that at high temperatures compound gases dissociated into their constituent elements, and Cailletet confirmed Deville’s theory by examining the gases emitted from the blast furnaces of his ironworks.

In all his communications to the Académie des Sciences, Cailletet stressed that his experiments benefited from the industrial context in which they were performed. His experiments were on materials that could not be prepared in laboratories, and the quantities used were on an industrial scale, so that the phenomena observed were intimately linked to manufacturing processes. Some chemical reactions occurred only in extreme conditions, such as the high temperatures produced in blast furnaces, or when large quantities of metals were involved. Although his first experiments were conducted during the normal operation of the ironworks where he worked, Cailletet later built a 350-litre cementation box with which he could experiment without depending on actual production processes. For his research he devised several experimental arrangements that allowed him to collect the gases emitted from the blast furnaces and replicate the various phenomena he had observed in a laboratory he set up in Châtillon-sur-Seine.

‘Chemistry at 300 atm’

In 1868 Deville became director of the chemistry laboratory at the École Normale Supérieure. A year later Cailletet started a new series of experiments on the influence of pressure on chemical processes that were not directly related to the phenomena observed in ironworks. This change in his research interests was due to Deville. Until 1869 Cailletet continued to stress the industrial context of his research and to insist on the benefits to be gained from working in such an environment rather than in a laboratory. However, from 1869, in his
experiments on high-pressure chemistry as presented to the Académie des Sciences, Cailletet never again mentioned the ironworks as a site where experimentation took place. It seems likely that Cailletet was seeking to refashion himself as a ‘scientist’ or a ‘savant’, a status he was not entitled to automatically because of his lack of proper institutional training.

Almost every Sunday afternoon, Deville entertained colleagues and other influential personalities in his laboratory and mounted experimental demonstrations for them. Cailletet’s first note on high-pressure chemistry, which was presented by Deville at the Académie des Sciences on 22 March 1869, described experiments that he had performed at one of Deville’s Sunday meetings, in the presence of the Minister of Public Instruction, Victor Duruy. They were also reported in the daily press a few days before their announcement in the Académie. According to an article by the zoologist and science popularizer Edmond Perrier in the daily newspaper *Le National*, Cailletet was one of the relatively new guests in Deville’s laboratory, where his experiments on high-pressure chemistry had been referred to by Deville as ‘une chimie nouvelle: la chimie à 300atm’.12

In *Comptes Rendus*, Cailletet described how pressure slowed down chemical action. He then concluded his account with his first theoretical remark: ‘...affinity is not a specific force, but the chemical combinations and decompositions depend directly on the mechanical phenomena in which they develop.’13 Cailletet’s views were similar to those of Deville, who in his *Leçons sur l’affinité* in 1867 declared that ‘The hypothesis of atoms, the abstraction of affinity, all kinds of forces… are pure inventions of our mind, …words to which we attribute reality.’14 Deville and Cailletet, like many nineteenth-century French scientists, confined themselves to the study of the observable facts and abstained from drawing any conclusions touching upon metaphysical issues.

The results of March 1869 were contested by the influential chemist Marcelin Berthelot (1827–1907), who referred to his own experiments in arguing that the action of pressure on chemical reactions could not be explained in purely mechanical terms but was due to, among other things, changes in the masses of the reacting bodies.15 Cailletet’s response recast the foundations of the discussion. He saw Berthelot’s intervention as a priority claim concerning experimentation in high-pressure chemistry. In his defence, he stressed that his aim was mainly to employ new apparatus that was easy to handle and safe to use, and with which he could perform chemical reactions in specific conditions of pressure and temperature. Even though Cailletet acknowledged the various scientific hypotheses with which the observed phenomena could be explained, he continued to prefer conclusions that were descriptive and independent of any hypotheses. His main argument, though, was based on the apparatus used and on his skills and knowledge in instrument making.16 From the very beginning, Cailletet’s work represented one of the main traits of nineteenth-century French experimental physics and chemistry, which was the building of apparatus in order to throw light on phenomena leading to the formulation of empirical laws. Although there was ostensibly little concern for the corroboration of hypothetical models, a great deal of attention was paid to questions about how apparatus and instruments worked.

Most of Cailletet’s subsequent publications dealt with the compressibility of gases at high pressures, and focused mainly on the design of experimental apparatus. Despite his doubts about the precision of the results attained because of undetermined parameters such as the compressibility of the glass tubes, Cailletet was able to show that Mariotte’s law did not hold at high pressures.17 During this period, Cailletet had already in mind the possibility of liquefying the permanent gases, despite the fact that the eminent physicist and chemist Victor Regnault (1810–78) had tried to discourage him from undertaking such a task.18
Cailletet’s ability in high-pressure experimentation was further exemplified in his research on liquid carbon dioxide, which was first liquefied by Faraday in 1823. With his apparatus, Cailletet succeeded in liquefying the gas and examining its properties. Although he showed that the liquid was a poor conductor of electricity and examined its solvent power, he could not determine its compressibility coefficient because of his inability to achieve the complete condensation of the gas.\(^{19}\)

A few years later, in 1877, Cailletet successfully attempted the liquefaction of acetylene and ethane with the same equipment. Although the liquefaction of the latter was relatively easy, Cailletet was insistent about the simplicity and safety of his apparatus, as well as its possible uses in the classroom or the laboratory for experimental demonstrations.\(^{20}\)

Cailletet’s experimental arrangement was based on the compression apparatus of Colladon and Andrews. It consisted of a steel cistern, in which there was a glass vessel whose upper end formed a tube (figure 1). The space between the cistern and the glass vessel was filled with mercury. The tube, sealed at the top and containing the perfectly dry, pure gas was placed into an open glass vessel containing a cooling mixture and was surrounded by a protective glass shield. Water was pumped into the space between the cistern and the first glass vessel, whose lower end was open, and the mercury in the space was forced into the tube, where it compressed the gas. The operator then opened a valve in the hydraulic pump, which led to a sudden fall of mercury in the gas tube and the cooling of the gas by its own expansion. It is said that Cailletet adopted the technique of lowering the temperature through expansion after an accidental leak or an unintentional release of the pressurized gas during his experimentation with acetylene.\(^{21}\)

In his brief note to the Académie, Cailletet scarcely mentioned the expansion of the gas as a decisive step towards its liquefaction. He emphasized instead the description of his liquefaction apparatus with almost no reference to the hydraulic pump used.\(^{22}\) In later publications, the size of the hydraulic pump in comparison with the liquefaction apparatus was given greater prominence, and it can be considered as an indication that Cailletet attached far greater importance to compression than to the lowering of the temperature by expansion (figure 2).\(^{23}\)

The next gas to be liquefied was nitrogen dioxide, followed soon afterwards by methane.\(^{24}\) A few days before the cautious announcement of the liquefaction of methane, Cailletet received a letter from Berthelot, who gave him instructions on how to purify the gas so as to make sure that the mist observed was indeed methane and that no other gas was contained in it.\(^{25}\)

In the discussion of Cailletet’s systematic work on the liquefaction of gases, Berthelot presented Cailletet’s achievement as the most important advance since Faraday, and looked forward to the eventual liquefaction of oxygen and carbon monoxide.\(^{26}\) In a letter to Cailletet, he expressed his conviction that Cailletet would be able to liquefy these gases by lowering the temperature of the gas tube and without needing to exceed 200 atm.\(^{27}\) Berthelot himself had attempted to liquefy some of the permanent gases by applying pressures of more than 800 atm. But he had failed, being unaware of the importance of the critical temperature, above which no gas could be liquefied at any pressure, no matter how great.\(^{28}\)
ON THE LIQUEFACTION OF OXYGEN

As we have seen, Cailletet and Pictet liquefied oxygen almost simultaneously in 1877, and the work of both scientists was presented to the Académie on 24 December. Employing his usual method of gas liquefaction, Cailletet placed oxygen and carbon monoxide into his liquefaction apparatus, cooled them to $-29$ °C and compressed them to 300 atm. He then let the gases expand rapidly, and calculated that the temperature drop would be 200 °C.
At the end of the expansion, he observed a thick mist, which he identified, after several trials, as the condensed form of both gases. He was, of course, aware that he was still unable to collect the gases in liquid form. However, he expressed his intention of using the necessary refrigerants to achieve this success in the near future.29

Pictet’s telegram, received by the Académie on 22 December, stated that he had liquefied oxygen at 320 atm and $-140^\circ$C, using a mixture of sulphuric and carbonic acids. Immediately afterwards, Pictet, who at the time held the chair of physics and mathematics of the University of Geneva, explained how he had achieved the liquefaction, using a procedure quite different from Cailletet’s. His apparatus consisted of a series of cold circuits known as the cascade method, which was later used by Zygmunt Wróblewski and Karol Olszewski, James Dewar (1842–1923) and Heike Kamerlingh Onnes (1853–1926).30

Regnault was impressed by Pictet’s apparatus, which he had seen half a decade before in Geneva.31 Moreover, the concerns that led Pictet to the problems of liquefaction were different from those of Cailletet. In contrast with Cailletet’s purely experimental approach, Pictet’s interest in the liquefaction of gases stemmed from a wider theoretical concern about the constitution of bodies. His friendship with the chemist and fervent supporter of atomism, Adophe Wurtz, during his student years in Paris may well have contributed to this position. In his extended paper on his liquefaction work, in *Annales de Chimie et de Physique*, Pictet described his microscopic approach to the laws of nature within the context of the mechanical theory of heat and Clausius’s kinetic theory of gases.32 Pictet referred to the term ‘critical point’ at least once in his works, an indication that he was aware of the work of Andrews and van der Waals.33 Cailletet, too, was aware of the
concept of the critical point, although he never made any claims about its underlying ontology, whether in Pictet’s or van der Waals’s work.  

The announcement of the liquefaction of oxygen by Cailletet and Pictet was received with enthusiasm. Although Pictet had reported the liquefaction of oxygen first, the Académie granted priority in the achievement to Cailletet. On 2 December, a few days before Pictet conducted his experiment, Cailletet had sent a letter to Deville, in which he announced the liquefaction of carbon monoxide and oxygen. Deville had the foresight to deposit the letter in a sealed envelope with the Académie des Sciences on the following day. Cailletet had successfully repeated his experiments on 16 December in the laboratory of the École Normale. The reason he did not make the announcement immediately was that on 17 December the Académie was busy electing to fill a vacancy in its mineralogy section, and he was one of the candidates. Although many academicians knew of his experiments because they were present at the École Normale, he thought that its announcement would influence the jury.

At that time there was no dispute over priority, at least between the two parties. In a letter to Cailletet, Pictet denied any priority claim. There was certainly no doubt that Pictet had arrived at almost the same result independently, and both of them received the Davy Medal, which was awarded to them in a ceremony at the Royal Society in London on 30 November 1878.

The extensive reports of the liquefaction of oxygen that appeared in the French periodical press were cast in distinctly patriotic terms. A journalist in the daily Télégraphe emphasized the importance of Cailletet’s experiments for France and the whole of Europe: ‘The successive discoveries with which you have enriched science have brought your name to the attention of France and the whole of Europe’, and, as one of the first journalists to report his achievements just after their announcement at the Académie des Sciences, he asked for information on Cailletet’s life and background. Other daily newspapers too, both in France and abroad, sought to get information about the ‘illustre savant’. And periodical publications, such as the popular science journals La Nature, Revue Scientifique and L’Univers Illustré, prepared articles on the liquefaction of oxygen. The editor of La Nature, Gaston Tissandier, commissioned an engraver to draw Cailletet’s instruments and asked Cailletet to prepare a brief summary of his work for use in the article on him. In an earlier article, on 5 January 1878, the geologist and scientific writer Stanislas Meunier had already summarized the achievement. After describing Pictet’s fourth demonstration of the liquefaction of oxygen, Meunier went on to state that his compatriot Cailletet was attempting the liquefaction of the other permanent gases, in particular nitrogen, air and hydrogen. According to Meunier, Cailletet had already succeeded in liquefying nitrogen (as a mist) under 200 atm pressure at 13 °C, and air and hydrogen at 280 atm and −29 °C.

Cailletet had indeed claimed that he had liquefied nitrogen and air and that there was convincing evidence that he had successfully liquefied hydrogen as well. Apparently, hydrogen that was compressed to 280 atm and then allowed to suddenly expand created an instantaneous very fine mist that disappeared immediately. Cailletet admitted that during his first attempts to liquefy hydrogen he had not observed anything in particular, but he believed that in the experimental sciences the habit of carefully observing phenomena finally led to the recognition of signs that had previously gone unnoticed. Cailletet’s experiments were conducted repeatedly before prominent members of the scientific community such as Berthelot, Deville and Mascart, all of whom had endorsed the (hasty) announcement of the liquefaction of hydrogen. In these experiments, testimony and repeatability were deemed necessary to validate the results. After Cailletet’s
announcement in *Comptes Rendus*, Berthelot confirmed that he had witnessed the liquefaction of nitrogen that left "no place for any uncertainty". He was more circumspect, however, in what he said about the liquefaction of hydrogen. Although the experiments on hydrogen "ont fourni des signes non douteux", they were less rigorous and more difficult than those with nitrogen.45

The publicity surrounding Cailletet’s achievements did not stem solely from publications in the daily and periodical press. A private letter from the instrument maker Eugène Ducretet to Cailletet shows that in addition to visitors to Ducretet’s atelier who admired the simplicity of Cailletet’s liquefaction apparatus, Ducretet himself took a smaller, mobile version of the apparatus and arranged demonstrations in Belgium and other neighbouring countries.46 This second version of the apparatus was the one that was presented at the Académie des Sciences and was normally used at the École Normale.47

**PRODUCING LIQUID OXYGEN IN A STABLE FORM**

Having provided the first tangible indications that oxygen could be liquefied, Cailletet continued his research in broadly the same direction. He improved his equipment, devised new experimental techniques, focused on the construction of better manometers, and studied, alone or in collaboration, the changes of state near the critical temperature and the properties of liquid gases and those of mixed gas hydrates.48 In 1882 he started using liquid ethylene as a cooling agent.49 The evaporation of ethylene had the merit of producing a very low starting temperature, and Cailletet used it (despite its high cost) as an important tool in his work on the liquefaction of oxygen. However, his first experiments with ethylene did not lead to conclusive results. Having cooled compressed oxygen to the boiling temperature of liquid ethylene ($-105^\circ\text{C}$) and then allowed it to expand, Cailletet observed a violent boiling and projection of a liquid in part of the cooled tube. But he could not determine whether this liquid pre-existed or was formed at the moment when the oxygen expanded.50

Cailletet initially used liquid ethylene in the form of a jet that struck the apparatus to be cooled and was therefore wasted in each experiment. In the following year, however, he referred to an improvement of his apparatus, which incorporated the circulation of the liquid in a steel cylinder. In his note to the Académie he announced the ultimate goal of this improvement, which was the preparation of boiling oxygen for use in the liquefaction of hydrogen.51

Small quantities of liquid oxygen were finally obtained by Zygmunt Wróblewski and Karol Olszewski in April 1883. Having been exiled for six years in Siberia because of his participation, as a student in Kiev, in an insurgence against the Russians, Wróblewski managed to complete his studies at Heidelberg and to gain his doctorate at the University of Munich in 1874. Before accepting a position at the Jagiellonian University of Cracow in 1882, he visited various laboratories in London, Oxford, Cambridge and Paris, to broaden his horizons. Similarly, Olszewski had completed his studies in Heidelberg under Bunsen and in 1876 was appointed Professor of Chemistry at the Jagiellonian University. Their collaboration, although it did not last long, yielded impressive results. Only a couple of months after they started working together, the two Polish scientists sent a note to the Académie in which they announced their success in liquefying oxygen in a stable form. Modifying Cailletet’s apparatus, Wróblewski and Olszewski had evaporated
ethylene in a vacuum and thereby obtained a temperature of \(-137 \, ^\circ\text{C}\), below oxygen’s critical point.\(^{52}\) On 18 April Wróblewski sent a cordial letter to Cailletet to thank him for the congratulatory letter he had received, and generously insisted that his own success should properly have been Cailletet’s.\(^{53}\)

**LIQUID OXYGEN: IN THE MI(d)ST OF A DEBATE**

Even a close reading of the published notes and memoirs in *Comptes Rendus* and the various scientific journals of the time provides us with an incomplete account of the events surrounding the liquefaction of the permanent gases. Although the announcement of the liquefaction of oxygen in a stable form by Wróblewski and Olszewski was received with moderate enthusiasm by the French scientific community, an extended article by Jules Jamin on the history of the liquefaction of air in the literary and cultural magazine *Revue des Deux Mondes* provoked a fierce reply by Wróblewski, which revealed many details of a debate that the ‘official sources’ had attempted to silence.\(^{54}\)

Jamin’s article, entitled ‘How air was liquefied’, gave a historical account of the liquefaction of air from the pneumatic experiments of the seventeenth century to the most recent developments. Although Jamin acknowledged the contribution of both Wróblewski and Olszewski to the liquefaction of oxygen in a stable form, his emphasis on the importance of Cailletet’s initial achievement and several pejorative insinuations concerning the originality of the work of the two Polish scientists aroused Wróblewski’s indignation.

According to Jamin’s account, in 1877 both Cailletet and Pictet had clear indications that oxygen could be liquefied, but neither of them had managed to collect liquid oxygen in a stable form. In the article Jamin argued that collecting liquid oxygen in a stable form called for refrigerants, such as ethylene, that were more powerful than carbon dioxide or nitrous oxide. As Jamin described it, Cailletet had already started working on ethylene and had announced his project publicly,\(^{55}\) when a year later the Académie received two telegrams from Cracow announcing the complete liquefaction of oxygen and nitrogen.\(^{56}\) Jamin referred to Wróblewski as one of Cailletet’s assistants in the laboratory at the École Normale, who, using Cailletet’s apparatus and with the collaboration of Olszewski, had managed to boil ethylene in a vacuum and so reached \(-150 \, ^\circ\text{C}\), a temperature sufficient for the complete liquefaction of oxygen.\(^{57}\) However, when asking who deserved to be recognized as having liquefied these gases, Jamin opted, to Wróblewski’s dismay, for Cailletet. For Jamin, Wróblewski and his collaborator Olszewski were until then

[two] unknown men, one of whom had assisted Cailletet in his work and with whom Cailletet had shared confidences…rushed to execute Cailletet’s most recent experiment that had been publicly announced…they had executed the work of skilful labourers, but they had not invented anything, and, even if they had wanted it, they had not taken anything from Cailletet.\(^{58}\)

In support of his view, Jamin reproduced a letter by J. B. Dumas, the deceased former secretary of the Académie des Sciences, in which Dumas urged an unnamed colleague to support Cailletet’s candidature for the prix Lacaze, particularly in view of Wróblewski’s and Olszewski’s achievements.\(^{59}\)

Wróblewski’s 30-page reply focused precisely on these issues: on his own research agenda that had led him independently to the study of the liquefaction of gases; on his
construction of experimental apparatus that, although similar to Cailletet’s, had introduced important modifications; on his stay in Paris; on the successful execution of a series of experiments using ethylene as a refrigerant that had eventually led to the liquefaction of oxygen and nitrogen; and finally on a debate concerning the paternity of the idea to use methane as an even more powerful refrigerant than ethylene.

WRÓBLEWSKI’S POINT OF VIEW

Wróblewski linked his current work on gas liquefaction to his previous research agenda on the absorption of gases by liquids and solids, which included the study of phenomena at high pressures and involved the liquefaction of the absorbed gases.60 His earlier experiments had required the construction of suitable apparatus, which was designed by Wróblewski and commissioned, at the beginning of April 1881, from the Parisian instrument maker Ducretet. The method and equipment were similar to those used by Andrews and Cailletet, but they had superior features; for example, the apparatus contained up to six times more gas.61 According to Wróblewski, Ducretet agreed to build the apparatus, which then had to be tested in a laboratory. Wróblewski visited the laboratory of the École Normale to obtain permission from Deville to test his new apparatus and experiment with it. However, because Deville was in Italy at the time, he was advised by the chemist Henri Debray (1827–88) to return in August, by which time Ducretet was expected to have finalized the apparatus.

On his return to Paris in August 1881, Wróblewski learned of Deville’s death and the appointment of Debray as director of the laboratory. He was accepted in the laboratory, and he began his experiments with his new apparatus. Because there was no suitable pump in the laboratory, Wróblewski bought a Cailletet pump from Ducretet, the 300th pump sold by that time. It was therefore obvious to Wróblewski that he could not be accused of improper behaviour when the instrument he used was already widely available. The same argument had already been made in his memoir on the liquefaction of oxygen, in which he insisted that the use of Cailletet’s apparatus was widespread in France and that Cailletet’s methods were not secret because he had presented them in public both at the International Electrical Exhibition in Paris in 1881 and later at Debray’s laboratory at the École Normale.62 Moreover, Wróblewski’s experiments had begun a year before Cailletet returned to Paris to work with ethylene.63

Wróblewski began his experiments on the solubility of carbon dioxide in water, mainly because he could use Andrews’s data for the relations between the volume, pressure and temperature of this particular gas. His experiments led him to the creation of the carbonic acid hydrate, and they were warmly received by the Académie.64 Having been praised by Debray, Wurtz and Troost and invited by the Société de Physique to demonstrate his experiments in public, Wróblewski wondered how Jamin could characterize him as ‘unknown’.65

By the time that Wróblewski published his first note on carbonic acid hydrate, at the beginning of February 1882, Cailletet had returned to Paris with a new pump to begin his experiments with ethylene. However, when he learned about Wróblewski’s experiments on hydrates, he decided to start working on hydrates as well, and to postpone his new series of experiments on the liquefaction of oxygen. Wróblewski described in rather derogatory terms Cailletet’s engagement with this new line of research and questioned his method. But Cailletet managed to produce the hydrate of hydrogen phosphate, and some
other substances that, according to Wróblewski, he was not able to identify. In fact, Cailletet, apart from announcing the production of the hydrate of hydrogen phosphate in 1882, described a process that yielded numerous other hydrates that he had not examined yet. In that way, he and his collaborator, Bordet, were laying the ground for a possible future priority claim with regard to the study of these substances. According to Wróblewski, however, Cailletet’s concern, more than anything else, was to stay in history as a trailblazer in high-pressure chemistry.

Once Cailletet’s ‘razzia’ (the term Wróblewski used) to establish his reputation in the field had simmered down, he started his experiments with ethylene. He conducted his experiments on the complete liquefaction of oxygen with the use of ethylene in March and April 1882 in Paris. However, as we have already seen, his efforts failed once again. Because of these unsuccessful attempts, Cailletet considered the possibility of liquefying other gases that were more difficult to liquefy than ethylene, so as to lower further the limit of ‘extreme cold’. In Wróblewski’s view, such a proposal was a sign that Cailletet had not thought of evaporating ethylene in a vacuum. A week after the publication of his note in *Comptes Rendus*, Cailletet left Paris for Châtillon-sur-Seine, and at the beginning of July he dismantled his apparatus and removed it from the laboratory of the École Normale.

Wróblewski described Cailletet’s attempts to use ethylene as a powerful refrigerant in disparaging terms. Cailletet, he wrote, was unsuccessful both because his technique was faulty and because he had failed to overcome the problems he encountered in his experiments. Hence, in the end, Cailletet succeeded in liquefying oxygen only after being introduced to Wróblewski’s and Olszewski’s method for the liquefaction of oxygen, nitrogen and carbon monoxide, which included the slow expansion of ethylene and the use of boiling ethylene in a vacuum. Wróblewski agreed with Jamin on one point, however: ‘[Cailletet] n’est point un savant de profession, mais bien un curieux.’ He had the material resources and wanted to make himself useful to science.

To show that he had the support of the French academic community, Wróblewski reproduced a series of letters addressed to him on the occasion of his liquefaction of oxygen. Moreover, he pointed to Dumas’s supportive presentation of his research before the Académie. The same position was taken in the French press, which published enthusiastic articles on Wróblewski’s achievements. In particular, Stanislas Meunier in an article in *La Nature* mentioned that although many members of the Académie regretted that Cailletet was not the first to produce liquid oxygen in stable form, his own opinion was that Wróblewski’s experiments indicated that Cailletet was not only good at conducting experiments but also good at training students, namely Wróblewski. On 9 April 1883 Cailletet himself had sent a congratulatory letter to Wróblewski, in which he also asked about the details of his experiments. In his reply Wróblewski insisted that the name of Cailletet would always be linked to the liquefaction of gases and that his own success in no way diminished Cailletet’s contribution. He described in general terms the apparatus he had used and reminded Cailletet that he must have seen it in operation at the laboratory of the École Normale before he left Paris. In the letter, Wróblewski also mentioned his use of the principle of the vacuum, which had already been employed by Johann Natterer in Vienna some 40 years earlier for the liquefaction of nitrous oxide.

The reproduction of letters in support of Wróblewski’s case continued with a letter of 24 April 1883, in which Debray regretted that Cailletet seemed to lack Wróblewski’s patience and perseverance. Cailletet, according to Debray, had an ingenious spirit but no truly scientific method. A few months later, on 1 January 1884, Debray replied to
Wróblewski’s note on the temperature of boiling oxygen in enthusiastic terms and underlined the latter’s great skill and remarkable determination.\(^{73}\)

In February 1884 Wróblewski wrote to Debray on the occasion of his note on the alleged liquefaction of hydrogen.\(^ {74}\) In Wróblewski’s view, to liquefy hydrogen, experimentalists had to proceed in a completely different way based on the construction of new apparatus and the simplification of the methods used. Being exhausted from the intense experimental work he had undertaken in recent years, Wróblewski considered that it was now for Cailletet to take up the baton, and he decided to take a break with a trip to Germany and Paris. On his arrival in Paris in April 1884, Wróblewski found Cailletet in a state of defeat. Although he had reported to the Académie on 19 November 1883 that he was about to construct new apparatus with which he would be able to liquefy oxygen in large quantities,\(^ {75}\) he confessed to Wróblewski that ‘oxygen did not want to flow’.\(^ {76}\) Wróblewski tried to encourage Cailletet to continue his research, insisting that research on the liquefaction of gases was just beginning and that Cailletet had plenty of time ahead of him for new achievements. Wróblewski also gave Cailletet practical advice concerning his new apparatus and the reasons why, in Wróblewski’s view, Cailletet’s experiments had failed. As Wróblewski believed, although the experiments were very expensive, Cailletet had had the resources to complete them and would have done so if only he had been more patient.\(^ {77}\)

Recognizing how valuable Wróblewski’s help would be, Cailletet asked him to spend a year in Paris so that the two of them would be able to complete the research together. However, Wróblewski’s refusal of Cailletet’s invitation led to a radical worsening of relations between them. It seems that the tension began when Wróblewski, in a paper on the density of liquid oxygen, argued that it was Pictet who had first obtained oxygen in a stable form.\(^ {78}\) This incident was aggravated by the introduction of a new procedure that involved the use of methane as a refrigerant. Not being able to obtain any quantity of liquid oxygen with his new apparatus, Cailletet started considering the use of methane. Without mentioning that he had discussed the use of methane with Wróblewski, Cailletet announced to the Académie on 30 June 1884 that he intended to use the gas, apparently as a way of ensuring his priority for the use of the technique.\(^ {79}\) Wróblewski soon afterwards sent a note to the Académie on the properties of methane, which did not appear in Cailletet’s note, but adding that he was aware that Cailletet was also considering using it as a refrigerant.\(^ {80}\) On 4 August Cailletet asked the Académie to open an envelope that he had deposited on 12 December 1881. In the sealed document he described a series of experiments that, as he claimed, made it possible to liquefy large quantities not only of carbon dioxide and nitrous oxide but also of ethylene and methane.\(^ {81}\) Wróblewski, however, showed very easily that the experiments could not actually have taken place, because in 1881 Cailletet did not have the means to conduct them; alternatively, if they had been successful, he would have had no difficulty in liquefying oxygen in a stable form.\(^ {82}\)

**CONCLUSION**

After 1877, priority disputes about the liquefaction of gases and related innovations in techniques and instrumentation were commonplace. After Cailletet’s and Pictet’s proof that oxygen had been liquefied, there was no doubt that the rest of the permanent gases could be liquefied as well. The liquefaction of hydrogen, finally achieved by James Dewar...
in 1898, was to provoke similarly intense controversy between early low-temperature researchers. Cailletet had claimed to have seen hydrogen mist in 1877, Raoul Pictet to have liquefied it in 1878 and Wróblewski to have done so in 1884, and Wróblewski’s former collaborator Olszewski claimed that he had succeeded in 1885. With the exception of Raoul Pictet, all of them seem to have been concerned about matters of priority. However, once oxygen had been obtained in a stable form in 1883, whoever wanted to claim priority in the liquefaction of hydrogen had to obtain something more substantial than a transient mist of the gas.

The liquefaction of hydrogen posed a great experimental challenge, because its critical temperature was estimated to be about $-243^\circ C$. As already mentioned, Cailletet had liquefied oxygen by compressing it and lowering its temperature through a simple expansion of the gas, without making use of the Joule–Thomson effect, known since 1852. It was Dewar who made systematic use of the Joule–Thomson effect after learning about its efficacy for cooling around 1895. In addition, Dewar made use of Wróblewski’s deductions regarding the critical point of hydrogen after the latter’s study of the isothermals of the gas. Hydrogen was finally liquefied in May 1898, by what has been called a ‘brute-force’ approach. To demonstrate the decisive role of van der Waals’s early work in the development of the field of low temperatures, Kostas Gavroglu has used as an example Dewar’s failure to liquefy helium and has contrasted it with the research programme of the Dutch physicist Heike Kamerlingh Onnes. In contrast with Dewar’s lack of programmatic claims, Kamerlingh Onnes’s main motivation for the liquefaction of helium was not the experimental challenge as such but the provision of supporting evidence for van der Waals’s law of corresponding states and the generalization he himself provided in 1881. The last of the permanent gases, helium, was liquefied by Kamerlingh Onnes in 1908.

In a similar manner, Cailletet’s failure to produce liquid oxygen in a stable form and his dispute with Wróblewski may also be grounded on the former’s ‘atheoretical approach’ and the theoretically informed approach of Wróblewski. It seems that the combination of the more ‘theoretically minded’ Wróblewski and the ‘dexterous and inventive’ Olszewski made up for the lack of resources and old equipment in Cracow. Moreover, Kurt Mendelssohn has argued that Wróblewski and Olszewski succeeded where Cailletet failed because they had a better understanding of the physical principles involved in gas liquefaction. Both of them worked on the estimation of the critical temperatures and other physical constants of gases, used van der Waals’s law of corresponding states, and measured their isothermals. Cailletet, in contrast, never seemed greatly interested in the theory behind experimentation, even though he had inspired Kamerlingh Onnes through the boldness of his experiments and techniques. The various comments both by Wróblewski and by Debray concerning Cailletet’s lack of ‘scientific method’, patience and perseverance may have alluded to this characteristic.

It is interesting to examine why priority disputes were so frequent between 1877 and 1908. The liquefaction of oxygen initiated the emergence of a new research field, characterized by the introduction of new experimental techniques, initially in the absence of any particular theory to ‘guide’ the experiments. The early experimentalists themselves were not entirely confident about the results they obtained, and the same was true of the eyewitnesses who were called to testify to the success of their experiments. An important element in this confused situation was that the new research field involved not only the liquefaction of all the permanent gases but also the investigation of the fundamental
properties of matter at very low temperatures. Work of such potential importance carried with it the promise of fame for its pioneers as well as of national pride. It is therefore not surprising that Cailletet aspired to a place in history as the ‘founder of high-pressure chemistry’ and that he was supported in his ambition by the French academic community. The 1870s in France were characterized by widespread perceptions that the nation’s science was in decline, a judgement that emerged strongly in reports by Louis Pasteur and Adolphe Wurtz, among others. The rhetoric of the declinists was mainly intended to persuade the French government to increase funding for the infrastructure of higher education. In these circumstances, the liquefaction of oxygen by Cailletet, even if he supported the work from his own resources, helped to raise the morale of the French scientific community and to foster perceptions of the achievement as a French success. This was evident in the praise that France’s leading savants bestowed on Cailletet’s work, even if it was clear that at times Cailletet himself did not stand up for science in the way his peers expected him to do.

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NOTES

3 Although the Polish spelling of his name is Zygmunt Wróblewski, in French publications his name usually appears as Sigismond Wroblewski.
5 The Second Empire in France (1852–70) was a period during which scientific research was closely linked to the industrial needs of the country. Deville had managed to gain the support of Napoleon III through his work on aluminium, which was of national interest mainly for its military uses. In 1854 he set up a laboratory at the chemical factory of Javel in Paris for the large-scale production of aluminium, which was initiated a couple of years later at the La Glacière plant. In 1857 the plant was relocated to Nanterre because of neighbourghood pollution. See also R. Fox, The savant and the state. Science and cultural politics in nineteenth-century France, p. 95 (Johns Hopkins University Press, Baltimore, MD, 2012); A. J. Rocke, Nationalizing science. Adolphe Wurtz and the battle for French chemistry, p. 289 (MIT Press, Cambridge, MA, 2001); E. Bardez, ‘Henri Sainte-Claire Deville (1818–1881)’ in Itinéraires de chimistes, 1857–2007. 150 ans de chimie en France avec les présidents de la SFC (ed. L. Lestel), pp. 475–481 (EDP Sciences, Les Ulis, 2007), at p. 476.
Letter from Henri Saint-Claire Deville to Cailletet, 2 February 1864 (Archives de l’Académie des Sciences [hereafter AAS]).


One of Cailletet’s aims was to examine the chemical phenomena that took place during case-hardening in a cementation box (a box of wrought iron in which case-hardening is effected).


Various local newspapers reproduced an article entitled ‘Le laboratoire’ first published by Edmond Perrier in Le National. See reprints of the article in the newspapers Le Bien Publique (20 Mars 1869), Le Châtillonnais et l’Auxois (25 Mars 1869) and L’Indépendant (28 Mars 1869) with the title ‘Une chimie nouvelle’.


Although the Joule–Thomson effect had been known since the 1850s, neither Cailletet nor Pictet made use of it. It was only in 1895 that William Hampson in Britain and Carl von Linde in Germany introduced it into their liquefying apparatus. J. S. Rowlinson, ‘James Joule, William Thomson and the concept of a perfect gas’, Notes Rec. R. Soc. 64, 43–57 (2010), at p. 50.

Cailletet, op. cit. (note 20).


Letter from Marcellin Berthelot to Cailletet, 21 November 1877 (AAS).

M. Berthelot, ‘Observations’, CR 85, 1017 (1877).

Berthelot, op. cit. (note 25).

In his study of the gas–liquid equilibrium, the Irish chemist Thomas Andrews (1813–85) indicated the existence of a critical point—corresponding to a critical volume, a critical pressure and most importantly a critical temperature—at which the phases of a substance are not distinguishable. Above the critical point, even the highest pressure cannot yield liquefaction. See J. S. Rowlinson, ‘The work of Thomas Andrews and James Thomson on the liquefaction of gases’, Notes Rec. R. Soc. 57, 143–159 (2003).


Ibid., p. 225. Andrew’s experimental results were interpreted in terms of molecular physics by Johannes van der Waals. See A. Kipnis, B. Yavelov, J. S. Rowlinson, *Van de Waals and molecular science* (Oxford University Press, 1996).

Many French experimentalists had an important role in the consolidation of the significance of the critical point after Andrews’s and van der Waals’s work. However, their work remained purely experimental and involved no theoretical considerations.

Cailletet was finally elected as a corresponding member at the Mineralogy section of the Académie on 17 December 1877.

Letter from Raoul Pictet to Cailletet, 19 January 1878 (AAS). In this letter Pictet made clear the theoretical assumptions that led him to the liquefaction of gases, declaring himself a fervent supporter of the atomic theory and the laws of molecular physics.

Letter from the Secretary of the Royal Society to Cailletet, 10 November 1878 (AAS).

See also letter by Pierre Giffard from the newspaper *Le Gaulois. Littéraire et Politique* to Cailletet, 18 January 1878 (AAS), asking him for an interview.

Letter from the editor of *L’Univers Illustre* to Cailletet, 25 January 1878 (AAS), asking him for a portrait photograph to be published with an article written by Joseph Decaisne on the liquefaction of gases.

Letter from Gaston Tissandier to Cailletet, 3 April 1877 (AAS).


Ibid., p. 1270.

M. Berthelot, ‘Note’, *CR* 85, 1271 (1877).

Letter from Ch. Avezon to Cailletet, 4 January 1878 (AAS).

Letter from the editor of *L’Univer sur les échanges dans le voisinage du point critique de température*, *CR* 92, 840–843 (1881), and L. P. Cailletet and P. Hautefeuille, ‘Recherches sur la liquefaction des mélanges gazeux’, *CR* 92, 901–904 (1881).


Ibid., p. 1226.


Letter from Wroblewski to Cailletet, 18 April 1883 (AAS).


By ‘public announcement’ Jamin was referring to a note published by Cailletet on the use of ethylene for the production of low temperatures: Cailletet, *op. cit.* (note 49).

Wroblewski and Olszewski, *op. cit.* (note 52).

Ibid., p. 102. The prix Lacaze for chemistry was indeed awarded in 1883 to Cailletet as the first to show that the so-called permanent gases could be liquefied, and because he provided a simple apparatus with which these experiments could be performed without danger: ‘Prix Lacaze’, *CR* 98, 1106–1109 (1884).

Ibid., p. 102.


Wróblewski’s studies on carbonic acid hydrate were published in 1882 in a series of notes in *Comptes Rendus*. Wróblewski used the notes to acknowledge the hospitality shown to him by Debray. See, for example, S. Wroblewski, ‘Sur la combinaison de l’acide carbonique et de l’eau’, *CR* 94, 212–213 (1882).


Cailletet, *op. cit.* (note 43).


One such instance was a supportive comment that Dumas inserted in *Comptes Rendus* just before Wróblewski and Olszewski’s note on the liquefaction of oxygen, nitrogen and carbon monoxide. It has to be noted, however, that Dumas, as well as all other French savants, always alluded to Cailletet as the initiator of this research field and presented Wróblewski as one of Cailletet’s followers.

One of the points that Wróblewski made in his reply to Jamin was that he had never been Cailletet’s student. Meunier was probably reporting the views of the members of the Académie, but adopting a milder position. S. Meunier, ‘Académie des Sciences—séance du 16 avril 1883’, *La Nature*, no. 516, pp. 335–336 (1883), at p. 335.


S. Wroblewski, ‘Sur la liquéfaction de l’hydrogène’, *CR* 98, 304–305 (1884). To this note Cailletet added a lengthy comment, in which he drew attention to his earlier attempts to liquefy hydrogen and the production of a fine mist, and stressed that Wróblewski’s results came as a corroboration of his own work: L. P. Cailletet, ‘Observations au sujet de la communication précédente’, *CR* 98, 305–306 (1884).

Cailletet, *op. cit.* (note 51).


Wroblewski and Olszewski, *op. cit.* (note 62).


James Dewar had also suggested the use of liquid methane as a coolant at the British Association for the Advancement of Science meeting at Southport in 1883: J. S. Rowlinson, *Sir James Dewar, 1842–1923. A ruthless chemist* (Ashgate, Farnham, 2012), p. 81. Wróblewski attributed the priority of its suggestion and use to Dewar and not to Cailletet.

Rowlinson, *op. cit.* (note 21).


