
Between Physics and Chemistry: Early-Low-Temperature Research, 1877-1908

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The early period of low-temperature research, that is from 1877 to 1908, when all the so-called permanent gases were finally liquefied, is commonly considered to be the period during which another sub-branch of physics, that of low-temperature physics, emerged. Indeed, it is the case that, after the discovery of superconductivity in 1911 and of the various properties of liquid helium below 2.9 K in the early 1930s, research at the low temperatures was almost completely dominated by physicists. However, this was not so for the period during which the liquefaction of the so-called permanent gases dominated low temperature research. The most important developments in gas liquefaction took place in a period characterised by the application of thermodynamics on physical and chemical research, the reappraisal of chemical theory and the elaboration and acquisition of increasingly complex experimental apparatus and skills. It appears that chemists were as much as physicists actively involved in early low-temperature research. What, then, has been the role of the chemists in the development of a series of practices, which eventually formed a branch of physics?

In this paper an attempt is made to show some aspects of a more general thesis that is that the history of low-temperature research, and especially the period between the liquefaction of oxygen in 1877 and the liquefaction of helium in 1908, has been an integral part of the history of physical chemistry. The period to be examined is the period when physical chemistry was also in search of its own identity. It was a period when physical chemistry was articulating its own autonomous language with respect to both physics and chemistry, when it was charting its own research agendas and formulating its own theoretical framework. It was also a time when the sub-disciplinary boundaries were drawn and re-drawn, and when these processes were deeply influenced by the different cultures of physicists and chemists.

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The inclusion of early-low-temperature research in the history of physical chemistry has not been previously discussed in the literature of the field. Similarly, historians of low-temperature physics have paid almost no attention to the ways in which low-temperature research has been influenced by the attempts to establish physical chemistry as a separate discipline. The first section of this paper reviews some of the basic assumptions made and some of the main historiographical issues raised among historians of physical chemistry. It will be argued that one of the main preoccupations of historians has been the examination of the emergence of physical chemistry as a new discipline under the influence of Wilhelm Ostwald, Svante Arrhenius and Jacobus Van't Hoff. However, such an approach has overshadowed the complex procedures related to the development of physical chemistry. Evidence from primary sources is provided in order to show that the links between early-low-temperature research and physical chemistry were also acknowledged by contemporary workers.

The second section deals with some aspects of the history of early-low-temperature research. Starting with the liquefaction of oxygen in 1877 by Raoul Pictet and Louis Cailletet, it will be argued that the interplay of both physics and chemistry, physicists and chemists, held an important role in the production, maintenance and use of low temperatures. However, physical chemistry is not characterised by the mere application of physical methods into chemistry and vice versa. Although this reductionist view has been sustained by the contemporary scientists, the liquefaction of helium by Kamerling Onnes in 1908 demonstrates that the success of his project did not depend only on the development of techniques for lowering the temperature and for purifying gases. The liquefaction of helium was the result of a research programme built upon a solid theoretical knowledge on the behaviour of gases, and combined with systematic research in instrumentation and thermometry, issues that have been intrinsically connected to the agenda of physical chemistry.

Historians and the emergence of physical chemistry

Historians traditionally identify the emergence of physical chemistry as a new discipline with the spectacular take-off of the work of Wilhelm Ostwald (1853-1932), Svante Arrhenius (1859-1927) and Jacobus Van't Hoff (1852-1911) in the 1880's.

Wilhelm Ostwald initiated his experimental work in the 1870s. He studied the problem of chemical affinity, paying special emphasis to electrochemistry and che-

mical dynamics. Critical of the descriptive character of chemistry, he aimed at redirecting the focus of chemists onto questions related to chemical change rather than on the nature of chemical compounds. His work was characterised by his determination to look for the general laws of chemical change, using physical techniques and presenting these laws in a mathematical language. Around the same period, in 1884, Svante Arrhenius submitted his doctoral thesis on the galvanic conductivity of electrolytes. His thesis demonstrated that electrolytes, when dissolved in water, dissociated into electrically positive and negative ions. The ions were supposed to be carriers of electricity and chemical activity. Arrhenius's thesis, although it almost failed to fully convince the faculty staff of the University of Uppsala, where it was submitted, gained quickly the support of Ostwald and Jacobus Van't Hoff. In fact, Van't Hoff used it in order to validate his own research on the extension of the laws of thermodynamics from gases to dilute solutions. This powerful ensemble of ideas and techniques –the new theory of solutions, the theory of electric dissociation and their approach through thermodynamics– that was created by the work of the three ionists (as Ostwald, Arrhenius and Van't Hoff were called) is considered to be the foundation stone of the discipline of physical chemistry.

The consolidation of the discipline was achieved through some well-orchestrated activities towards the institutionalisation of the field. From 1884, Wilhelm Ostwald wrote textbooks in which he attempted to promulgate his vision for a reformed chemistry, and numerous other scientific works on analytical chemistry, electrochemistry, and inorganic chemistry. Along with his writing of textbooks, he founded, in 1887, the first *Journal of Physical Chemistry* (the *Zeitschrift für physikalische Chemie*), and around the same time he was put in charge of the organisation of the Department of Physical Chemistry at the University of Leipzig. Similar developments took place in Great Britain and France, and contributed to the further establishment of physical chemistry. By the end of the nineteenth-century, the new discipline had gained important institutional space. Physical chemistry grew rapidly also in the United States, after some of Ostwald's American students gained positions and power in America's expanding University system.

The founders of the discipline used a carefully crafted rhetoric in order to promote and consolidate their field. As Diana Kormos Barkan has shown, the programmatic texts of the prime movers of physical chemistry stressed the links between physical chemistry and its ancestors.¹ In these works, physical chemistry was presented as the natural outcome of the 'progress' in both sciences of physics and che-

mistry, and their interaction through the systematic approach of research questions laying between the two sciences.²

Some historians, such as Erwin Hiebert and R.G.A. Dolby, have paid attention to the creation of the discipline of physical chemistry within the context of a growing professionalisation and the emergence of other sub-disciplines (such as pharmaceutical and medical chemistry, experimental psychology, etc.) during the second half of the 19th century.³ Their approach was characterised by a careful examination of the scientific work and the network activities of the three ionists. Similarly, John Servos' seminal book on physical chemistry focuses almost exclusively on the growth of physical chemistry in the US.⁴ In his introductory chapter, Servos briefly discusses the emergence of the discipline, placing emphasis on the discontinuities rather than the continuities between older scientific traditions and the physical chemistry of the 1880s. For Servos the physical chemists of the 1880s altered the balance between theory and experiment, affirmed the role and use of mathematics in chemistry, revealed the relations of chemistry with other sciences, and changed the topography of chemistry itself.⁵

Most of the secondary literature treats physical chemistry from either the point of view of its emergence as a new discipline, or the point of view of individual contributions to its main research topics such as the theory of solutions, chemical kinetics and chemical thermodynamics.⁶ The story seems a straightforward and a rather unproblematic. Despite the analysis of various debates that inevitably sprung from the enforcement of the new theories to the scientific community, there is little reflection on the process of legitimisation of the language of physical chemistry and the praxis of its practitioners.⁷

The task to narrate the emergence of physical chemistry as a new discipline with respect to the works of the three ionists seems to have been accomplished. What is still missing is, perhaps, a better understanding of the rich ontological, epistemic and conceptual commitments that underpinned the emergence of physical chemistry. The emergence of physical chemistry as a new scientific field cannot be identified with the mere application of physical theory and techniques to chemistry. This reductionist view sounds far too simplistic to justify the emergence, consolidation and endurance of an autonomous discipline. Even the founders of the discipline did not give a clear answer to whether physical chemistry emerged as an attempt to unify chemistry under general principles, or whether they wanted to develop a new specialty that would stand apart from chemistry and would make use of physical methods in order to better understand chemical processes. As John Servos has pointed out, Ostwald's use of both the terms 'General chemistry' and 'Physical chemistry' is indicative of his ambivalence of whether physi-

cal chemistry could be conceived as part of chemistry, or reduced to the domain of physics.⁸

During the period under examination, there were plenty of investigations that fell into the borderland between physics and chemistry, such as the study of the physical properties of compounds: the measurements of specific heats, the index of refractivity, the rotation of polarised light etc. During the same period we have the emergence of a new research field –the low temperatures– created by the liquefaction of the permanent gases. Both chemists and physicists, employing chemical and physical techniques, became interested in using the low temperatures for probing into the properties of matter and extending their theoretical understanding of these properties. Despite the importance of the development of highly complex physical and chemical techniques for lowering the temperature and for purifying gases, early-low-temperature researchers seems to have participated in, and contributed to the articulation of a new theoretical framework that was to accommodate the latest developments in the theory of thermodynamics and its various applications.

Low-temperature research and physical chemistry in primary sources

An obvious place to look for connections between low-temperature research and physical chemistry would be in the newly founded journals of Physical Chemistry. However, it is not surprising if such information is not readily available. We must not forget that the early journals on physical chemistry were instrumental in the consolidation of the emerging discipline, but also for the promotion of the research agendas of its editors. Therefore, Ostwald's journal of physical chemistry founded in 1887 was mainly concerned with the main topics dealt by his research school. Similarly, Wilder Bancroft's *Journal of Physical Chemistry*, founded in 1896 at Cornell University, reflected its editor's rather idiosyncratic conception of physical chemistry, which stressed the need for a qualitative understanding of its principles and its usefulness in industry and medicine.⁹ However, papers on liquefaction and the thermodynamic properties of gases and gaseous mixtures were occasionally accommodated in both journals.¹⁰

Such papers were also included in the Swiss *Journal de Chimie Physique*. Correspondence between the editor of the journal, the chemist Philippe Guye (1862-1922) and the Dutch physicist Heike Kamerlingh Onnes (1853-1926), is again indicative that research in the low temperatures was not considered unre-

lated to physical chemistry. Philippe Guye had asked Kamerlingh Onnes to lend his support to his journal not only by allowing him to include his name among the principal collaborators of the journal, but most importantly by sending him articles on the work conducted at the Leiden Cryogenic Laboratory.¹¹ Guye wanted to include in his journal articles related to physical chemistry, especially articles on the equation of state, a 'question that he wished to treat extensively in the journal'.¹²

Perhaps the most convincing evidence is to be found in general journals. The fact that both physicists and chemists were involved in early-low-temperature research is made evident from an examination of articles that were related to the low temperatures published in the *Comptes Rendus (CR)* of the Academy of Sciences in Paris. From 1877 to 1908 low-temperatures related articles were classified under both the categories of 'chemistry' and 'physics'. These articles referred to the liquefaction of gases, the use of special instrumentation and thermometric methods, the study of the properties of matter at low temperatures, and the application of the low temperatures in industry. Although most of these articles fell under the headings of 'chemistry' and 'physics', it is hard to identify them as 'purely' chemical or 'purely' physical research. This apparent difficulty is partially resolved in 1901, when the category 'physical chemistry' appears for the first time in the *CR*, and under which some of these articles (especially articles dealing with the measurement of the densities of liquid gases at low temperatures as well as the measurement of atomic volumes and molecular weights) were thereafter classified.¹³

Interesting information is derived when one attempts to classify the authors of the scientific papers inserted in the *CR* according to their background. Although one can single out a greater number of chemists compared to physicists working in the low temperatures, the difficulty of identifying someone as a physicist or a chemist reinforces the hypothesis that the development of research in the low temperatures, at least for sometime, could have played an important role in the making of the culture of physical chemistry. What remains to be seen is how research in the low temperatures has contributed to the emergence of physical chemistry. A brief examination of some aspects of the history of low temperature research may shed light on the way in which the challenge of the liquefaction of the permanent gases led to the articulation of a theoretical framework, a theoretical agenda and an autonomous language with respect to both physics and chemistry.

Aspects of early low-temperature research and the emergence of physical chemistry

The liquefaction of oxygen by the French Louis Cailletet (1823-1913) and the Swiss Raoul Pictet (1846-1926), simultaneously in 1877, is often considered to be the date of the birth of low-temperature research. The first systematic attempts to liquefy gases are traced back to Michael Faraday's liquefaction of chlorine in 1823. Until 1845, Faraday had managed to liquefy almost all known gases, apart from six that were then named the 'permanent gases'. These were the oxygen, nitrogen, hydrogen, nitrogen dioxide, methane, and carbon monoxide. Until 1877, attempts to liquefy the so-called permanent gases had all failed. The Austrian physician Johannes Natterer (1821-1901) had attempted liquefaction by the exertion of pressures reaching up to the enormous number of 3,000 atmospheres. Similarly, the French chemist Marcelin Berthelot (1827-1907) had attempted to liquefy some of the permanent gases by applying pressures of over 800 atm without success.

The key to the liquefaction of the permanent gases was given by the experimental work of the Irish chemist, Thomas Andrews (1813-1885). Andrews's work was mainly concerned with the calorimetry of chemical reactions, and the properties and constitution of ozone. However, around the late 1850s and probably through the influence of James Thomson, he became interested in the liquefaction of the permanent gases.¹⁴ He undertook the study of the gas-liquid equilibrium using carbon dioxide. In this study, Andrews pointed to the existence of a critical point, which corresponds to a critical volume, a critical pressure and most importantly a critical temperature, at which point the phases of the substance are not distinguishable. Above the critical point, even the highest pressure cannot yield liquefaction. In 1869 Andrews submitted a paper for the Bakerian lecture of the Royal Society, where he reported his experiments on carbon dioxide and stated his belief on the continuity of the gaseous and liquid states of matter.¹⁵

Andrews's experimental results were interpreted in terms of molecular physics in Johannes Van der Waal's thesis, defended in 1872 under the same title as Andrews's Bakerian lecture. Van der Waal's worked substantially on the law of the ideal gas. The reformulation he provided gave a fairly adequate explanation of Andrew's experimental results, and demonstrated the continuity of the transition from the gaseous to the liquid state. The great virtue of Van der Waals's equation was that it applied to every substance. Some years later, in 1880, Van der Waals was able to show not only the continuity of the transition from one state of aggregation to another, but also their identity. His formulation of the law of corresponding states implied a similarity among all gases and liquids.¹⁶

Various experimentalists, especially in France, played an important role in consolidating the significance of the critical point after Andrew's and Van der Waal's work.¹⁷ Emile Amagat, perhaps the most systematic among them, started his experimental work examining the influence of temperature on the deviations from Boyle's law. His work was purely experimental, and he did not proceed to any theoretical claims. By the early 1890s he had compiled his data in 70 comprehensive tables, which were widely used by his contemporaries.¹⁸

Before going into the implications of Van der Waals's work for low-temperature research, it is useful to first take a look into the liquefaction of oxygen. Upon the simultaneous announcement of the liquefaction of oxygen by Raoul Pictet and Louis Cailletet at the Academy of Sciences in Paris, it was primarily chemists who stepped in to applaud the achievement. Jean-Baptiste Dumas, reminded them of the prediction of Lavoisier, the 'immortal creator of modern chemistry', that air, or at least part of its constituents, could be liquefied at very low temperatures.¹⁹ Sainte-Claire Deville testified that he was present at Cailletet's experiments, conducted in his chemical laboratory at the Ecole Normale.²⁰ Marcelin Berthelot praised Cailletet for his systematic work that led to the liquefaction of the permanent gases, and used Pictet's results in order to lend support to some of his own views on high-pressure chemistry.²¹ But how did research in the low temperatures relate to both physics and chemistry for these early experimentalists? Both Raoul Pictet and Louis Cailletet, although they followed different paths to achieve the liquefaction of oxygen, had clear understandings of the importance of the critical point. Let us not forget that in the minds of people Van der Waals's equation is a reformulation of an equation that is known by the name of the doyen of chemistry, Robert Boyle.

After studying physics and chemistry in Geneva and Paris, Pictet returned to his hometown and started experimenting in the low temperatures, while at the same time he followed closely the lucrative refrigeration industry.²² His interest in the liquefaction of gases stemmed also from a wider theoretical concern about the constitution of bodies. His extended memoir on the liquefaction of oxygen, published in the *Annales de chimie et physique* in 1878, includes a rather long exposition of his microscopic approach to the laws of nature, within the context of the mechanical theory of heat and Clausius's kinetic theory of gases.²³

For Pictet, the identification of heat with motion required an understanding of the laws that govern the behaviour of the ultimate particles of matter. His approach was non-mathematical, mostly qualitative and highly speculative. He often complained that the use of mathematics obscured the physical meaning of the problems under examination, and sought to present his work with a minimum use of

mathematics and in simple terminology.²⁴ He resorted to a mechanical explanation of physical theory, making use of a molecular model with a specific configuration of the particles and the forces that acted between them, very close to the one conceived by Van der Waal's. Pictet considered bodies to be constituted of impermeable molecules, submitted to the force of cohesion, and set in motion. The liquefaction of gases was usually achieved by mere compression, during which the particles of the gas were brought close enough for the force of cohesion to act upon them. Brought to a certain distance, and upon the influence of the force of cohesion, the molecules of the gas precipitated one upon another and formed a liquid. In order to explain the impossibility of liquefying all gases by mere pressure, Pictet argued that it was the motion of the particles of the body, which counteracted the force of cohesion. Since temperature was directly related to the motion of the particles, he reasoned that the lowering of the temperature of the body would reduce the motion of the particles. Two conditions had, therefore, to be fulfilled for the liquefaction of gases: the exertion of great pressures, and the obtaining of great cold.²⁵ Although, Pictet must have been aware of Andrew's and probably Van der Waal's work, he never mentioned them explicitly. He only once referred to the term 'critical point'; a concept, he believed, that was logically deduced from his own theory.²⁶

The liquefaction of oxygen was presented by Pictet as a proof of the validity of his microscopic theory of matter. Despite his non-rigorous theoretical exposition, Pictet provided an exhaustive description of the experimental apparatus and set-ups employed. His virtuosity in experimentation and dexterity in the construction and manipulation of his experimental apparatus was highly appraised. Even Victor Regnault was highly impressed by Pictet's remarkable experimental apparatus.²⁷ In fact, it was his liquefaction of oxygen, the experimental apparatus and the method employed, that seemed to be of interest at least to the French scientific community rather than his speculations about the nature of bodies and the action of the force of cohesion.

After the liquefaction of oxygen, and his unsuccessful attempts to liquefy hydrogen, Pictet used his skills in the obtaining of low temperatures in order to probe into the properties of matter and further his theoretical investigations.²⁸ His interests lay in the domains of both physics and chemistry, and rested on the hypothesis that all physical and chemical phenomena result from the interplay of two attractions, namely, the attraction of matter to matter, and the attraction of matter to the ether. His investigations were characterised by strong ontological and methodological commitments. He believed that it was possible to account for all physical phenomena on a celestial, terrestrial, and molecular scale in terms of

central forces between particles. His main concern was to give thermodynamics a physical imagery, making a minimal use of mathematics, but seconding his reasoning by empirical data.²⁹

Although Pictet's theories had no impact on his contemporaries, his preoccupations may be considered as relevant to the emergence of physical chemistry. In Pictet's mind, research in the low temperatures clarified issues about the constitution of bodies, gave a physical imagery to the laws of thermodynamics, and submitted the study of physical and chemical phenomena under the same principles. It was not a matter of reducing chemistry to the laws of physics, rather than articulating a framework within which both physical and chemical phenomena were treated in a similar fashion.

Let us now pass to the second experimentalist, Louis Cailletet, who had liquefied oxygen independently and almost simultaneously with Pictet. Contrary to Pictet, Cailletet's initial interest in the liquefaction of gases seems to be almost exclusively due to the experimental challenge imposed, rather than for any theoretical concerns. His interest in gases had its roots in the training he received by the chemist Henri Sainte-Deville, and his first professional steps as an industrialist.

Cailletet attended courses at the *École de Mines* as an 'auditeur libre', and frequented the chemical laboratory of Henri Saint-Claire Deville. However, he soon returned to his birthplace, Châtillon-sur-Seine, to work at his father's ironworks. There, he continued to pursue his scientific interests that were closely connected to Saint-Claire Deville's work on the phenomenon of dissociation.³⁰ Work on dissociation had revealed that there was a strict analogy between chemical decomposition and the change of the physical state of matter, when it passed into the solid, liquid and gaseous condition.³¹ Cailletet provided supportive evidence for his mentor's theory by having the gases suddenly cooled at the moment of their collection, and demonstrated that at very high temperatures these gases were indeed dissociated to their elements.³²

His interest in the liquefaction of gases began from his research on liquid carbon dioxide.³³ A few years later, in 1877, he attempted and succeeded the liquefaction of acetylene by pure pressure.³⁴ During his work with acetylene an accidental leak of the pressurised gas from a tap caused a sudden cooling of the gas, which led to momentary condensation. The production of abrupt cold by the expansion of a compressed gas, led Cailletet to contemplate upon the possibility of using such a technique in the liquefaction of the permanent gases.³⁵

Cailletet's research on chemical phenomena at high pressures, and the compression of gases led him gradually to get interested in the liquefaction of gases. His

work on chemistry, the dexterity he obtained with his involvement in high-pressure chemistry, as well as his expertise in building apparatus for the manipulation of such phenomena, were all useful experience for his later work. Contrary to Pictet, Cailletet's experimental work was followed neither by theoretical claims, nor by ontological commitments.³⁶ Although he was aware and made use of the notion of the critical point, he never made any claims about the underlying ontology in Van der Waal's work.

As already mentioned, the estimation of the critical points was crucial for the liquefaction of gases, and many experimentalists were drawn into the study of isotherms in order to calculate the critical temperatures under which liquefaction was achievable. The liquefaction of hydrogen posed an even greater experimental challenge since its critical temperature was estimated to be around -243°C . It was finally the British chemist James Dewar who succeeded its liquefaction in 1898. For this, Dewar made extensive use of Zygmunt Wroblewski's deductions regarding the critical point of hydrogen following from a study of the isothermals of the gas. In his paper "Liquid Hydrogen", Dewar stated that Wroblewski's results were "a signal of triumph for the theory of Van der Waals and a monument to the genius of the Cracow physicist".³⁷

Despite the occasional references to the importance of Van der Waals's work in Dewar's writings, Kostas Gavroglu has argued that Van der Waals's considerations played only a very small part in Dewar's experimental work. The British chemist had not published a single theoretical work, nor was there any reference to the measurement of isotherms despite the reporting of the values of a large number of physical parameters at low temperatures.³⁸ In order to demonstrate the decisive role of Van der Waals's early work in the development of the field of the low temperatures, Gavroglu used as an example, Dewar's failure to liquefy helium and compared it to the research programme of the Dutch physicist, Heike Kamerlingh Onnes.

Just after his appointment to the Chair of Experimental Physics at the University of Leiden in 1882, Heike Kamerlingh Onnes established the first cryogenic laboratory and initiated his work on the low temperatures with an aim to liquefy hydrogen. When Dewar managed to liquefy hydrogen, Kamerlingh Onnes turned to the liquefaction of the newly-discovered gas helium. Contrary to Dewar's lack of programmatic claims, Kamerlingh Onnes's main motivation for the liquefaction of helium was not the experimental challenge imposed but the provision of supporting evidence to Van der Waal's law of corresponding states, and the generalisation he himself provided in 1881.³⁹ Kamerlingh Onnes did not ascribe only to the phenomenological implications of Van der Waals's theory but also to its onto-

logical and methodological commitments. In his paper 'General theory of the fluid state' where he discussed the law of corresponding states, he suggested that corresponding states could be visualised as states of similar molecular movement. In other words, the motion of the molecules of substances at the corresponding states, was considered to be dynamically similar.⁴⁰ Like Van der Waals, Kamerlingh Onnes was interested in drawing conclusions from physical-mechanical-arguments rather than sophisticated mathematics.⁴¹

In practice this meant that one could explore the possibilities of liquefying gases by applying the law of corresponding states to the results of working with other substances in higher temperatures. The liquefaction of helium in 1908 was achieved through the systematic research of Kamerlingh Onnes based on the work started by Van der Waals. Around 1900 Kamerlingh Onnes had started investigating the isotherms of monoatomic, diatomic gases and their binary mixtures. These investigations, along with considerable improvement of the cryogenic apparatus, led the Dutch physicist to arrive at a fairly good estimate of the critical point of helium, which was necessary prior to any attempt to liquefy it.⁴²

As Kostas Gavroglu has shown, the measurements of isotherms had been decisive for the liquefaction of helium. For Kamerlingh Onnes the liquefaction of helium was not an aim by itself, but a proof of the validity of the law of corresponding states. On the contrary, Dewar's work on the liquefaction of gases seems not to have been guided by strong theoretical considerations. Dewar did not explore the possibilities offered by the law of corresponding states. In the case of helium, his 'brute force' approach did not prevail. Dewar's approach to low-temperature research is delineated in his presidential address to the Society of Chemical industry in Glasgow. There, he referred to the two schools of chemistry: one of organic chemistry, and another in which physical chemistry was predominant. According to Dewar, physical chemistry examined the physical relations of chemical action, as well as the effect of the physical action of the constituents taking part in chemical changes.⁴³ For Dewar, chemical changes were considered to be parallel and similar to physical operations, and therefore measurable with physical accuracy.⁴⁴ The liquefaction of gases was a good example of the analogy between chemical and physical transitions, while research in the low temperatures followed strictly the consideration of the physical side of chemistry.⁴⁵ However, Dewar never went beyond the notion of physical chemistry as a way of adopting physical techniques for chemistry.⁴⁶

On the contrary, for Kamerlingh Onnes the law of corresponding states was not only a useful tool for the estimation of the critical points, but provided also a completely novel way of dealing with phenomena lying between physics and che-

mistry.⁴⁷ Like Pictet's rather crude considerations, Kamerlingh Onnes's work was not characterised by the mere application of physical laws in the molecular scale, but by the articulation of a framework within which both physical and chemical phenomena were treated in a similar fashion.

Concluding remarks

This paper attempts to present some preliminary results concerning the emergence of low-temperature research within the context of physical chemistry. Traditionally historians identify the emergence of physical chemistry with the work of Wilhelm Ostwald, Svante Arrhenius and Jacobus Van't Hoff on the theory of solutions, chemical kinetics and chemical thermodynamics in the 1880s. The institutionalisation of the field was achieved through the establishment of specialised journals, and research departments. Current historiography on physical chemistry focuses mostly on the emergence of this new research field as a new discipline, and on individual contributions to its main research areas.

It has been shown that other research areas, and especially low-temperature research, have also contributed to the establishment of physical chemistry as an autonomous field in respect to both physics and chemists. Such a thesis questions also the commonly assumed position that the various developments in early low temperature led in a straightforward manner to the establishment of a new branch of physics, that of low-temperature physics.

The involvement of both chemists and physicists in low-temperature research concerning the low temperatures is indicative of a continuous negotiation about the identity of this emerging field. Although the first successful attempts to liquefy the permanent gases were mostly due to the employment of complex experimental apparatus and skills, the liquefaction of helium by Kamerlingh Onnes in 1908 was not simply a matter of improving the existing techniques of liquefaction. The liquefaction of helium was the outcome of the study of a series of theoretical issues explicitly expressed or implied by the work of Johannes Diderik Van der Waals on the equation of state and the law of corresponding states. Kamerlingh Onnes and his collaborators in the cryogenic laboratory of the University of Leiden developed a rather characteristic culture and characteristic laboratory practices in which theoretical research was in direct relationship to experimental studies and vice versa.

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Notes

¹ Diana Kormos Barkan, "A Usable Past: Creating Disciplinary Space for Physical Chemistry," in *The Invention of Physical Chemistry*, eds Mary Joe Nye et al. (Dordrecht: Kluwer, 1992), 175-202.

² It is interesting to note that the only recent accounts of a general history of physical chemistry, written by authors trained as physical chemists, trace the origins of the field in past scientific activity dating back to Robert Boyles's natural philosophy. See Keith Laidler, *The World of Physical Chemistry* (Oxford, New York: Oxford University Press, 1993) and Cathy Cobb, *Magick, Mayhem and Mavericks. The Spirited History of Physical Chemistry* (Amherst, NY: Prometheus books, 2002).

³ Erwin Hiebert, "Developments in Physical Chemistry at the Turn of the Century," in *Science, Technology and Society in the Time of Alfred Nobel*, eds Carl Gustav Bernhard et al. (Oxford: Pergamon Press, 1982), 92-115; R.G.A. Dolby, "The case of physical chemistry," in *Perspectives on the Emergence of Scientific Disciplines*, eds G. Lemaine et al. (Hague: Mouton, 1976), 63-73.

⁴ John Servos, *Physical Chemistry from Oswald to Pauling: The Making of Science in America* (Princeton: Princeton University Press, 1990).

⁵ Servos, *Physical Chemistry*, 40.

⁶ See for example H.A.M. Snelders, "The Dutch Physical Chemist J.J. van Laar (1860-1938) versus J.H. van't Hoff's 'osmotic school'," *Centaurus* 29 (1986): 63-71 and Helge Kragh, "Before Quantum Chemistry: Erich Hückel and the Physics-Chemistry interface," *Centaurus* 43 (2001): 1-16.

⁷ See for example: R.G.A. Dolby, "Debates over the theory of solutions," *HSPS* 7 (1976): 297-404 and "Thermochemistry vs Thermodynamics: the 19th century controversy," *History of Science* 22 (1984): 375-400.

⁸ John Servos, "A Disciplinary Program that Failed: Wilder D. Bancroft and the Journal of Physical Chemistry, 1896-1933," *ISIS* 73 (1982): 230.

⁹ Servos, "A disciplinary program", 3.

¹⁰ See for example: Pierre Duhem, "On the liquefaction of a mixture of two gases," *Journal of Physical Chemistry* 5 (1901): 91-112; F.G. Cottrell, "On air liquefiers," *Journal of Physical Chemistry* 10 (1906): 264-274.

¹¹ Letter 30 avril 1903 from Philippe Guye to Heike Kamerling Onnes. Museum of Boerhaave, archives of Kamerlingh Onnes, inv. no 297.

¹² Letter 9 October 1903 from Philippe Guye to Heike Kamerling Onnes. Museum of Boerhaave, archives of Kamerlingh Onnes, inv. no 297 (my translation from French).

¹³ See for example: Ph.-A. Guye, Ed. Mallet, "Constantes critiques et complexité moléculaire d'hydrocarbures élevés," *CR* 133 (1901): 1287; A. Ponsot, "Chaleur spécifique des corps au zéro absolu," *CR* 134 (1902): 703; Ph.-A. Guye, "Application de la méthode des densités limites aux gaz liquéfiables," *CR* 147 (1907): 1360; Joseph de Kowalski, "La phosphorescence progressive à basse température," *CR* 151 (1910): 810.

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- ¹⁵ Thomas Andrews, "On the continuity of the gaseous and liquid states of matter," *Phil. Trans. R. Soc. Lond.* 16 (1869): 575-590.
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