Thomas Andrews

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RESUMEN. Thomas Andrews (1813-1885) realizó importante investigaciones en el área de la termoquímica, la termodinámica del equilibrio de fases y la naturaleza y propiedades del ozono. Sus trabajos sobre calor de reacción entre bases y ácidos son notables por su avanzada técnica y buenos resultados numéricos, a pesar haberse realizado antes de las teorías de Arrhenius y del establecimiento de la ley de conservación de la energía. Sus contribuciones más importantes son el establecimiento del estado crítico del equilibrio líquido-vapor, la continuidad en el cambio de fase, la correcta definición de los conceptos de vapor y gas, y el hecho de que el ozono es un estado alotrópico del oxígeno.

ABSTRACT. Thomas Andrews (1813-1885) performed important research in the area of thermochemistry, thermodynamics of phase equilibrium, and the nature and properties of ozone. His work on the heat of reaction between acids and bases is notable for its high technique and good numerical results, in spite of having been done at the time before the advent of the Arrhenius theory and when the law of conservation of energy were unknown. His most important contributions are the establishment of the critical state in vapor-liquid equilibrium, the continuity in the change of state, the correct definition of the concepts of vapor and gas, and the fact that ozone is an aIlotropic state of oxygen.

LIFE AND CAREER

The best information about the life, career, and scientific publications of Thomas Andrews is found in the recollection of Andrews's papers prepared by Peter Guthrie Tait (1831-1901), his friend and collaborator.[1]

Thomas Andrews, the eldest son of Thomas John Andrews, a linen merchant in Belfast, and Elizabeth Stevenson, was born at Belfast, on the 19th December 1813. Andrews was first educated at the Belfast Academy and the Belfast Academical Institution, where he studied Mathematics under James Thomson (1822-1892) and classics under the Rev. Dr. Hincks. His most intimate companion was Thomas O'Hagan (1812-1885), afterwards Lord Chancellor of Ireland; and the close friendship lasted through life. After working for a short time in his father's office during 1828, he left to study chemistry under Thomas Thomson (1773-1852), Regius Professor of Chemistry at the University of Glasgow. In a letter of introduction to Thomson, Dr. James McDonnell (1762-1845), founder of the Belfast Medical School, described Thomas Andrews as a modest, silent, and very capable boy, who wished to study chemistry profoundly, not merely as being connected with his professional business, but as a great branch of human knowledge. Andrews attended the Chemistry Class during the winter session 1828-1829, and one of his teachers, William Meikleham (1771-1846), professor of Natural Philosophy, certified that in the Public Class of Natural Philosophy "*he distinguished himself for ability*".[1]

After this first college session, and while only fifteen years old, Andrews published his first scientific paper, *On the Action of the Blowpipe on Flame.*[2] Although the action of the flame produced by the blast of the blowpipe had been tried upon almost every substance, yet its influence upon the flame itself had never been examined. Andrews directed the flame of a candle urged by a mouth blowpipe upon that of another candle of equal size, and found that on applying the blast, the flame of the second candle was inverted and exhibited nearly the same appearances as a flame acted on immediately by the blowpipe.

This publication was shortly afterwards followed by a note *On the Detection of Baryta or Strontia when in Union with Lime,*[3] characterized by the care and analytical skill so typical of all his experimental work.[1]

After graduation Andrews spent a short period in Jean-Baptiste André Dumas's (1800-1884) laboratory in Paris in 1830. In addition to his chemical work, Andrews spent some time each day in the *Hôpital de la Pitié* (Today: *Hôpital de la Salpêtrière*). During his stay abroad McDonnell wrote to Thomas's father that his son "*should enter Dublin College, and return home from that, without pursuing the usual course of study there. He should at the same time be bound nominally to a surgeon...after which he should go to France and Italy, and remain there until he has satisfied his own mind; and, returning from thence, should attend as many terms in Dublin as would qualify him for taking the degree of Bachelor of Arts, and either or both the other degrees in Surgery and Physick; taking care, in these pursuits, never to relinquish the idea of becoming ultimately a merchant if it became his duty or interest to do so*". It is probable that this letter, coupled to a severe attack of fever, resulted in Thomas' return to England and enrollment at Trinity College, Dublin, for a four-year course in Medicine. In Dublin he distinguished himself in classics as well as in science, and was awarded several prizes. He attended at the same time lectures in the School of Physics in the Meath Hospital, and in the Richmond Surgical Hospital. In 1834 Andrews attended hospital and dispensary practice in Belfast; he spent the ensuing winter and summer sessions in Edinburgh, where he studied under the physicians R. S. Allison, Thomas Graham (1805-1869), John Thomson, Robert Knox (1791-1862), and William Turner (1832-1916), Professor of anatomy.[1]

In 1835, Andrews obtained the diploma of the Royal College of Surgeons of Edinburgh and the degree of M.D. of the University of Edinburgh. His thesis was entitled *On the Circulation and the Properties of the Blood* and among other items, reflected his work on the composition of the blood of cholera patients[4] and the changes in the composition of blood that took place as a consequence of repeated bleedings.[5]

The information available on the changes that occurred in the blood of cholera patients was incomplete and contradictory, and Andrews took advantage of a cholera outbreak in Belfast to perform new experiments on the subject. Andrews believed that the discrepancies were actually due to the analytical methods employed. He analyzed blood samples taken at different stages of advancement of the illness and found that the only difference between the blood of cholera patients and that of healthy ones was that in the former there was a deficiency of water in the serum and a consequent excess of albumin, that the saline ingredients of the serum was the same as in healthy blood, that the red globules and fibrin were normal, and that the lack of fluidity of the blood, its dark color, and the bulk of the crassamentum (blood clots), were a result of the increased viscosity of the serum.

In 1835 he was offered, and declined, the Chairs of Chemistry in the Richmond School of Medicine and in the Park Street School of Medicine, Dublin. In the same year, having settled in Belfast as a physician, he was the first Professor appointed to teach chemistry in the Royal Belfast Academical Institution. During the next ten years he delivered extended courses of lectures and gave instruction in practical chemistry to a large number of students.

In 1842 Andrews married Jane Hardie Walker and three years later gave up both his medical practice and his teaching post to become the first vice-president of Queen's College, Belfast. He also became professor of Chemistry at Belfast when teaching started in 1849, and did not retire until 1879.

During the next few years Andrews published a number of original papers connected with voltaic circuits[6-8] where he concluded that contact with an electronegative metal increased the ordinary action of an oxyacid on an electropositive metal if the acid is so dilute that the metal becomes oxidized from the decomposition of water, and retards the action if the acid is so concentrated that the metal is oxidized from the decomposition of the acid itself. In a paper on *Galvanic Cells with Strong Sulfuric Acid*[8] he showed that the composition of the gas given off at the cathode varied in a remarkable manner with the temperature. His results on the subject are more valuable when consideration is taken that of the fact that at that time there was no knowledge on the constitution and dissociation of strong sulfuric acid.[1]

Early in 1845 Andrews was informed of the wish of several of the Fellows of King's College, London that he should present himself as a candidate for the Chair of Chemistry there. He declined however to do so, but in the autumn of the same year he resigned his connection with the Belfast Institution and gave up his private practice, on his appointment as Vice-President of the Northern College, now Queen's College, Belfast.[1]

It had been understood from the first that Andrews was to the Professor of Chemistry in Belfast, but he was required (as a matter of form, merely) to produce a few testimonials. These he obtained at once, in the highest terms, from such prominent scientists as Thomas Graham, Humphrey Lloyd (1800-1881), James Mac Cullagh (1809-1847), Justus von Liebig, and Dumas.[1]

Shortly after this Andrews initiated his detailed researches on ozone, which were communicated to the British Association for the Advancement of Science and the Royal Society with the titles *On the Polar Decomposition of Water by Common and Atmospheric Electricity*[9] and *On the Constitution and Properties of Ozone.*[10]

In 1852 Andrews was elected a member of the committee appointed by the British Association *"to propose such general views regarding a more systematic method of publishing scientific papers as may assist in rendering the records of facts and phenomena published in the United Kingdom more complete, more continuous, and more convenient than they are at present"*.[1]

Andrews resigned the offices of Vice-President and Professor of Chemistry in Queen's College, Belfast, on October 1879. The grave debility from which he had long been suffering increased so much that in October 1885 he was confined to bed and sank gradually, until passing away on November 26. His grave is in the Borough Cemetery, Belfast where a granite obelisk now marks the spot. His wife, three daughters and two sons survived him. The elder son became Major in the Devonshire Regiment and the younger a member of the Irish Bar.[1]

HONORS AND AWARDS

Andrews received many honours for his contribution to science and academic life. He was awarded degrees of LL.D. by Trinity College, of Dublin (1872), the University of Glasgow (1877), and the University of Edinburgh. In 1844 the Council of the Royal Society awarded him a Royal Medal for his paper entitled *On the Thermal Changes Accompanying Basic Substitutions* and received an award of 1 000 francs from the Académie des Sciences for his memoir on the determination of the quantity of heat disengaged in chemical combination. This was given *á titre d'indemnité* as the greater part of the contents had already been published. He was elected a member of the Royal Irish Academy in 1839: an original member of the Chemical Society in 1841; honorary member of the *"Societé des Sciences Naturelles du Canton de Vaud"*; fellow of the Royal Society (1849); Honorable Fellow of the Royal Society of Edinburgh (1870) to succeed Graham; and in 1884 he was elected corresponding member of the Royal Society of Sciences of Göttingen.

His most famous paper, *The Continuity of the Liquid and Gaseous States of Matter"*,[11] was selected by the Royal Society as the Bakerian lecture for 1867. A Grace of the Senate of the Queen's University, Ireland, was passed on 1879, conferring on him the honorary degree of Doctor in Science. In 1867 Andrews was President of the Education Section of the Belfast Meeting of the Social Science Congress. In 1880, Andrews received a letter from the Duke of Marlborough, then Lord Lieutenant of Ireland, offering him, by Her Majesty's gracious permission, the honor of civil knighthood; Andrews declined the distinction on account of his bad health.[1]

In 1883 the Andrews' Studentship for the promotion of the study of Chemical and Physical Science was established. Andrews' portrait now hangs in the Examination Hall of the College.[1]

SCIENTIFIC AND ACADEMIC CONTRIBUTION

Andrews published over 50 papers in different areas of thermodynamics and physical chemistry. Andrews's physicochemical researches fell broadly into four groups: (a) galvanic studies of the action of acids on metals, (b) the constitution and properties of ozone, (c) calorimetry, and (d) the continuity of the gaseous and liquid states.[12] His most significant results will be discussed below, after summarizing his contributions in the subjects of sociology and academic planning and philosophy.

Social and University affairs

Andrews's main contributions in these two subjects were published in 1867.

During the Belfast Meeting of the Social Science Congress he read a paper entitled *Suggestions for Checking the Hurtful Use of Alcoholic Beverages* where he discussed the physical and mental damages produced by drinking in the working classes, and the intensification of this produced by insufficient food, impure air, and strong forms of alcohol. In his words: *"No one will be inclined to dispute that the public-house and gin palace, as they now exist, are an outrage to society and a disgrace to the country, and that the mischief they do to the working classes...is incomparably greater than any advantage they afford as places of refreshment. With the view of abating this great evil, I propose in the first place, to have them changed into places truly of refreshment, the only purpose for which they ought to be licensed. No house should, according to my view, be licensed as a public house for the sale of alcoholic beverages, unless it be provided with ample appliances for cooking and serving food, and the license should be withdrawn if it be found that these appliances are not made use of, and that the public-house is devoted solely to the sale of stimulants."*

Andrews's only writings bearing in any way on political matters are *Chapters of Contemporary History*. The first, entitled *Studium Generale* and published in 1867, is a historical and critical discussion of the function and mission of a University, with special reference to the Queen's Colleges. Many of the points he raises are also valid today. The immediate occasion of its publication was the issue of a supplementary charter to the Queen's University, completely changing the relations of the Colleges to the University and enabling the senate of the University to confer degrees on any person who had matriculated in the University and was deemed qualified by the service, although he had not studied in any of the colleges.[1]

In this work, Andrews sketched the history of the University of London, the Queen's University, and the Catholic University in Ireland, specially comparing the constitution of the latter with that of the Catholic University at Louvain (founded in 1833). Andrews had studied the question of the function of Universities and of the duty of Governments to the higher education. He regarded the system of grouping a number of teaching institutions and placing them under the care of a so-called University, as fatal to freedom and progress. Here are his words on this subject: *"The admirers of the institutions which have arisen in France...will not view with favor the proposal to establish a third university in Ireland...According to their views, the present institutions for higher education ought rather to be assimilated to one another and combined into a national university, like the Imperial University of France. Considering the great control over the education of the country such a system would give to the executive government, it is not surprising to find it regarded with favor in some influential circles. It may, perhaps, be said that it would afford facilities for the prevention of abuses and for the introduction of new methods of teaching. But such advantages would be a poor compensation for the depressing influence a gigantic organization of this kind would exert upon the free play of thought and action. Universities, if properly conducted, ought to be what they are in Germany, centers of intelligence scattered over a country, each shining brightly with its own peculiar light, and not coldly reflecting the rays of a distant luminary. The only considerations, which ought to limit their number, are the requirements of the country and the means of sustaining them in efficiency. From their nature, they must always be costly institutions, for they will utterly fail in their object and fall into disrepute, if conducted by inferior men, or with insufficient appliances... few...are aware of the immense advantages England herself has derived from them... It may indeed be said, without exaggeration, that England would long ago have been forced to establish universities, after the Scottish or German model, for the use of the middle classes, if the universities of Scotland and Germany had not furnished her with a large supply of men, well versed in the sciences connected with the useful arts. The United States of America have followed in the same path and have covered their vast territories with universities, some of which are already favorably known. Canada and Australia have likewise not failed in this respect to perform their duty, and have fully supplied their inhabitants with the means of university education."*

"As regards the internal arrangements and methods of teaching, it is desirable...that they should be as varied as possible in different universities...Education and training must form the foundation of civilized life in every country...The imperial institutions of France, from their magnitude and imposing form, may captivate the rulers, and even the people of a country; but similar institutions were coincident with the decline of the Roman Empire, and literature and art soon withered under their protection...the chief end of higher education, the cultivation of habits of accurate and independent thought, will be best attained by allowing the fullest freedom of action, to those who are engaged in the difficult task of training the youth of a country in the noble walks of literature and science".[1]

Andrews strongly advocated the foundation of a true teaching University for London and the conversion of the Owens College, Manchester, into a University of the Scottish or German type. If some such scheme as this were carried into effect, Andrews believed that ten times the present number of candidates would qualify themselves annually for this distinction, by passing through a well-digested undergraduate course, to the great advantage of the community and the elevation of the middle class of English society.[1]

Thermochemistry

Around 1840 Andrews started working in thermochemistry and in the period of 1841-1848 published his main contributions on the heat of neutralization of diluted solutions of acids and bases,[13] on the heat of reaction between chlorine, bromine, and iodine and metallic compounds,[14] the heat of formation of chlorine derivatives,[15] on the heat of reaction during basic substitutions,[16] the heat of reaction of different compounds with oxygen and chlorine,[17] metallic substitutions,[18] and a general view of the state of art of thermochemistry.[19] His work took place at about the same time as that of Hermann Hess (1802-1850) of Saint Petersburg, and, interesting enough, although their experimental results were similar, their interpretation was not usually so.

Andrews's memoirs show his careful design of the experiments, identifying all the possible sources of errors and efforts to reduce them to a minimum. Thus, among possible sources of errors he mentions the facts that all reagents must be initially at the same temperature; accounting for the heat losses through the walls of the reaction vessel; the thermal capacity of the latter, the mercury, and the glass in the thermometer, and the fact that the heat capacity of the final solution is different from that of the reagents. In order to properly understand his knowledge of the pertinent physics, attention must be paid to the fact that he conducted his experiments at a time when the first law of thermodynamics was still not an accepted fact, and years before the concept of entropy and available energy would become known.

Already in his first incursion in the area,[13] he realized that the heat of neutralization of acids and bases must be a function of the concentration and for this reason he confined himself to the study of highly diluted solutions. His experimental technique was very simple: the reagents were put in two separate vessels, one containing the quantity of alkali whose heat of reaction was sought and the other slightly more than the equivalent of acid (nitric) required to neutralize the alkali (KOH). After both vessels were at the same temperature they were mixed and the increase in temperature observed with a delicate thermometer. Andrews remarked that it should be clear that the same amount of heat was realized if the two reagents were in stoichiometric ratio, or one was in slight excess. A slight excess was used to make the reaction faster and to have a more uniform solution. A correction was also applied for the heat absorbed by the glass and mercury of the thermometer and heat losses to the atmosphere, and the fact that the final solution is a diluted solution of potassium nitrate and not pure water.

Andrews came to the following conclusions:

(a) The heat of neutralization is determined by the base and not by the acid; the same base producing when combined with an equivalent of different acids, nearly the same quantity of heat; but different bases a different quantity, (b) When a neutral salt is converted into acid salt by combining with one or more atoms of acid, no change in temperature occurs, (c) When a neutral salt is converted into a basic salt by combining with an additional proportion of base, the combination is accompanied with the evolution of heat (exothermic).[13,20]

It is interesting that Hess[21] obtained similar results but interpreted them in the opposite manner. The principle, as stated by Hess was that different bases disengage the same quantity of heat in combining with the same acid. According to Andrews, experiments performed with concentrated acids were not adapted to yield simple results, since the mere circumstance of dilution with water products produced the evolution of large quantities of heat in the case of some acids and none or a very slight change in temperature, in the case of others. It was for this reason that when an alkaline solution was neutralized by the addition of an equivalent of nitric acid, the heat disengaged was very different according to the concentration of the acid, while the same circumstances produced little or not effect when tartaric acid was employed. In many apparently simple reactions it was difficult to ascertain with certainty all the combinations and decompositions which occurred. The liquids before mixture were, in fact, solutions of the acid and the alkali in the state of hydrates, and as large quantities of heat were evolved during their subsequent solution, an equal absorption of heat would take place when these combinations were destroyed.

According to Mackle[12,22] the difference of interpretation between Andrews and Hess was due that neither of them had really good experimental grounds for making either assertion; they were studying the reaction between two electrolytes in pre-Arrhenius days when the fundamental neutralization process was not understood.

Andrews gave a table of the experimental results for potassium and sodium hydroxide and ammonia, with 14 acids, barites with four acids, and also for bases which are insoluble and slightly soluble in water, such as magnesia, calcium hydroxide, zinc oxide, and lead oxide, with acids such as sulfuric, nitric, hydrogen chloride, hydrogen iodide, and acetic acid.[13] Andrews's obtained the value −13.1 kcal/mol for the reaction HCl/NaOH, with the currently accepted value of −13.34 kcal/mol for the reaction at infinite dilution.

New experiments were performed for determining the accuracy of this principle using dilute solutions of potash hydrate, and salts of calcium oxide, magnesia, barites, strontia, manganese, iron (ferrous and ferric), mercury, lead, copper, silver, and iron. All the results justified the principle that when one base displaced another from its neutral combinations, all taken in the state of dilute solution, the heat effect was always the same with the same bases, but in general different with different bases. The only significant deviation (which Andrews was unable to explain) was the great development of heat that took place during the neutralization of dilute sulfuric acid by alkaline solutions.[16]

In a following work,[17] Andrews studied the heat of reaction of oxygen with hydrogen, carbon monoxide, methane, ethylene, carbon, sulfur, methanol, phosphorus, zinc, iron, tin, copper, and cuprous oxide, and the heat of reaction of chlorine with potassium, tin, antimony, arsenic, mercury, copper, zinc, and cuprous oxide. In every case he reported the value of the heat of reaction in different units, (one liter or one gram of oxygen or chlorine, or with one liter or one gram of the substance in question), in order to compare his results with the ones reported by Pierre-Louis Dulong (1785-1838).[17,23] For the oxidation of one mole of hydrogen Andrews reported the value 67.62 kcal/mol, compared with today's value of 68.815; for the combustion of one atom mole of carbon he obtained 92.12 instead of today's value of 94.054 kcal/mol. According to Mackle[22] his value for carbon is low probably because he worked at atmospheric pressure, and even with the 30 atm oxygen pressure of modern bomb calorimetry, graphite is not always oxidized stochiometrically.

Having originally observed that although a very limited number of bases (potash, soda, barites, and strontia) developed nearly the same quantity of heat when they combined with an acid, yet that the greater number of bases differed most widely from one another, when so treated, while on the other hand that different acids (diluted) produce with the same base nearly the same amount of heat, Andrews ventured to draw the general inference that the thermal effects produced were more intimately connected with the basic or electropositive than with the acid or electronegative element. In conformity with this view, it appeared probable that in the decomposition of solutions of neutral salts by the addition of bases or metallic bodies, the nature of the acid or electro negative element of the compound would exercise no special influence on the results. The general result of the whole investigation was stated as follows: When an equivalent of one and the same metal replaces another in a solution of any of its salts of the same order (the metal exists in the same state of oxidation), the heat developed is always the same, but a change in either of the metal produces a different development of heat.[18]

Andrews studied the reaction of salts of copper black oxide salts (sulfate, chloride, acetate, and formiate) with metallic zinc, iron, lead, and silver; the salts of silver with metallic copper; salts of lead, mercury, and platinum with metallic zinc; and concluded that if three metals A, B, and C were so related that A was capable of displacing B and C from their combinations, and also B capable of displacing C, then the heat developed in the substitution of A for C would be equal to that developed in the substitution of A for B, added to that developed in the substitution of B for C, and a similar rule could be applied to any number of metals similarly relate.[18]

His last memoir[19] was intended to give a general view of the state of knowledge on the subject of thermochemistry. General propositions of the state of the art were as follows: (a) The solution of a crystallized salt in water is always accompanied by heat absorption; (b) If equal weights of the same salt are dissolved in succession in the same liquid, the heat absorbed will be less on each addition of salt; (c) The heat absorbed by the solution of a salt in water, holding other salts dissolved, is generally less that absorbed by its solution in pure water; and (d) The heat absorbed by the solution of a salt in the dilute mineral acids is generally greater than that absorbed by its solution in water.

Ozone

In 1799 Martinus van Marum's (1750-1837) reported that oxygen gas that had been arced acquired a peculiar odor and the property of attacking mercury.[24] This subject attracted no further attention until 1840 when Schönbein[25] announced the discovery of ozone in a memoir presented to the Academy of Munich. He reported that during the electrolysis of water oxygen was released at the positive pole accompanied by an odorous substance, which could be preserved for a long time in well-closed vessels. The production of this material was influenced by the nature of the metal that served as the pole, by the chemical properties of the electrolytic fluid, and by the temperature of that fluid as well of the electrode. He also remarked that the odor was the same that accompanies a flash of lightning. In his memoir Schönbein speculated that the odorous body was a new electro-negative element, belonging to the same class as chlorine and bromine, and for which he proposed the name ozone (from the Greek, *ozein*: smell). In a following paper, he suggested that ozone might be one of the constituents of nitrogen. Schönbein soon afterwards discovered that ozone is also formed when phosphorus oxidizes slowly in the presence of moist air or oxygen.[26]

Further investigations on the new substance were conduced by Jean-Charles Marignac (1817-1894), Auguste Arthur de la Rive (1801-1873), Jöns Jacob Berzelius (1779-1848), Edmond Frémy (1814-1894), Antoine Henri Becquerel (1852-1908, 1903 Nobel Prize for Physics), Alexander Williamson (1824-1904), and Friedrich Moritz Baumert (1818-1865). Marignac and de la Rive established that ozone is formed by the passage of electrical sparks through pure and dry oxygen gas; Frémy and Becquerel[27] showed that pure oxygen, contained in a tube inverted over a solution of iodide of potassium, is entirely absorbed by that liquid if electrical sparks are passed for a sufficiently long time through the gas; and Baumert maintained that water is always formed when dry ozone prepared by electrolysis is destroyed or decomposed by heat. Williamson tried the thermal decomposition of carefully dried ozone and found that there was a significant gain in weight; also that ozone obtained by electrolysis decomposed when passed over water. Baumert tried to determine the composition of ozone by determining the increase in weight of a solution of iodide of potassium when it is decomposed by ozone. He concluded that two distinct bodies had been confounded under the name of ozone: allotropic oxygen, formed by the passage of the electrical spark through oxygen, and a teroxide of hydrogen, HO_3, produced in the electrolysis of water. Baumert's experiments and conclusions attracted a great deal of attention at the time they were published. Schönbein's hypothesis that ozone is an oxide of hydrogen was manifestly inconsistent with the production of that body by the passage of electrical sparks through pure and dry oxygen.[26]

When Andrews begun his research on ozone its nature was still unknown and it was not clear if the ozone obtained by electrolysis, by the action of electric sparks, or formed during the slow oxidation of phosphorus, were the same substance or different ones having very similar properties. Some experiments seemed to show that ozone contained nothing but oxygen, others that it was an oxide of hydrogen containing a larger proportion of oxygen than water does.

In 1855 Andrews communicated to the Royal Society a paper of great importance and interest on ozone.[10] He reported that one of the most remarkable properties of ozone was its destruction by heat, or rather its conversion into ordinary oxygen. Andrews found that the amount of ozone produced in his apparatus started to diminish after the temperature attained 230 ^{o}C and almost reached zero at 240 ^{o}C . Ozone brought into direct contact with water vapor at its boiling point was instantly destroyed. The action of water at common temperatures and of alkaline solutions upon ozone was remarkable. Pure water had the property of destroying a small quantity of ozone. If ozone produced by electrolysis of water or by the action of the electrical spark or by means of phosphorus, was largely diluted with atmospheric air, it would completely disappear, if collected in a jar inverted over water. The odor of ozone, from whatever source derived, was the same. The same remark applied to its property of bleaching, without producing at first an acid reaction. Potassium iodide was decomposed forming potassium iodate, and oxidable substances in solution, such as ferrous acid sulfate, were brought to a higher state of oxidation. Andrews's final conclusion was that "ozone, from whatever source derived, is one and the same body, having identical properties and the same constitution, and is not a compound body, but oxygen in an altered or allotropic condition" (Andrews, 1856).

Andrews's work into the nature of ozone was continued with Tait and the results published in several papers.[28-31] In the first one[28] they reported their first attempts to determine the density of ozone by measuring the change in volume that took place when exposing a mixture of oxygen and ozone to a temperature of 230 °C (at which ozone would decompose). They found that the volume of the gas after this treatment invariably increased, and from the change in volume they estimated that the density of ozone (assumed to be an allotrope of oxygen) was at least four times larger than that of oxygen. The following memoir was a detailed description of the properties of ozone and reported that *"dry silver in the state both of leaf and of filings, has the property of entirely destroying ozone, whether prepared by electrolysis or by the electrical machine. If a stream of electrolytic ozone is passed over silver leaf or filings contained in a tube, the metal becomes altered in appearance where the gas first comes into contact with it, but no appreciable increase in place takes place, however how long the experiment may be continued. Arsenic also destroys dry ozone, but, as it likewise combines with dry oxygen, its separate action on ozone cannot be observed. Most of the other metals examined, such as gold, platina, iron, zinc, tin, etc., are without action on dry ozone. Iodine brought into contact with oxygen contracted by the electric discharge, instantly destroys the ozone reactions, and a yellowish solid is formed; no change in volume accompanies this action. Peroxide of manganese and copper oxide have the property of destroying ozone, apparently without limit. Hydrogen gas, purified with care and perfectly dry was not changed in volume by the action either of the electrical spark, or the silent discharge (obtained from the common friction machine)...Ozone decomposes a solution of potassium iodide liberating the iodine...Paper moistened with manganese sulfate becomes brown from the formation of the hydrated peroxide. Solutions of thallium oxide are in like manner converted into the brown peroxide...".*[29]

The next memoir[30] was of more fundamental nature and its results led directly to the theory of the constitution of ozone now universally held; according to Tait, Andrews and Tait, state that theory distinctly, although not further discussed on account of its supposed improbability.[1] The changes produced by ozone on mercury were remarkable. The metal instantly lost its mobility, and if gently shaken, covered the interior of the tube with a brilliant mirror. As the action continued the mirrored surface broke up and the coating became a blackish semi pulverulent substance. Andrews and Tait believed that if ozone was an allotropic form of oxygen, then it when mercury would came into contact with it, a contraction would take place, equal to the volume of ozone, which entered into combination with the metal. This prediction was not realized; no change in volume took place.[30]

Since the reaction of ozone with mercury and silver was evidently very complex (the mercury and silver combined partly with the gas and the resulting products appeared to exercise a catalytic action) Andrews and Tait tried to find an elementary body that would instantly stop the ozone reactions, and at the same time be without action on dry oxygen. After some trials they found that iodine possessed the required properties. Iodine showed very little affinity for oxygen but in the presence of ozone present, it was immediately attacked; a grayish-yellow compound was formed and all ozone reactions were instantly stopped.[30]

Assuming the allotropic hypothesis correct then these experiments led to the conclusion that ozone must have a density at least 50 times as great as that of oxygen. This was an unavoidable conclusion, unless it was assumed that simultaneously with the combination of one portion of the ozone with the iodine, another portion changed back into oxygen, and that these quantities were so related to one another that the expansion due to one was exactly compensated by the contraction arising from the other.[30]

It was known that ozone may be formed under conditions which exclude the possibility of its containing as a constituent any element except oxygen. Andrews and Tait believed that their experiments could be reconciled with the allotropic view and an ordinary density, but still greater than that of oxygen, if it was assumed that when ozone comes into contact with such substances as iodine, or solutions of potassium iodide, one portion of it, retaining the gaseous form, is changed back into oxygen while the remainder enters into combination; and that these are so related to one another, that the expansion due to the formed is exactly equal to the contraction arising from the latter *"...It remains to be considered whether in the formation of ozone, oxygen does not undergo a more profound molecular change that is involved in an allotropic modification, whether...this supposed element may not be actually decomposed. If we confine our attention to the phenomena, which present themselves when the electrical discharge is passed through oxygen, this attractive hypothesis will be found to furnish a simple and plausible explanation of them all. It will be observed at once, that the conditions under which ozone is formed from oxygen under the electrical discharge, are precisely those under which other gases, known to be compound, are decomposed...If we assume that oxygen is resolved by the electrical discharge into a new compound (ozone) containing the same constituents as the oxygen itself, but in a different proportion, and into one of the constituents themselves, in the same manner that* CO_2 *is resolved into CO and oxygen, or nitric oxide into hyponitric acid and nitrogen, the results of our experiments will admit of an easy explanation. One of the simplest suppositions we can make for this purpose is that two volumes of oxygen consist of one volume of U and one volume of V, united without condensation (U and V being the supposed constituents of oxygen) and that one volume of ozone consists of two volumes of U and one volume of V, and further, that by the action of heat, iodine, etc., ozone is resolved into U and oxygen".*[30]

Andrews and Tait realized that if a procedure could be found for completely converting the ozone formed into nonvolatile product(s), the ratio of the volume increase observed on thermal decomposition of an ozone-oxygen mixture to the volume decrease when ozone from a second sample of the same mixture reacted completely, would provide the ratio of the density of ozone to that of oxygen. The problem was to find a suitable reaction for complete consumption of ozone. They attempted to use mercury or silver; the volume change was negligible; leading to the conclusion that since a measurable weight of ozone thus appeared to occupy zero volume, it seemed that its density was infinite (more than fifty times as great as that of oxygen). This perplexing result led, however, to a proposal of the true solution by William Odling (1829-1921 in 1861,[31] Jacques Louis Soret (1827-1890), found the actual solution to the problem by first confirming Andrews and Tait's results on volumetric relationships.[32] While experimenting in 1866 upon the mixture of oxygen and ozone obtained by electrolysis, Soret made the important discovery that if this mixture is brought into contact with oil of turpentine or oil of cinnamon, a diminution of volume takes place equal in amount to twice the augmentation of volume which the same mixture would sustain if the ozone were converted by heat into ordinary oxygen. In other words, the volume of ozone, measured by its absorption by the essential oil, is twice as great as the difference between the volume of the same ozone and oxygen. Hence, Soret concluded that the density of ozone is one and a half times that of oxygen gas and its formula is O_3.[26,33] Benjamin Collins Brodie (1817-1887) confirmed Soret's in 1872.[34]

An additional important result was that ozone is not condensed at common pressures by the cold produced by a mixture of solid CO_2 and ether.

Soon after the discovery of ozone, Schönbein, having observed that the air of the country frequently colored a delicate ozone test paper in the same manner, inferred that ozone is a normal constituent of the atmosphere. Andrews went on to check this hypothesis, remarking that since other substances such as nitric acid and chlorine, which may possible exist in the atmosphere had the same property, no certain conclusion could be drawn from this fact alone. Hence, his test was based on the fact that ozone was quickly destroyed at 237 °C . Since the same effect was obtained with atmospheric air Andrews concluded that the body in the atmosphere, which decomposes potassium iodide, is identical with ozone.[35]

In an 1858 letter to Faraday, Schönbein[36] proposed the existence of another form of oxygen, which he called antozone. The two species, ozone and antozone, purportedly reacted together to give ozone. He considered antozone to be oxygen possessing permanently positive properties, while ozone itself he regarded as negative oxygen. On the assumption that both were formed under ozone-producing conditions, the low yield of ozone obtained was explained by its destruction by antozone. Schönbein considered this body to be oxygen possessing permanently positive properties, while ozone itself he regarded as negative oxygen; ordinary or inactive oxygen, was formed by the union of ozone and antozone. These views were not been supported by later investigations, leaving little doubt that the antozone of Schönbein was identical with the peroxide of hydrogen of Thénard.[26]

A detailed history of the discovery of ozone, its composition, and properties has been published by Rubin[37] (Rubin, 2001).

Continuity of the liquid and gas states

Starting in the late 1700's many scientists looked for ways of reaching lower and lower temperatures and liquefying gases. In 1799 van Marum and van Trovstwyk performed experiments trying to determine if the Boyle-Mariotte law was applicable only to air or for all gases.[24] For this purpose they chose ammonia and proceeded to compress it in a system piston-cylinder. When the pressure reached about seven atmospheres they noted that although the volume of the gas continued to decrease, the pressure did not change. From this result they understood that ammonia had been liquefied ammonia by a simple compression process without resorting to cooling. In the same year, Louis-Bernard Guyton de Morveau (1737-1816) liquefied ammonia by simple cooling to about –50 °C with a freezing mixture of calcium chloride and ice[38] while Antoine-François Fourcroy (1750-1809) and Louis Nicolas Vauquelin (1763-1829) failed to liquefy hydrogen chloride, hydrogen sulfide, and sulfur dioxide.[39] In 1801 Gaspar Monge (1746-1818) and his assistant Louis Clouet, succeeded in liquefying sulfur dioxide by passing a stream of SO_2 through an U tube submerged in a refrigerant mixture of ice and salt; they noticed that the tube filled up little by little with a colorless and high mobile liquid, similar to water.[40] In 1822 Charles Cagniard de la Tour (1777-1859) observed that certain liquids, such as ether, alcohol, and water, when heated in hermetically sealed glass tubes, they would dilate and their mobility become gradually greater. After compression to nearly twice its original volume, the liquid completely disappeared and was converted into a vapor so transparent that the tube appeared to be quite empty. On allowing the tube to cool, a very thick cloud was formed, after which the liquid reappeared in its former state became apparently reduced to vapor in a space from twice to four times the original volume of the liquid.[41]

Thereafter, many scientists tried to liquefy gases by a compression process. The next important step were the results obtained in 1823 by Michael Faraday (1791-1867), while investigating the influence of heat on chlorine hydrate.[42] Faraday noticed that the crystals first melted and then released a yellow gas that on cooling yielded a heavy bright yellow fluid floating of top of a solid phase. Faraday understood that chlorine gas had separated from the hydrate and condensed under its own pressure.

Faraday's equipment was limited to the production of very small amounts of liquefied gas; in 1834 a very smart modification by Charles Sainte-Ange Thilorier (1797-1852) allowed increasing substantially the amount of liquefied gas, particularly liquid CO_2.[43] In 1845, Faraday combined the two liquefying methods (cooling and compression) into one by taking advantage of Thilorier's mixtures to produce low temperatures, and was thus able to not only to liquefy gases such as HCl, HBr, SiF_4, PH_3, AsH_3, and ethylene, but also to solidify others such as H_2S, N_2O, and HClO. He was unsuccessful to liquefy hydrogen, nitrogen, oxygen, carbon monoxide, and, methane at 50 atmospheres and –110 °C .[44]

By mid-nineteenth century all but six of the known gases had been liquefied; the six remaining gases (oxygen, nitrogen, carbon monoxide, nitrous oxide, methane, and hydrogen) were called *permanent gases* and believed to be non-condensable. Helium was not considered then because this gas was discovered only in 1869 when observing the sun's corona. William Ramsay (1852-1916) discovered the first deposits in the earth in a sample of pitchblende, a dark rock containing radium and uranium.[45]

George Aimé (1810-1846) tried, without success, to liquefy oxygen and nitrogen by immersing recipients containing air in the sea, to a depth corresponding to more than 200 atmospheres.[46] In 1844 Johann August Natterer (1821-1900) succeeded in producing large quantities of liquid nitrous oxides but he failed to liquefy air by compressing it to pressures between 1 300 to 2 800 atmospheres.[47]

In 1850 Victor Regnault (1810-1878)[48] made some experiments on the discharge of a gas through a capillary tube and observed a small cooling effect, which he dismissed as experimental error. Two years later, James Prescott Joule (1818-1889) and William Thomson (1824-1907, Lord Kelvin)[49] would report the same result and understand its significance (the Joule-Thomson effect). Based on his findings on the behavior of the compressibility of gases Regnault predicted[50] that application of insufficient pressure was the only obstacle for the liquefaction of oxygen and nitrogen. Also, that if hydrogen was cooled, it would show enough compressibility to be liquefied.

It took the experiments of Andrews to understand the reason of the failure to condense the remaining gases.[11,51-54] Andrews studied the behavior of gases under high pressures and different temperatures and was able to formulate the concept of coexistence of the vapor-liquid equilibrium and the constancy of temperature during a phase change (Andrew's isotherms). He demonstrated that for every gas there exists a temperature (which he called the *critical temperature*) above which it was impossible to condense the gas, no matter how high a pressure was applied. For this purpose he used CO_2 partly because of the facility with which it can be produced in a pure state (by the action of boiling sulfuric acid over marble, and dried by passing through sulfuric acid) and its critical temperature being 31 °C .

The first printed account of Andrew's work appeared as a result of a communication he sent to William Allen Miller (1817-1870), who published it in his textbook.[55] After a graphic description of the appearance of carbon dioxide in a state intermediate between gas and liquid, he concluded *"that there exists for every liquid a temperature at which no amount of pressure is sufficient to retain it in the liquid form...On partially liquefying carbonic acid by pressure alone, and gradually raising at the same time the temperature to 88 °F, the surface of demarcation between the liquid and gas became fainter, lost its curvature, and at last disappeared. The space was then occupied by a homogeneous fluid, which exhibited, when the pressure was suddenly diminished or the temperature slightly lowered, a peculiar appearance of moving or flickering striæ throughout its entire mass. At temperatures above 88° no apparent liquefaction of carbonic acid, or separation into two distinct forms of matter, could be effected, even when a pressure of 300 or 400 atmospheres was applied. Nitrous oxide gave analogous results.".*[11]

Figure 1 is the graphical representation of Andrews's experiments and shows the behavior of the CO_2 isotherms. The dotted lines represent a portion of the curves of an ideal gas for the temperatures of 13.1, 31.1, and 48.1 °C . As seen, the volume of the gas at 31.1 °C diminishes regularly but much faster than according to Boyle's law, until a pressure of about 73 atm is attained. During this fall there is no indication at any stage that a phase change has taken place. Beyond 77 atms CO_2 at 31.1 °C yielded much less than before to pressure, its volume having become reduced nearly to that which it ought to occupy as a liquid at the temperature at which the observations were made.[11]

The simpler and more prominent results of Andrew's research may be briefly summarized as follows: (a) When CO_2 is maintained at any temperature above 30.9 °C, it cannot be condensed into liquid no matter what pressure is applied to it; (b) When the temperature is below 30.9 °C, the gradual increase of pressure ultimately leads to liquefaction; the temperature at which the phase change occurs decreases as the pressure is diminished; (c) A cycle of operations, in Carnot's sense, can be performed on liquid CO_2 in such a way that during the first stage of the expansion there is optical proof of the existence of liquid and gas side by side in the same vessel; while, on cooling down to the original temperature and volume, the whole contents are once more liquid, though at no stage of the latter part of the operation is there any appearance of the joint presence of two different states of matter; and (d) At a temperature below the critical one, the value of the product of the pressure and the volume, Pv, first decreases with increase in pressure until a minimum is reached; thereafter the value of Pv rises rapidly as the pressure is further increased. At temperatures above the critical one, the product Pv always increases as the pressure is increased.

Later on, additional series of careful experiments were made at 31.1, or 0.2 °C above the point at which, by compression alone, CO_2 is capable of assuming visibly the liquid form. These experiments allowed Andrews to determine mode precisely the critical temperature of CO_2: *"Since I first announced this fact in 1863, I have made careful experiments to fix precisely the temperature of this critical point in the case of carbonic acid. It was found in three trials to be 30.92° . Although for a few degrees above this temperature a rapid fall takes place from increase of pressure, when the gas is reduced to the volume at which it might be expected to liquefy, no separation of the carbonic acid into two distinct conditions of matter occurs, so far as any indication of such a separation is afforded by the action of light...It is easy so to adjust the pressure that one-half of the tube shall be filled with uncondensed gas and one-half with the condensed liquid. Below the critical temperature this distinction is easily seen to have taken place, from the visible surface of demarcation between the liquid and gas...But above 30.92° no such appearances are seen, and the most careful examination fails to discover any heterogeneity in the carbonic acid, as it exists in the tube".*[11]

According to Andrews: *"There can, however, be little doubt that all bodies, like mercury and water, are capable of existing in the three physical states. We may indeed live yet to see, or at least we may feel some confidence that those who come after us will see such bodies as oxygen and hydrogen in the liquid, perhaps even in the solid state, and the question of their metallic or non-metallic nature thereby finally settled".*[1]

The presence of a critical point allowed Andrews to propose a sharper definition of a gas and a vapor: *"The distinction between a gas and vapor has hitherto been founded on principles which are altogether arbitrary. Ether in the state of gas is called a vapor, while sulfurous acid in the same state is called a gas, yet they are both vapors, the one derived from a liquid boiling at 35°, the other from a liquid boiling at -10°...The critical point of temperature affords a criterion for distinguishing a vapor from a gas...Many of the properties of vapors depend on the gas and liquid being present in contact with one another and this, we have seen, can only occur at temperatures below the critical point. We may accordingly define a vapor to be a gas at any temperature under its critical point. According to this definition, a vapor may, by pressure alone, be changed into a liquid, and may therefore exist in presence of its own liquid; while a gas cannot be liquefied by pressure, that is, so changed by pressure as to become a visible liquid* distinguished by a surface of demarcation from the gas, If

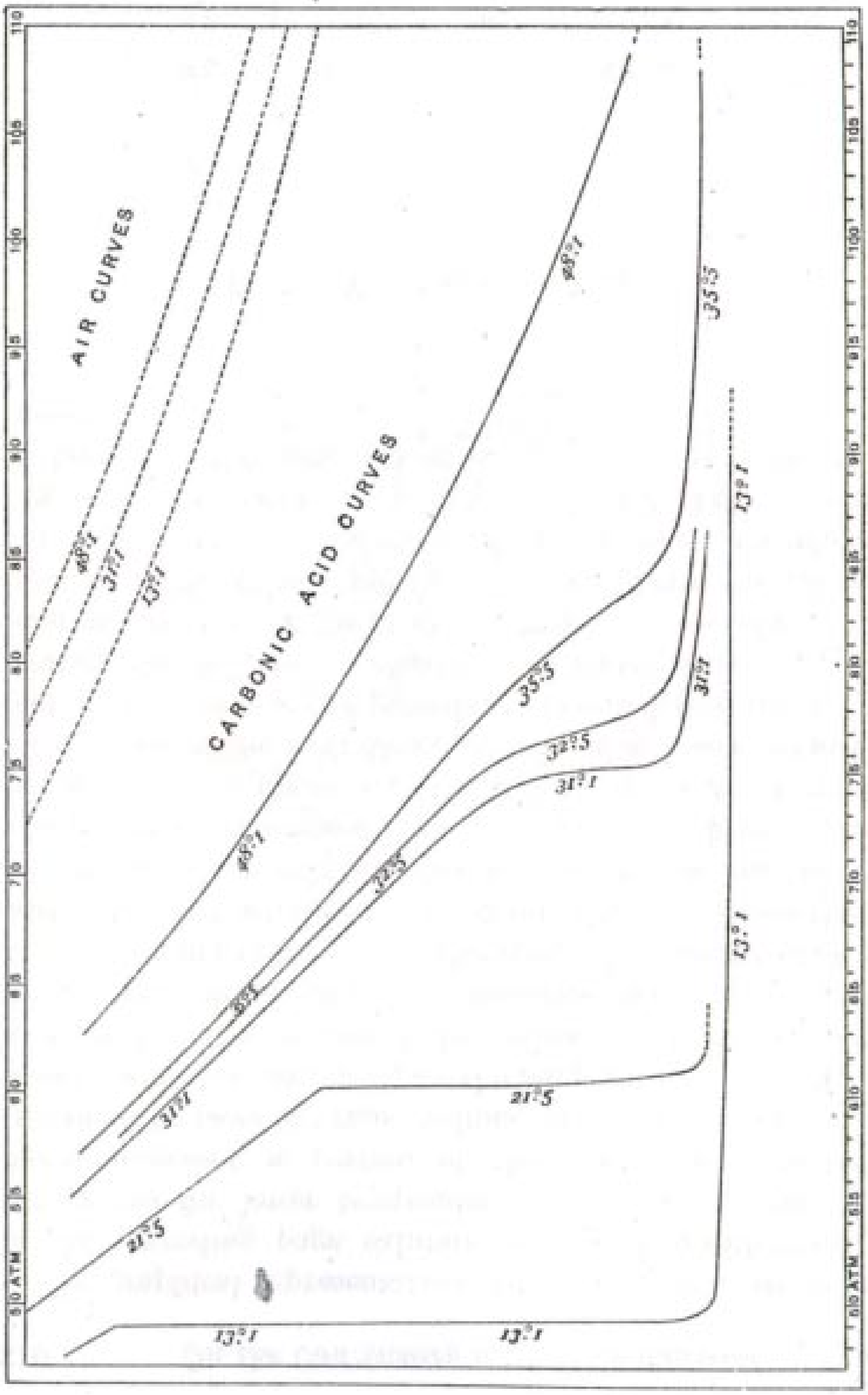

Fig. 1. *CO_2 isotherms.*[11]

this definition be accepted, carbonic acid will be a vapor below 31^0, a gas above that temperature; ether, a vapor below 200°, a gas above that temperature".[11]

Another important experimental result was that the gaseous and liquid forms of matter could be transformed into one another by a series of continuous and unbroken changes. According to Andrews: "*We are now prepared for the consideration of the following important question. What is the condition of carbonic acid when it passes, at temperatures above 31° from the gaseous state down to the volume of the liquid, without giving evidence at any part of the process of liquefaction having occurred? Does it continue in the gaseous state, or does it liquefy, or have we to deal with a new condition of matter? If the experiment were made at 100°, or at a higher temperature...the probable answer which would be given to this question is that the gas preserves its gaseous condition during the compression; and few would hesitate to declare this statement to be true, if the pressure, as in Natterer's experiments, were applied to such gases as hy-*

drogen or nitrogen. On the other hand, when the experiment is made with carbonic acid at temperatures a little above 31°, the great fall which occurs at one period of the process would lead to the conjecture that liquefaction had actually taken place, although optical tests carefully applied failed at any time to discover the presence of a liquid in contact with a gas. But against this view it may be urged with great force, that the fact of additional pressure being always required for a further diminution of volume, is opposed to the known laws, which hold in the change of bodies from the gaseous to the liquid state. Besides, the higher the temperature at which the gas is compressed, the less the fall becomes, and at last it disappears".[11]

"The answer to the foregoing question...is to be found in the close and intimate relations, which subsist between the gaseous and liquid states of matter. The ordinary gaseous and ordinary liquid states are, in short, only widely separated forms of the same condition of matter, and may be made to pass into one another by a series of gradations so gentle that the passage shall nowhere present any interruption or breach of continuity. From carbonic acid as a perfect gas to carbonic acid as a perfect liquid, the transition...may be accomplished by a continuous process, and the gas and liquid are only distant stages of a long series of continuous physical changes. Under certain conditions of temperature and pressure, carbonic acid finds itself, it is true, in what may be described as a state of instability, and suddenly passes, with the evolution of heat, and without the application of additional pressure or change of temperature, to the volume...There is no difficulty...in distinguishing between the liquid and the gas...Carbonic acid, at...35.5º, and...108 atmospheres, is reduced to 1/430 of the volume it occupied under a pressure of one atmosphere; but if anyone asks whether it is now in the gaseous or liquid state, the question does not, I believe, admit of a positive reply. Carbonic acid at 35.5º, and under 108 atmospheres of pressure stands nearly midway between the gas and the liquid; and we have no valid grounds for assigning it to the one form of matter any more than to the other. In the original experiment of Cagniard de la Tour, that distinguished physicist inferred that the liquid had disappeared, and had changed into a gas. A slight modification of the conditions of his experiment would have led him to the opposite conclusion, that what had been before a gas was changed into a liquid...In the foregoing observations I have avoided all reference to the molecular forces brought into play in these experiments. The resistance of liquids and gases to external pressure tending to produce a diminution of volume proves the existence of an internal force of...resisting character. On the other hand, the sudden diminution of volume, without the application of additional pressure externally, which occurs when a gas is compressed, at any temperature below the critical point, to the volume at which liquefaction begins, can scarcely be explained without assuming that a molecular force of great attractive power comes here into operation, and overcomes the resistance to diminution of volume...When the passage from the gaseous to the liquid state is realized by the continuous process described, these molecular forces are so modified as to be unable at any stage of the process to overcome alone the resistance of the fluid to change of volume".[11]

The discovery of the critical temperature, or critical point, soon led to the liquefaction (and in certain cases even to the solidification) of the gases, which had been called "non-condensable." Andrews's work had supplied all the necessary hints for the adaptation of his apparatus to such a purpose. The work of Marc-Auguste Pictet (1752-1806), Louis Paul Cailletet (1831-1913), and Zygmunt von Wroblewski (1845-1888), on this subject, followed as a natural and almost immediate consequence of that of Andrews.[1]

In I871, James Thomson[56] analyzed theoretically Andrews's results on the critical point[11] and suggested that *"although there is a practical breach in continuity in crossing the boiling point curve from liquid to gas or gas to liquids, there should be a theoretical continuity across the breach having some real and true significance; the sharp breaks at the gas and liquid ends of isotherms below the critical temperature could be avoided if the two segments of the isotherm that lay in the homogeneous fluid states were joined by a continuous curve, presenting a maximum and a minimum pressure in the two-phase region. The outer parts of his continuous curve could represent metastable states of supercooled vapor and superheated liquid, but that the central part, between the minimum and the maximum, was a region where pressure was an increasing function of volume, and so must be unstable"* (in modern terms, the loci of the spinodal curve). Thomson went on to speculate, however, that this state, although clearly inaccessible in the bulk fluid, might be realizable in the *"extremely thin lamina of gradual transition from a liquid to its own gas"*.

In 1873 the continuity of the gas and liquid state was be the subject of Johannes Diderik van der Waals' (1837-1923) doctoral thesis.[57] Van der Waals' cubic equation of state (and most modern ones) would provide an analytical tool for describing the continuity between the liquid and gas phases for temperatures below the critical one.

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