

High Temperature Gas Thermometry and the Platinum Metals

SOME ASPECTS OF NINETEENTH CENTURY DEVELOPMENTS

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The Johnson Matthey Group

The present day importance to both science and industry of resistance thermometers and thermocouples utilising the electrical and thermoelectrical properties of the platinum metals is so well known that it has tended to overshadow the use of these metals for crucial components in gas pyrometers. For perhaps one hundred and fifty years gas thermometers, mostly incorporating noble metal bulbs, have provided a most accurate means of determining high temperatures. This article gives a selective account of early developments in temperature measurement involving gas thermometry and the platinum metals, one result of which was the adoption of the first internationally recognised standard scale of temperatures, in October 1887.

The origins of the platinum resistance thermometer and the work that led to it being used in 1927 to define the temperature range -190 to 660°C on the first practical International Temperature Scale has been admirably covered in this journal previously (1). For a hundred years prior to this event the most accurate way of determining high temperatures was by means of gas thermometry. This relies upon the fact that for a suitable gas a quantitative relationship exists between an increase in temperature of the gas, when expanding under either constant pressure or constant volume, and the amount of heat required to produce that temperature increase. Indeed the general acceptance of the platinum resistance thermometer was due in part to the fact that it performed favourably when compared with a gas thermometer, which incorporated hydrogen in an iridium-platinum bulb.

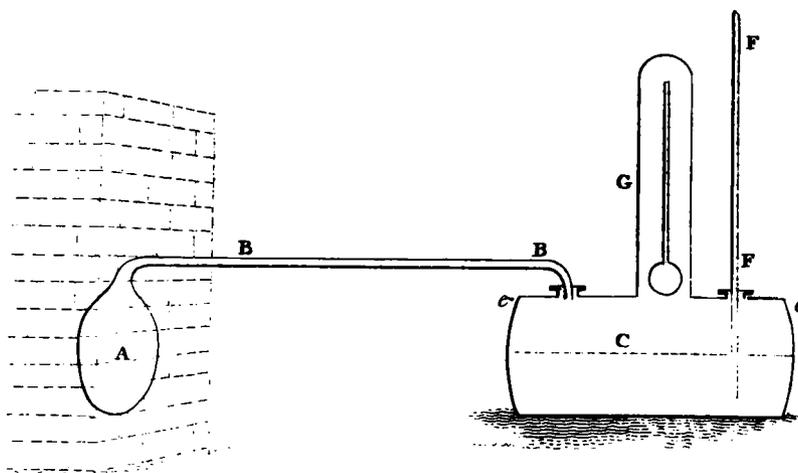
In the early years of the nineteenth century no satisfactory method of measuring high temperatures existed, and as a result many manufacturing processes could not be controlled satisfactorily. For a long time the most popular means of monitoring high

temperatures, particularly of enclosed furnaces, was by the use of cylindrical clay pieces devised by the English potter Josiah Wedgwood. These made use of the fact that clay was believed to contract in proportion to the intensity of the heat to which it was subjected. Thus by measuring the permanent change in length of a standard clay piece removed from a furnace the temperature to which it had been exposed could be determined.

However, it was not easy to obtain clay pieces of uniform composition, while an even greater disadvantage of this method was the discovery that if such a piece were heated for a long time at a low temperature the contraction produced could be the same as that resulting from a shorter time at a higher temperature. The problem caused wide concern. In 1815 Samuel Parkes wrote:

“The want of a good pyrometer is severely felt by the manufacturers of Birmingham. Cases daily occur of losses sustained in consequence of their not knowing the precise degree of heat in high temperatures.”(2)

The situation had not improved significantly by 1821 when J. F. Daniell, introducing his



The illustration that accompanied the account of the Schmidt air pyrometer showed it to consist of the same fundamental parts as later gas thermometers. The platinum bulb was joined by a platinum tube "of as fine a bore as possible" to a water-filled vessel. When the bulb was placed in a heated furnace, the air expanded forcing water up the graduated tube. Once due allowance had been made for the temperature of the air prior to the experiment, the true expansion of the air could be used to indicate the relative temperature of the furnace

new platinum expansion pyrometer, noted:

"It would be needless to preface much upon the utility of an instrument to measure the higher degrees of heat, as nothing in science has been more eagerly desired, and nothing, it is generally allowed, would tend more to the perfection of many of the arts."⁽³⁾

During this period many people had tried to find a solution to the problem, and not surprisingly platinum, the recently available high melting point metal, had featured in a number of the proposals. Indeed as early as 1805 Nicholson's *Journal of Natural Philosophy, Chemistry, and the Arts* carried an account of a platinum pyrometer said to be capable of indicating the temperature of a furnace. This had been submitted by Mr. J. G. F. Schmidt of Jassy, in Moldavia, and it included a drawing of his apparatus ⁽⁴⁾. Having considered which substances were "capable of regularly contracting or expanding, without altering their chemical properties, when subjected to elevated temperatures" he concluded that "the permanently elastic aeriform fluids appear to me to be superior in those respects to any other

body" and his pyrometer was based upon moisture-free air contained in a vessel of platinum. Whether or not such an apparatus was ever made or used by Schmidt is not known by this writer. However a treatise published in 1832 contained a description of his pyrometer, but commented:

"It is so evidently a mere theoretical proposal, and is, besides, an expensive, clumsy, and probably not very accurate mode of ascertaining high temperatures"⁽⁵⁾

None the less the book included a redrawn figure of the Schmidt pyrometer.

It seems to be generally accepted ⁽⁶⁾ that the first practical pyrometer utilising the expansion of gases for the measurement of high temperatures was due to James Prinsep, and described by him in the year 1827; but a footnote in his relevant paper tends to suggest that this may not have been the case.

Prinsep was a man of wide interests and great abilities; as a youth he had started to train as an architect but the close work damaged his eyesight, so it was necessary for him to seek another profession. He attended the chemical

lectures of Dr. A. J. G. Marcet, at Guy's Hospital, and afterwards was entered as a fee apprentice to Mr. Robert Bingley, the Assay Master of the Royal Mint, London from whom he received a certificate of proficiency (7). In 1819 he was appointed as Assistant to Dr. H. H. Wilson, Assay Master of the Calcutta Mint, and the following year he was nominated Assay Master at the Benares Mint (Varanasi, India). While he was resident at Benares he pursued his interest in science, to keep pace with developments in Europe, and it was during this period that he prepared a paper on the measurement of high temperature which was communicated to the Royal Society in London by Dr. P. M. Roget, on 13 December 1827, and afterwards published in the *Philosophical Transactions* (8).

Prinsep's Pyrometric Alloys

In the first part of this most interesting and informative paper Prinsep explained his use of pyrometric alloys to indicate the relative intensity of different heats. As the melting points of

pure silver, gold and platinum are determinate and unchangeable these three points can form the basis of a temperature scale, while intermediate points can be established from the melting points of a series of binary alloys of different proportions. Between the melting points of gold and platinum Prinsep proposed 100 degrees, each indicated by an alloy containing an additional one per cent of platinum. He found, however, that 45 per cent gold-55 per cent platinum was the highest melting point alloy which could be fused in his forge.

Before use the specimens were flattened and individually identified, then to establish a relative temperature an appropriate selection of alloys was positioned where the temperature had to be determined. Any samples that became molten at that temperature were readily identified, and:

"the heat of any furnace may be expressed by the alloy of least fusibility which it is capable of melting."

Although the melted alloys could easily be reflattened for further use the silver and gold



James Prinsep 1799–1840

In addition to his official duties, Prinsep engaged in a wide range of pursuits. Having skilfully amended the plans for the new mint to be built at Benares he was subsequently involved in a number of major public works. In contrast to this, he is also credited with making an assay balance capable of measuring to an accuracy of three thousand parts of a grain. Despite such technical contributions, Prinsep is remembered largely for his literary works and for his studies of the antiquities of India, especially numismatics and the deciphering of inscriptions carved in rock and on pillars

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alloys lost weight during long exposure to heat, but Prinsep observed that "the platina alloys are very durable".

By themselves these alloys could not give absolute temperature values, but with them Prinsep was able to indicate relative heats. Indeed, the use of such alloys for pyrometry continued into the twentieth century (9).

The "Golden Bulb" Thermometer

Having explained his method of determining the relative heat of his furnace Prinsep went on to describe his determination of the melting point of pure silver using his gas thermometer. Clearly he was most anxious to avoid any possibility of being charged with plagiarism for he noted that:

"Dr. Ure has recommended an air thermometer made of platinum; but I cannot learn whether his plan has ever been carried into effect".

and this comment was qualified by the footnote referred to previously which leaves open the possibility that Prinsep was not the first to use such a thermometer, for he recorded:

"I find since, that the instruments have been made for sale; but I have seen no statements of experiments made with them."

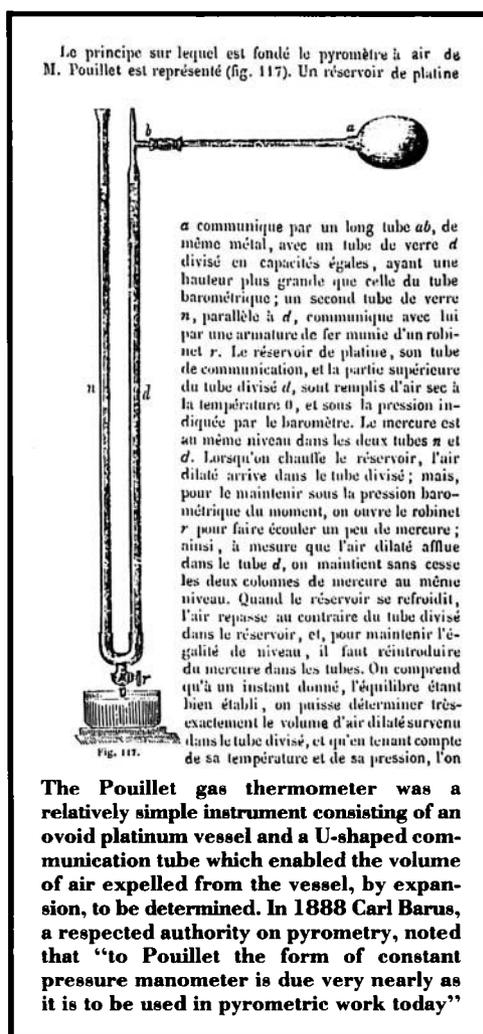
His own thermometer used air as the gas, which was contained in a bulb of pure gold, nearly ten cubic inches in volume and weighing approximately 6500 grains troy. This was connected to a reservoir containing olive oil, and to a sensitive manometer so that the air could be maintained at a constant pressure; the absolute temperature being calculated from the weight of oil displaced as the air in the gold bulb expanded.

Small bone ash cupels containing silver and silver-gold alloys were arranged in the furnace adjacent to the bulb to monitor that the furnace had in fact melted the pure silver, but that the temperature had been insufficient to melt any of the gold-containing alloys. Prinsep found the average figure for the melting point of silver to be 1830°, which compared with 2233° as determined by Daniell, and 4717° by Wedgwood. Although Prinsep used his air thermometer to establish the melting point of many of his

pyrometric alloys, its usefulness was limited by the relatively low melting point of the gold.

Pouillet's Platinum Bulb Thermometer

Prinsep was followed by several other workers all using thermometers based upon the expansion of air at constant pressure, but none made any significant improvement to Prinsep's apparatus until 1836 when Professor Claude-Servais-Mathias Pouillet (1790–1868) reported to the Académie Royale des Sciences his research on the measurement of high temperatures (10). At this time he was assistant



professor of physics at the Faculty of Science in Paris and also administrator of the Conservatoire des Arts et Métiers, and many of his lectures were regarded as important surveys of the state of the various branches of physics and of recent developments in them. A key component of his air thermometer was an ovoid shaped bulb, with a capacity of 60 cc, made from a single piece of platinum. This bulb was soldered with gold to a platinum capillary tube, which in turn was joined by a silver tube to a manometer. The use of a platinum bulb enabled him to measure higher temperatures than previously, including the melting point of gold; indeed he is credited with establishing gas thermometry on a sound footing (9).

In this paper Pouillet also put forward the idea of a "magnetic pyrometer". This was a crude iron-platinum thermocouple, the platinum wire being enclosed in an iron gun barrel which served as the second metal of the junction and also shielded the platinum from the action of the furnace gases. The story of this amazing instrument has been reported briefly in this journal previously (11). In addition Pouillet made other contributions to pyrometry, one being his anticipation of the method of temperature measurement through determinations of the specific heat of platinum.

This idea was subsequently developed by Jules Violle (1841-1923) who used a gas thermometer to determine the specific heat of platinum at a number of temperatures up to 1200°C, then extrapolating with this constant he determined the melting points of palladium and platinum to be 1500 and 1775-1779°C, respectively.

Over the following years advances in gas thermometry continued. During his classic researches on heat, Henri Victor Regnault (1810-1878) made a number of improvements to the constant pressure gas thermometer, his studies establishing the validity of the idea (12) and it is believed that the first constant volume gas thermometer was devised by Silbermann and Jacquelin in 1853 (9). However gas thermometry was soon to suffer a serious setback.

Over a number of years from about 1857 Henri Sainte-Claire Deville, whose major

pioneering contributions to the metallurgy of the platinum metals have been noted here previously (13), and L. J. Troost (1825-1911) worked to determine a number of constant temperatures. Wishing to use a heavier gas than air in their gas thermometer they chose iodine. In addition they rejected the use of platinum for the containment vessel because it "is generally considered as having the property of condensing on its surface the gases with which it comes in contact" (14) and instead they used a bulb of porcelain. With this they measured the boiling points of cadmium and zinc which they found to be 860° and 1040°, respectively. However disagreements arose in 1863, when Pouillet's work using air as the expanding gas in a platinum bulb was continued by Edmond Becquerel (1820-1891). Remembered for his work on the platinum-palladium thermocouple first proposed by his father Antoine Cesar Becquerel, Edmond concluded that cadmium boiled at 746.3° and zinc at 932°. These figures were not accepted by Deville and Troost who set out to discover why Becquerel's results were so different from the ones they had obtained.

The Great Platinum Controversy

Deville and Troost undertook a series of gas diffusion experiments, initially using a homogeneous tube drawn from a well-worked ingot of platinum prepared by the traditional process of consolidating spongy platinum by hammering. However they were later able to repeat their experiments with a cast platinum tube having a wall thickness of 2mm made by George Matthey and sent to them "for the benefit of science", and the results were exactly the same:— at high temperatures the platinum tube was porous to hydrogen. Apparently this problem had been avoided by Pouillet who had "heated his apparatus in an iron muffle very nearly closed" (15). Thus, in the opinion of Deville and Troost, platinum was quite unsuitable for the construction of gas pyrometers that were "to come into contact with the reducing gases, or with the hydrogen of a furnace". This was the first announcement of the permeability of hot platinum by hydrogen (16).

* While this paper was printing, we received from Mr. Matthey, the great London manufacturer, a cast platinum tube weighing 1070 grammes, 60 centims. long and about 2 millims. thick. All the experiments which we have already described have been repeated with this tube, and gave exactly the same result, causing the formation of water by means of hydrogen and at the expense of the air, and producing a vacuum in the annular space, &c. The immense thickness of this tube and its quality have in no respect altered the phenomena, either in their direction, in their intensity, or in their activity. Mr. Matthey, knowing what we were in need of, has had this tube manufactured with part of the ingot of 100 kilogs. of cast platinum which he exhibited in 1862, and, anticipating our wishes, has obligingly sent it to us for the benefit of science. We publicly express our obligations to him.

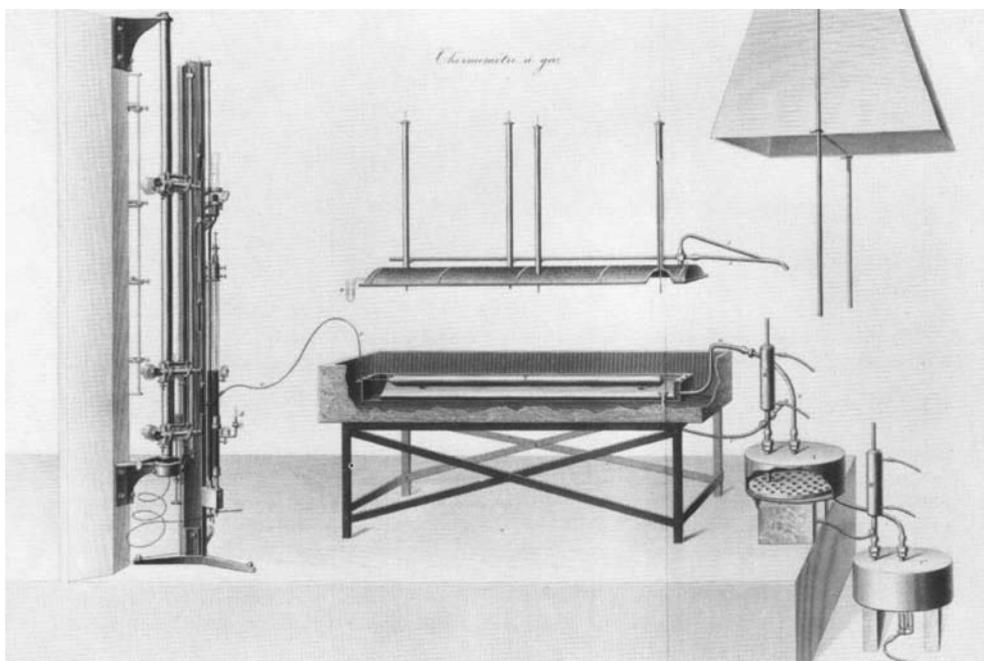
It is not at all surprising that George Matthey contributed a cast platinum tube for Deville's investigation of the diffusion of hydrogen through platinum, because a "great bond of sympathy" existed between the two men. Although the British patent for the French process of melting platinum in a lime crucible had been assigned to Johnson Matthey in 1857, several years of co-operation between the two parties were required before the operation was successfully achieved in London. In fact, Deville was present in Hatton Garden during March 1862 when a huge ingot measuring twelve by eight by six inches, and weighing 100 kilogrammes, was cast; it was this ingot that was displayed at the Second International Exhibition of Industry, in London

A bitter controversy developed between Becquerel on the one hand and Deville and Troost on the other. Both sides continued their temperature measurements, and obtained results which they claimed supported their earlier figures, and it was to be many years before the situation was resolved. In time very precise experiments showed that platinum was quite impermeable to all gases other than hydrogen (17) which, although frequently present in flames due to incomplete combustion, could be avoided, for example by electrical resistance heating. Also it was established that iodine vapour does not obey the gas laws of Mariotte (Boyle) and of Gay-Lussac, the vapour density decreasing as the temperature increases (18), a property that makes it unsuitable for use as the expanding medium in a pyrometer. However, at the time the unfortunate result of this dispute was that platinum bulbs were discredited and porcelain substituted, a "backward step which was not retrieved for more than thirty years" (19).

Clearly, in gas thermometry the choice of a suitable gas and an appropriate material for the

bulb are both important considerations. Ideally the expansion of the gas should vary continuously and uniformly with temperature change. Although no strictly "perfect gas" has been found, hydrogen is very close to this, while the accuracy obtained with nitrogen, which can be used over a greater temperature range, is "of the order of magnitude of a single degree" at 1100°C (20). It has already been noted that the bulb must be made from a material which has a sufficiently high melting point, and it must be impermeable to gases under pressure. In addition its coefficient of expansion must be both small relative to that of the gas and also accurately known at the temperatures which are to be determined, in order that the unavoidable changes in the volume of the bulb which occur with changes in temperature can be allowed for.

The selection of porcelain by Deville and Troost was unfortunate because it was found to be porous unless it had been glazed. Also such a glazed surface coating could be incomplete, as well as being susceptible to cracking after heating to about 1000°C. In addition porcelain



In the Chappuis hydrogen thermometer the gas containment vessel, seen in the middle of this illustration, consists of a platinum-iridium tube just over one metre long arranged horizontally. This is connected to the manometer, on the left, by a platinum capillary tube. The complexity of the manometer and the amount of ancillary equipment perhaps give an indication of the efforts that had to be made to upgrade earlier gas thermometers into an instrument that could measure temperatures with an accuracy that was internationally acceptable

Courtesy of the Bureau International des Poids et Mesures, Sèvres

dissolves some gases, including water vapour, which can then readily pass through the container wall, while inconsistent results may also arise due to variations in the coefficient of expansion of different samples. As has been mentioned earlier, their choice of gas was also a mistake. However, despite the misunderstanding that resulted from the investigations of Deville and Troost, work on gas thermometry was later revived.

Chappuis' Hydrogen Thermometer

Accepting the need for an international agreement on an accurate and reproducible temperature scale, the Comité International des Poids et Mesures met in Paris exactly one hundred years ago to consider the advantages and disadvantages of the various devices then available for the measurement of temperatures. Having done so, on the 15th October 1887 they

adopted as their standard the Centigrade scale of the hydrogen thermometer at Sèvres, the so-called Chappuis hydrogen thermometer. The official text of the resolution was in French (21); an English translation reads:

"The International Committee on Weights and Measures adopts as the standard thermometric scale for the international service of weights and measures, the Centigrade scale of the hydrogen thermometer, having for fixed points the temperature of melting ice (0°) and that of the vapour of boiling distilled water (100°) under standard atmospheric pressure; the hydrogen being taken at an initial pressure of 1 m of mercury, that is to say at $1000/760 = 1.3158$ of the standard atmospheric pressure". (22)

The constant-volume thermometer employed included two essential parts, a bulb to contain the gas and a manometer to measure its pressure. The former was a platinum-iridium tube 1.10 metres long with an outer diameter of 0.036 metres, the volume being 1.03899 litres at the temperature of melting ice. In use the



Pierre E. Chappuis
1855–1916

Born in Bremblens near Morges, in Switzerland, Chappuis studied first at the University in Basel and later in Leipzig, where he received a doctorate for his work on the solidification of gases on glass surfaces. After his move to Paris in 1882 he at first did further work in the same field but it then fell to him to carry out the principal work of research on thermometry, work that was still incomplete some twenty years later when he returned to Basel, for family reasons. However he built and equipped a private laboratory in the garden of his house, and there continued his scientific investigations. In addition he made his considerable experience available to the Swiss scientific community, and accepted a seat on the board of the Swiss Office for Weights and Measures

Courtesy of the Trustees of the Science Museum, London

bulb was contained in a bath held at the temperature that had to be determined, the bulb being connected to the manometer by a platinum capillary tube with a diameter of 0.7 mm. The apparatus is reproduced here, from Chappuis' principal publication on gas thermometry (23).

At the Bureau International des Poids et Mesures thermometry was an essential interest, related to one of its original objectives, namely the comparison of national prototypes of length with the international prototype. To enable the temperature of the standard metre bars and the coefficient of expansion of the platinum-iridium from which they were fabricated to be measured, two very accurate mercury-in-glass thermometers were supplied with each national prototype metre, and it was therefore necessary to establish a uniform temperature scale against which these could be compared. For almost two decades Chappuis devoted himself to this most exacting task and the extent of his major contributions to thermodynamic and practical

temperature scales can be learnt from an account of his life and work written in 1916 by the then Director of the Bureau (24) and from two Swiss obituaries (25), all of which emphasise the painstaking care and precision of his measurements; while further details of the so-called "normal hydrogen scale", and of more up-to-date gas thermometry, are contained in a recent publication (26).

The Measurement of Higher Temperatures

Work to improve the techniques of temperature measurement did not stop with the adoption of this standard scale in 1887; indeed it was continued with great ingenuity as scientists in several countries sought to overcome the limitations of the hydrogen thermometer, in particular the restricted temperature range over which it could be used and the accuracy of the results. The year 1887 also saw the publication of the first of four now famous, but then controversial papers by H. L. Callendar in which he described the essential requirements for precise resistance thermometry (27); and over the next four decades much notable work was done on various means of determining high

temperatures, and again the platinum metals had important contributions to make.

Brief mention has already been made of early thermocouples, which resulted from an observation of Thomas Johann Seebeck (1770–1831) that if one of the junctions of two dissimilar metals was heated by the warmth of his hand then an electric current was generated in the circuit. Following work by the Becquerels, Professor P. G. Tait and especially Professor H. Le Chatelier and Carl Barus, and others, the procedure of measuring the electromotive force generated when a junction of two dissimilar platinum metals or alloys was heated developed into an effective practical means of determining temperature, and after calibration against a gas thermometer such a thermocouple could be used in an intermediary role to measure other temperatures. Indeed in 1927 the temperature scale between 660 and 1063°C was defined by means of a 10 per cent rhodium-platinum against pure platinum thermocouple (28).

At the Physikalisch-Technische Reichsanstalt in Charlottenburg, an institute devoted both to theoretical research and to finding solutions to industrial problems, Professor Ludwig Holborn (1860–1926) and his colleagues, who included Wilhelm Wien and the American physicist Arthur Louis Day, pursued with vigour the investigation of gas thermometry. For temperatures up to 550°C they employed a borosilicate glass bulb and used hydrogen as the expanding gas, but to extend the range up to 1100°C they initially tried porcelain bulbs glazed inside and out, and filled with either hydrogen or atmospheric nitrogen. Later they changed to platinum for the bulb material and employed nitrogen as the expanding gas, which of course could not diffuse through the container wall (29). Their use of electrical resistance heating overcame any possibility of contamination or diffusion by furnace gases, and also increased the uniformity of the temperature around the bulb.

As platinum was found to be too soft for this purpose the famous firm of Heraeus, in Hanau, made a bulb from a platinum-iridium alloy which “contained as much iridium as could be

alloyed with the platinum and allow of its being properly worked—about 20 per cent” (30). The bulb which had a volume of about 208 cc and a wall thickness of 0.5 mm was made from three pieces of sheet welded together and the seams were “afterwards protected by a thick layer of platinum, melted and dropped on to the hot bulb—it then proved and has since remained perfectly tight”. The capillary stem that served to connect the bulb to the manometer was also made of platinum-iridium. The first 10 cm had an iridium content of 20 per cent, but for the remainder of the length only 5 per cent was employed, this alloy being less brittle and therefore more convenient to use. Later, to avoid any possibility of the vessel being distorted at the high pressures involved, a bulb with walls 1 mm thick was made, the material being platinum-10 per cent iridium, and this proved to be as satisfactory as the first (31).

Despite many difficulties the researchers at the Reichsanstalt renewed their efforts to extend the gas scale from 1150°C towards 1600°C. In fact using a pure iridium bulb with a capacity of only 50 cc, which had been made specially for the purpose by Dr. W. C. Heraeus, who took a great personal interest in their high temperature research, Holborn and his co-workers made several determinations of temperatures as high as 1680°C, a magnificent achievement for 1906 (32).

Work in the United States

Work on gas thermometry and the measurement of high temperatures was not confined to Europe. In order to be able to study the conditions of mineral and rock formation with greater accuracy than previously possible, Carl Barus of the U.S. Geological Survey undertook a comprehensive investigation of high temperature measurement (33). A literature survey of previous work probably helped him to appreciate the crucial importance of a uniform temperature distribution around the thermometer bulb, which he was able to achieve by enclosing the bulb in an iron muffle that was revolved rapidly inside a gas fired furnace. Thus every part of the bulb was protected

Arthur Louis Day
1869–1960

After receiving his doctorate in 1894, Day remained at Yale as an Instructor in physics until he moved to Charlottenburg in 1897. In the same year that he returned to the U.S.A. he married Helene, the daughter of Friedrich Kohlrausch—who was President of the Physikalisch-Technische Reichsanstalt between 1895 and 1905. While Director of the Geophysical Laboratory, Day made extensive studies of lavas and volcanic gases in Hawaii, and Californian geysers and hot springs; he also played a prominent part in establishing and advancing seismological investigations, particularly in California. In addition to his academic activities he was appointed a Vice President of the Corning Glass Works in 1919. Many honours were bestowed upon him including, in 1941, the Wollaston Medal of the Geological Society

Courtesy of the Carnegie Institution of Washington



from direct exposure to any temperature irregularity in the furnace.

This elaborate arrangement meant that thermocouples had to be used as intermediaries to compare unknown temperatures with the gas thermometer, and for this reason Barus made an extensive study of thermocouples, as a result of which he selected limbs of pure platinum and 90 platinum-10 iridium for his work.

In 1892 Barus published his final memoir on gas thermometry and thermoelements, and turned his attention to other matters when he moved to the U.S. Weather Bureau. However some time later, in 1900 Arthur Day was recalled from Charlottenburg to the U.S. Geological Survey to equip a laboratory where the methods of physics and physical chemistry could be applied to the study of minerals, and when the new Geophysical Laboratory provided by the Carnegie Institution of Washington was completed in 1907 he was appointed the first Director, and set out to establish petrology as a quantitative science. Indeed his own researches were largely responsible for perfecting the methods of high temperature measurement and standardising the thermometric scale to cover the whole range of mineral formation (34).

After being exhibited in 1900 at the Congrès Internationale de Physique in Paris, a platinum-10 per cent iridium bulb made by Dr. Heraeus was loaned to the American investigators who used it in an initial attempt to eliminate or substantially reduce the errors that had previously occurred in gas thermometry measurements (35). The instrument was generally similar to that at the Reichsanstalt but the entire furnace was enclosed in a gas tight container, so that the gas containment bulb could be filled with nitrogen and also surrounded by nitrogen at the same pressure. Thus there was no tendency for gas to diffuse through the walls of the bulb, or for the bulb to deform.

However when the gas containment bulb was made from iridium, or an alloy containing even small amounts of iridium, a problem arose when a noble metal thermocouple, which had been standardised against the gas thermometer, was used for the actual temperature determination. Above about 900°C the limbs of the thermocouple became contaminated by vapour from the iridium, thus changing the electrical

characteristics of the junction which then indicated erroneous temperatures.

To avoid this contamination U.S. workers later used an alloy of platinum-20 per cent rhodium. Although less rigid than platinum-iridium at temperatures above 1000°C, the platinum-rhodium bulb performed entirely satisfactorily up to 1550°C provided equal pressure was maintained inside and outside (36).

Making the Standard Scale Available

It may be apparent from this review that gas thermometers are cumbersome and complicated precision instruments, and belong in the standards laboratory rather than in the factory. Indeed at many stages during their development it must have seemed that the early criticism of Schmidt's pyrometer was correct. Nevertheless the genuine limitations of gas thermometers have not always been appreciated. In the early part of this century "a well-known engineer" asked Day what the cost of a dozen gas thermometers would be. Day was obliged to answer that he:

"knew of but one in this country, and this one had cost us upward of four thousand dollars to date and might cost even more before we had finished with it" (37).

However once it was accepted that gas thermometers could provide an accurate standard it was then possible to use them to calibrate other intermediary devices which, being more practical, fulfilled the needs identified in the early nineteenth century by Parkes, Daniell and others. Initially the Chappuis hydrogen thermometer was made more generally available when it was used to calibrate a series of very accurate mercury in verre dur thermometers made by Tonnelot, of Paris in the late 1800s, a number of which are still preserved (38). Later other precision mercury-in-glass thermometers made by Baudin, about 1900, were also calibrated in this way. At times these high-precision mercury-in-glass thermometers were designated "primary standards", but of course this was a misnomer. Later, platinum thermocouples and resistance thermometers were

employed to compare temperatures with the gas thermometer, and their use has become widespread for scientific and industrial applications. This part of the contribution of the platinum metals to temperature measurement is already well known (39).

Some of the investigations mentioned here were carried out during the first ten years of this century, and are therefore outside the stated period of this review. This work is included because of the major role played by the platinum group metals, and because it was a logical sequence to the late nineteenth century work.

Gas thermometry is still an accepted method of relating absolute measurements of temperature to thermodynamics, in accordance with the definition of the unit of thermodynamic temperature, the kelvin (40). Additionally, in anticipation of a future need for an updating of the International Practical Temperature Scale a number of standards institutes are currently undertaking work which may be relevant to such a revision (41). In the last century when Holborn and Day were engaged in their investigations of gas thermometry at the Reichsanstalt they were hindered by the fact that few studies had been made of the expansion of materials at high temperatures, and the results were not very accurate. They therefore devised an improved method of determining the expansion of materials, and used it to study some platinum metals and alloys (42). It is therefore interesting to note that a recent paper from the National Bureau of Standards at Gaithersburg has described a technique for the accurate measurement of linear thermal expansions over the temperature range -27 to 55°C, and determinations of the thermal expansion of platinum and two platinum-rhodium alloys; this work being carried out in support of the National Bureau of Standards Gas Thermometry Program (43).

Thus the platinum metals continue to contribute to the usefulness of gas thermometry for the most accurate determination of temperature.

Acknowledgements

The author has gained much information from three standard texts on the measurement of high temperatures, these being "Bulletin No. 54, U.S. Geological Survey" by C. Barus, "The Measurement of High Temperatures" by G. K. Burgess and H. Le Chatelier, and "High Temperature Gas Thermometry" by A. L. Day and R. B. Sosman, as well

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References

- 1 L. B. Hunt, *Platinum Metals Rev.*, 1980, **24**, (3), 104; see also R. Price, 1959, **3**, (3), 78
- 2 S. Parkes, "Chemical Essays", Baldwin, Cradock and Joy, London, 1815, p. 376
- 3 J. F. Daniell, *Quart. J. Sci.*, 1821, **XI**, 309
- 4 J. G. F. Schmidt, *J. Nat. Phil., Chem. & Arts (Nicholson)*, 1805, **XI**, 141
- 5 Thermometer and Pyrometer, in "Library of Useful Knowledge, Natural Philosophy" Baldwin and Cradock, London, 1832, p. 31
- 6 For example, see A. L. Day and R. B. Sosman, "High Temperature Gas Thermometry", Carnegie Inst. Washington, Washington D.C., 1911, p. 4
- 7 H. T. Prinsep, "Memoir of the Author", in "Essays on Indian Antiquities, Historic, Numismatic, and Palaeographic", by the late James Prinsep, ed. Edward Thomas, London, John Murray, 1858, Vol. 1, pp. i-xvi
- 8 J. Prinsep, *Phil. Trans.*, 1828, **118**, 79
- 9 Op. cit., (Ref. 6), p. 5
- 10 C. S. M. Pouillet, *Comptes rendus*, 1836, **3**, 782
- 11 L. B. Hunt, *Platinum Metals Rev.*, 1964, **8**, (1), 23
- 12 R. C. Mackenzie, *Thermochim. Acta*, 1984, **73**, (3), 290
- 13 J. C. Chaston, *Platinum Metals Rev.*, 1981, **25**, (3), 121; D. McDonald, 1958, **2**, (2), 55; B. Swindells, 1975, **19**, (3), 110
- 14 H. St.-C. Deville and L. J. Troost, *Phil. Mag.*, 1863, **26**, 4, 336
- 15 Op. cit., (Ref. 14), 339
- 16 W. W. Randall, *Am. Chem. J.*, 1897, **19**, 682
- 17 G. K. Burgess and H. Le Chatelier, "The Measurement of High Temperatures", 3rd Edn., 1912, Wiley, New York, p. 54
- 18 Op. cit., (Ref. 17), p. 85
- 19 Op. cit., (Ref. 6), p. 6
- 20 A. L. Day, *Metall. Chem. Eng.*, 1910, **8**, (5), 257
- 21 Comité Intern. Poids et Mesures, Procès-Verbaux des Séances de 1887, 1888, 85
- 22 J. A. Hall, The International Temperature Scale, in "Temperature Its Measurement and Control in Science and Industry", Vol. 2, ed. H. C. Wolfe, Reinhold, New York, 1955, p. 115
- 23 P. Chappuis, "Etudes sur le thermomètre à gaz et comparaison des thermomètres à mercure avec le thermomètre à gaz", *Trav. Mem. Bur. Int. Poids Mes.*, 1888, **VI**
- 24 Ch.-Éd. Guillaume, "Pierre Chappuis et le Développement moderne de la Thermométrie", Extrait de la Revue Générale des Sciences, Avril 1916, O. Doin et Fils, Editeurs, Paris
- 25 A. Hagenbach, *Verh. Naturforsch. Ges. Basel*, 1916, **XXVII**, 86-92; H. Zickendraht, *Verh. Schweiz. Naturforsch. Ges.*, 1917, 1-7
- 26 T. J. Quinn, "Temperatures", Academic Press, London, 1983
- 27 H. L. Callendar, "On the Practical Measurement of Temperature", *Phil. Trans.*, 1887, **178**, 160, as quoted in E. F. Mueller, "Precision Resistance Thermometry" in "Temperature Its Measurement and Control in Science and Industry", Reinhold, New York, 1941, p. 162
- 28 Op. cit., (Ref. 22), p. 118
- 29 L. Holborn and A. L. Day, "On the Gas Thermometer at High Temperatures," *Am. J. Sci.*, 1899, 4th Series, **8**, (45), 165
- 30 Op. cit., (Ref. 29), p. 186
- 31 Op. cit., (Ref. 17), p. 69
- 32 Op. cit., (Ref. 6), p. 12
- 33 C. Barus, *Bull. U.S. Geological Survey*, 1889, 54
- 34 C. E. T., *Proc. Geol. Soc., (London)*, 1959-60, (1582), 130-132
- 35 Op. cit., (Ref. 6), p. 15
- 36 Op. cit., (Ref. 6), p. 50
- 37 Op. cit., (Ref. 20), 258
- 38 J. A. Chaldecott, "Temperature Measurement & Control", Science Museum, London, 1976, 2nd Edn., (II), p. 15, item 43
- 39 D. McDonald and L. B. Hunt, "A History of Platinum and its Allied Metals", Johnson Matthey, London, 1982
- 40 "Le Système International d'Unites (SI)", 5th Edn., (French and English texts), 1985, BIPM, p. 106
- 41 P. P. M. Steur and M. Durieux, "Constant-Volume Gas Thermometry between 4K and 100K", *Metrologia*, 1986, **23**, (1), 1
- 42 L. Holborn and A. L. Day, "On the Expansion of Certain Metals at High Temperatures", *Am. J. Sci.*, 1901, Fourth Series, **11**, (65), 374
- 43 R. E. Edsinger, M. L. Reilly and J. F. Schooley, "Thermal Expansion of Platinum and Rhodium-Platinum Alloys", *J. Res. Natl. Bur. Stand.*, 1986, **91**, (6), 333