The Early History of the Thermocouple

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The name of Seebeck is indissolubly associated with the discovery of thermoelectricity and the thermocouple. But how did Seebeck's researches fit into the general background of contemporary scientific work, and how did they lead on to the development of the modern thermocouple pyrometer? This article outlines the early history of the couple up to the time when it became accepted as an accurate and reliable means of measuring high temperatures.

At this distance from the events, and looking back from our present understanding of the nature and applications of electricity, it is almost impossible to appreciate the excitement and enthusiasm that prevailed in the little world of physics around the year 1820. Until Volta announced the discovery of his pile in 1800 physicists had had no means of studying the effects of a steady current. This, and the voltaic cell which rapidly succeeded it, provided for the first time a simple means of maintaining a continuous current, and led to a burst of activity in the study of the chemical effects of electricity.

Oersted and Ampère

As this first wave of enthusiasm was perhaps dying away, Oersted discovered that a current of electricity flowing in a wire lying parallel with, and close to, a magnetic needle had the power of deflecting the needle. This discovery was announced in 1820, and it immediately set off a new wave of interest all over Europe, this time in the mechanical effects of a current.

Arago, in the same year, produced the first electromagnet, while Ampère, within a week of hearing of Oersted's experiment, had shown that one electric current had a magnetic influence upon another. No doubt was left that magnetism was essentially an electrical phenomenon.

Among the small band of physicists who were active in this way was Thomas Johann Seebeck. Born at Reval in Estonia on April 9th, 1770, the son of a wealthy merchant, he left his native town at the age of 17 and took up the study of medicine in Berlin. His strong inclination for natural science, together with his financial independence, caused him to change his plan, however, and he embarked on a career of private research, first in Bayreuth and later in Jena. Here he worked on optics and on the nature of colour, but in 1810 he left Jena for Nuremberg, and it was here that Oersted spent some time as Seebeck's guest. In 1818 he accepted a position with the Berlin Academy of Sciences, and moved to that city.

Seebeck's Discovery

Here it was, of course, that he learned of Oersted's discovery, and at once applied himself to the study of electromagnetism; in December of the same year, 1820, he read a paper to the Academy dealing with the magnetic influence of a current. Only a few months later, in August 1821, he announced to the Academy (1) his discovery that two different metals forming a closed circle, in the absence of moisture, showed magnetic properties when subjected to a difference of temperature at the point of contact. He had experimented with a number of combinations of metals (finding an antimony-bismuth combination the most effective), and had ascertained the effects of both heating and cooling one of the junctions. He established that the deflection of the magnetic needle arose from the difference in temperature of the metallic junctions, that the effects varied for different metals, and were greater for greater differences of temperature. In his results he reported the movement of the needle in terms of an easterly or a westerly deflection, and he described the phenomenon as "thermo-magnetism", taking objection in later years to the expression "thermo-electricity".

Second in importance at the time only to Oersted's experiment, Seebeck's discovery also spread rapidly among European physicists, and it was repeated in every centre of research.

Faraday and Ohm

Among others, Faraday carried out the experiment, and he records it in his diary as follows:

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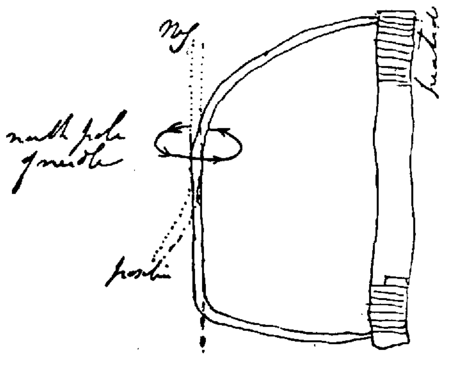
Dr. Seebeck's Expt. An. Phil. N.S. Vol. iv. p. 318

Bar of Antimony and brass wire; the bar being heated at one end the north pole of a needle would go round it as represented in the lower figure—the effect on the needle very decided, powerful even and constant.

The dotted lines represent the state of the wire as ascertained from former experiments.



At this time Ohm was working on the propagation of electricity through a conductor and on the concept of resistance, but he was having trouble in his experiments owing to the variations in the current obtained from his batteries. A suggestion was made to him by Poggendorf that he should replace the batteries by a thermo-electric circuit, and this idea Ohm adopted in his classical research in 1826. He used a circuit of bismuth and copper, one junction being immersed in a steam jacket and the other in ice.

The First Measurement of High Temperature

The first recorded suggestion to make use of Seebeck's discovery as a means of measuring high temperatures came from A. C. Becquerel (2) in a paper read to the Academie Royal des Sciences in Paris on March 13th, 1826. His investigations included observations of the needle deflection obtained with a number of combinations of metal wires when one junction was heated in a spirit lamp, and he deduced that, for certain of these combinations, the intensity of current developed was proportional to the rise in temperature. The most suitable combination, he decided, was a circuit consisting of platinum and palladium wires.

Becquerel further showed that the characteristics were independent of the diameter of the wire, and also that an impure platinum wire would give rise to a current if coupled with a pure platinum wire; he pointed out, in fact, the necessity for cleaning the platinum in nitric acid to avoid spurious effects due to contamination.

The Magnetic Pyrometer

In 1836 Professor C. S. M. Pouillet (3), of Paris, also before the Academie Royal des Sciences, put forward his "magnetic pyrometer" and detailed its construction. This instrument, almost incredible by today's standards, comprised a platinum wire sealed into the breech of a gun, the wire passing up the barrel but prevented from touching the sides by a filling of magnesia or asbestos. The breech of the gun was then to be inserted into the hot zone.

In the course of his long and classic researches on heat Henri Regnault (4) made use of Pouillet's iron-platinum couple, but he found such irregularities that he emphatically condemned the whole idea of the thermo-electric method. Regnault's unhappy experiences were due partly to his use of iron as one element, and also to his failure to employ a high-resistance galvanometer. Later, in 1862, Edmond Becquerel (5) took up the study of his father's platinum-palladium thermocouple and used it as an intermediary with an air thermometer in determining the melting points of a number of substances. As a result of his researches he succeeded to some extent in rehabilitating the reputation of the thermocouple, and he derived an expression—much too complex—for the relationship between temperature and electromotive force.

E.m.f. – Temperature Relationship

Avenarius (6) also investigated this relationship, working with the rather curious combinations of steel and nickel-silver, and copper and zinc. He arrived at a parabolic formula of the type:

$$E=a+bt+ct^2$$

but a few years later apparently realised his error and withdrew his arguments.

In the meantime Professor P. G. Tait (7) of Edinburgh University had conducted a series of experiments in an attempt to construct "thermo-electric diagrams", and concluded that the electromotive force is in general a parabolic function of the absolute temperature. He also reported that a very small amount of impurity, or even of permanent strain, is capable of considerably altering the line of a metal in the diagram.

Professor Tait used "platinum-iridium alloys containing respectively 5, 10 and 15 per cent of the latter metal. These were prepared for me from pure metals by Messrs. Johnson and Matthey". This constitutes the first reference to the use of iridium-platinum alloys in thermocouples.

Henry Le Chatelier

The father of the modern thermocouple, Le Chatelier was the first to employ a rhodium-platinum alloy against platinum and to recommend calibration in terms of the fixed points of melting or boiling of pure substances

The Work of Le Chatelier

And so to 1885 and Henry Le Chatelier (8), whose name, together with that of Seebeck, will always be associated with the thermo-electric pyrometer and with the use of a rhodium-platinum alloy. Born in Paris in 1850, Le Chatelier studied chemistry under Sainte-Claire Deville, but in 1870 was called into the army and took part in the siege of Paris. Subsequently he practised as a mining engineer, but in 1877 joined the French School of Mines to teach chemistry, becoming Professor of Industrial Chemistry some nine years later. Many years afterwards Le Chatelier recalled the origins of his work on thermocouples in the following words:

> "In 1885, when I attacked the problem of the measurement of high temperatures, it is

fair to say there existed nothing definite available on this important question; we possessed only qualitative observations for temperatures above 500°C. Engaged at that time in industrial studies relative to the manufacture of cement, I sought a method which above all would be rapid and simple, and decided on the use of thermo-electric couples, intending to determine the order of magnitude of the sources of error noticed by Regnault. The readings of even a crude galvanometer might be very useful in technical work, provided the limitations of its accuracy were appreciated. I soon recognised that the errors attributed to this method could easily be eliminated by discarding in the construction of the couples certain metals, such as iron, nickel, and palladium, which give rise to singular anomalies. Among the different metals and alloys studied, pure platinum and the alloy of platinum and rhodium which are still used today, gave the most satisfactory results. . . . I recommended also the calibration of the couples, not against the air thermometer directly, as Becquerel had tried to do, but in terms of the fixed points of boiling or fusion of certain pure substances, in such a way that, when these temperatures should be known more exactly, as is the case since my earlier researches, the results could be corrected with certainty."

Le Chatelier devoted considerable time and effort to the development of the thermocouple pyrometer, and arranged for the instrument to be manufactured by Carpentier, the successor of the famous Ruhmkorff, at 20 Rue Delambre, Paris. The reputation of these instruments spread rapidly and widely. In 1890, for instance, the great American metallurgist, Professor H. M. Howe wrote (9):

"Thanks to the labors of M. Le Chatelier, we have at last a pyrometer capable of measuring easily, accurately and rapidly extremely high temperatures, indeed, those approaching the melting point of platinum. And this is not an apparatus which each must construct for himself; it is for sale ready made. Indeed, it is so far simplified that it has actually entered into practical use for the control of high temperatures in steel works, glass works and gas works."

American Investigations

Contemporary with Le Chatelier but quite independently of him, Dr. Carl Barus (10) was engaging himself actively in the measurement of high temperatures. In 1882 a new physical laboratory had been set up within the organisation of the United States Geological Survey with the objective of studying the physical constants of rocks. Barus was put in charge of this laboratory, which was located first in New Haven, Connecticut, but moved to Washington two years later. He realised that few important steps in the study of this branch of geology could be made until methods for the accurate measurement of high temperatures and pressures had not only been perfected but rendered easily available, and he therefore undertook a most comprehensive study of temperature measurement; this was published as a memoir of some 300 pages in 1889. Numerous alloys of platinum were investigated as thermocouple elements, most of them having additions of 2, 5 and 10 per cent of other elements, but he came to rest for general use on platinum against 20 per cent iridium-platinum. Barus was aware of the importance of purity and homogeneity in

Sir William Roberts-Austen

Chemist to the Royal Mint, Professor of Metallurgy at the Royal School of Mines and first investigator to the Alloys Research Committee of the Institution of Mechanical Engineers, Roberts-Austen was quick to appreciate the usefulness of Le Chatelier's thermocouple pyrometer his thermocouple materials, and he drew upon the resources of the Bishop and Co. Platinum Works at Malvern, Pa., for the preparation of his materials. The couples were then calibrated at the boiling points of mercury, zinc and certain organic substances.

Roberts-Austen's Contribution

At this time the Institution of Mechanical Engineers had established its Alloys Research Committee, with the initial objective of studying the effects of alloying elements on the properties of metals, and had appointed W. C. Roberts-Austen, who combined the posts of Chemist to the Royal Mint and Professor of Metallurgy at the Royal School of Mines, as investigator. In his first report (11) in 1890 to the Institution, Professor (later Sir William) Roberts-Austen said:

> "In the present investigation it is necessary to measure much higher temperatures; and fortunately an accurate method is at hand. Early in 1889 I had occasion to employ the pyrometer devised by M. H. Le Chatelier, and was satisfied as to its being extremely trustworthy and convenient up to temperatures over 1000°C. or 1800°Fahr. The instrument in fact enabled me to confirm the fundamental observations of M. Osmond respecting the critical points of iron and steel, and to demonstrate the results in a lecture delivered before the members of the British Association in September 1889."

Since 1875 Roberts-Austen had interested himself in the problems of liquation or segregation of the constituents of alloys, and had been most painstaking in his measurement of temperatures using the laborious calorimetric methods then available. He therefore welcomed most readily the new type of instrument and proceeded to adapt it for the production of autographic records of the cooling and solidification of molten metals and alloys.

Problems of Homogeneity

Some doubt still remained, however, concerning the absolute reliability of the rhodium-platinum alloy, and Roberts-Austen referred to this:

Edward Matthey

Investigated the homogeneity of rhodium-platinum alloys and confirmed the findings of Le Chatelier and Roberts-Austen as to their suitability for thermometric use

> "It is asserted that even long wires of the platinum-rhodium alloy are homogeneous, and therefore do not give rise to subsidiary currents which would disturb the effect of the main current produced by heating the junction; but very careful experiments to determine whether this is the case have yet to be made."

This uncertainty aroused the interest of Edward Matthey, who carried out a lengthy investigation (12) on the liquation of alloys of the platinum metals. On the rhodium-platinum alloys he had the following comment to make:

> "Much attention has lately been drawn to an alloy of pure platinum, with 10 per cent of rhodium, which has become important from the excellent service it has rendered in the determination of high temperatures. The alloy of platinum with 10 per cent of rhodium is used with pure platinum as a thermocouple, and it is, therefore, interesting to be able to set at rest any doubt which might arise as to this alloy being uniform in composition when melted and drawn into wire."

Matthey prepared a melt of one and a half kilograms of 10 per cent rhodium-platinum, which he cast into a sphere of two inches diameter. The sphere was then sectioned, and samples were taken for analysis from a number of locations between the surface and the centre. The maximum difference between the centre and the outside was found to be 0.06 per cent of platinum and 0.04 per cent of rhodium. He concluded:

> "This result proves that the alloy is not subject to liquation, and fully justifies the high opinion that H. Le Chatelier and Roberts-Austen have formed as to its suitability for thermometric measurements."

At much the same time, 1892, Edward Matthey was concerning himself with the extraction and refining of bismuth and he contributed a series of papers on this subject to the Royal Society. An extract from one of these papers (13), dealing with the temperature at which arsenic can be oxidised off from bismuth, reads as follows:

> "The work of Roberts-Austen has shown that a thermo-junction is practically the only form of pyrometer that can be used for delicate thermal investigations of this kind, but the question arose which particular thermo-junction should be adopted. Was it well to use the platinum-iridium one as advocated by Barus, or the platinum-rhodium one suggested by H. Le Chatelier? My previous work on the alloys of platinum and rhodium, lately published in the 'Philosophical Transactions', settled the question in favour of the rhodium-platinum thermo-junction, for I was satisfied that the alloy of platinum with 10 per cent of rhodium is as homogeneous as any known alloy could well be, and is therefore admirably adapted for use as a thermo-junction, pure platinum being the opposing metal."

The instrument employed was obtained from Paris and was used in the full scale operation of the oxidation process in the works of Johnson Matthey, being one of the first such pyrometers to be used in industry.

The only earlier record of a Le Chatelier pyrometer being used in this country is that given by Sir Robert Hadfield (14), who purchased one from Carpentier in April 1890. This gave excellent service in the steel works of Hadfields Ltd. in Sheffield until British-made pyrometers became available just after the turn of the century.

The first mention of thermocouples being available for temperature measurement in this country appears in a Cambridge Instrument Company catalogue of 1898, but the manufacture of them did not begin until 1902, when special stocks of platinum and rhodium-platinum were procured from Johnson Matthey and marketed in suitable porcelain tubes (15).

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