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## CHAPTER XI.

## STANDARDIZATION OF PYROMETERS.

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## HIGH TEMPERATURES

## INTRODUCTION.

WEDGWOOD, the celebrated potter of Staffordshire, the inventor of fine earthenware and of fine china, was the first to occupy himself with the exact estimation of high temperatures. In an article published in 1782, in order to emphasize the importance of this question, he considered at length certain matters a study of which would be well worth while even to-day.

"The greater part of the products obtained by the action of fire have their beauty and their value considerably depreciated by the excess or lack of very small quantities of heat; often the artist can reap no benefit from his own experiments on account of the impossibility to duplicate the degree of heat which he has obtained before his eyes. Still less can he profit from the experiments of others, because it is even less easy to communicate the imperfect idea which each person makes for himself of these degrees of temperature."

Joining example to precept, Wedgwood made for his personal use a pyrometer utilizing the contraction of clay. This instrument, for nearly a century, was the only guide in researches at high temperatures. Replaced to-day by apparatus of a more scientific nature, it has been perhaps too readily forgotten.

Since Wedgwood, many have undertaken the measurement of high temperatures, but with varying success. Too indifferent to practical requirements, the early experimenters above all regarded the problem as a pretext for learned dissertations. The novelty and the originality of methods attracted them more than the precision of the results or the facility of the measurements. Also, up to the past few years, the confusion was on the

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increase. The temperature of a steel kiln varied according to the different observers from  $1500^{\circ}$  to  $2000^{\circ}$ ; that of the sun from  $1500^{\circ}$  to  $1,000,000^{\circ}$ . More recently there has been great improvement in methods.

First of all, let us point out the chief difficulty of the problem. Temperature is not a measurable quantity in the strict sense of the term. To measure a length or a mass, is to count how many times it is necessary to take a given body chosen as a unit (meter, gram) in order to obtain a complex system equivalent either as to length or mass of the body in question. The possibility of such a measurement presupposes the previous existence of two physical laws: that of equivalence and that of addition. Temperature obeys well the first of these laws; two bodies in temperature equilibrium with a third, and thus equivalent with respect to exchanges of heat in comparison with this third body, will also be equivalent, that is to say, equally in equilibrium with respect to every other body which would be separately in equilibrium with one of them. This law allows determination of temperature by comparison with a substance arbitrarily chosen as a thermometric body. But the second law is wanting; one cannot, by the juxtaposition of several bodies at the same temperature, realize a system equivalent, from the point of view of exchanges of heat, to a body of different temperature; thus temperature is not measured, at least insomuch as one considers only the phenomena of convection.

In order to determine a temperature one observes any phenomenon whatever varying with change of temperature. Thus for the mercury centigrade thermometer the temperature is defined by the *apparent expansion of mercury* from the *point of fusion of ice* measured by means of a unit equal to  $\frac{1}{100}$  of the dilatation between the temperature of the *fusion of ice* and that of the *ebullition of water* under atmospheric pressure.

**Thermometric Scales.** — For such a determination there are four quantities to be chosen arbitrarily: the *phenomenon* measured, the thermometric *substance*, the *origin* of graduation, and the *unit* of measurement; while in a measurement properly

so called there is but one quantity to be arbitrarily chosen, — the magnitude selected as unity. It is evident that the number of thermometric scales may be indefinitely great; too often experimenters have considered it a matter of pride for each to have his own.

Here are some examples of thermometric scales chosen from among many:

Author.	Phenomenon.	Substance.	Origin.	Unit.
Fahrenheit	Dilatation	Mercury	{ Very cold winter }	1/18° ice to B. P.
Réaumur	Dilatation	Mercury	Ice.....	1/80 ice to B. P.
Celsius	Dilatation	Mercury	Ice.....	1/100 ice to B. P.
Wedgwood	{ Permanent contraction }	Clay	Dehydrated	1/2400 init. dimens.
Pouillet	Dilat. at const. p.	Air	Ice	1/100 ice to B. P.
(Normal ther.)	Dilat. at const. v.	Hydrogen	Ice	
(Thermodynamic scale)	{ Reversible heat scale }	Anything	Heat = 0	
Siemens	Electric resistance	Platinum	Ice	

The enormous differences above mentioned in the estimations of high temperatures are much more the result of the diversity of the scales than due to the errors of the measurements themselves. Thus the experiments on solar radiation which have led to values varying from  $1500^{\circ}$  to  $1,000,000^{\circ}$  are based on measurements which do not differ among themselves by more than 25 per cent.

To escape from this confusion it was first necessary to agree upon a single scale of temperatures; that of the gas thermometer is to-day universally adopted, and this choice may be considered as permanent. The gases possess, more than any other state of matter, a property very important for a thermometric substance, — the possibility of being reproduced at any time and in any place identical with themselves; besides, their dilatation, which defines the scale of temperatures, is sufficient for very precise measurements; finally, this scale is practically identical with the thermodynamic scale. This last is in theory more important than all the other properties because it is independent of the nature of the phenomena and of the substances employed. It gives, too, a veritable measure and not a simple comparison; its

only inconvenience is for the moment not to be experimentally realizable, at least rigorously, but this will probably not always be the case.

The adoption of the scale of the gas thermometer does not in any way imply the obligation to use this instrument actually in all measurements. Any thermometer may be taken, provided that in the first place its particular scale has been standardized by comparing it with that of the gas thermometer. According to the case, there will be advantage in employing one or another method; practically also one almost never employs the gas thermometer by reason of the difficulties inherent in its use, which result principally from its great dimensions and the onerous manipulation required.

For the estimation of very high temperatures the gas scale can be used only by an indirect extrapolation in terms of some property of matter whose variation has been studied within the range of the gas scale attainable experimentally and which variation is assumed to obey the same law at temperatures beyond which control cannot be had with the gas thermometer.

The fact that certain of the radiation laws, to which resort must be had for the estimation of the highest temperatures, have a thermodynamic basis and may therefore be considered an extension of the thermodynamic scale, is of the greatest importance in the extrapolation for temperatures above the attainable limit of the gas scale.

There are several series of temperature measurements on the gas scale in good agreement to  $1100^{\circ}\text{C.}$ , and two series reaching nearly to  $1600^{\circ}\text{C.}$  which differ by  $25^{\circ}$  at this temperature. Beyond  $1600^{\circ}\text{C.}$  the most infusible substances permanently alter their properties, and we are forced to measure temperature in terms of the radiations coming from heated bodies for the reason that we have not been able to find any other than the radiating properties of such excessively heated bodies whose variations can be measured without destroying or permanently altering either the substance used as pyrometer or the substance examined. Perhaps also chemical methods may be employed eventually.

It is in the realm of the laws of radiation and their applications to pyrometric methods that some of the most recent and important advances in high-temperature measurements have been made, so that, with certain restrictions which will be treated in the chapter on the laws of radiation, it is possible to measure on a common scale the temperatures of bodies heated to the highest attainable limits.

It is our purpose, in this introduction, to pass in review rapidly the different pyrometric methods (that is to say, thermometers utilizable at high temperatures) whose employment may be advantageous in one or another circumstance; we shall then describe more in detail each of them, and shall discuss the conditions for their employment. But in the first place it is necessary to define within what limits the different scales may be compared to that of the normal gas thermometer; it is the insufficiency of this comparison which is still to-day the cause of the most important errors in the measurement of high temperatures.

**Fixed Points.** — The standardization of the different pyrometers is the most frequently made by means of the fixed points of fusion and ebullition which have been determined in the first place by means of the gas thermometer; the actual precision of the measurements of high temperatures is entirely subordinate to that with which these fixed points are known; this precision was for a long time most unsatisfactory because these fixed points could only be determined in an indirect manner with the gas thermometer, and some of them only by aid of processes of extrapolation, always very uncertain. Recent researches, however, by various observers, in which improved methods of heating have been used, as well as greater purity of materials and more carefully constructed and calibrated apparatus, have led to much more concordant results, in the determination of fixed points, even by most varied methods.

Violle was the first to make a series of experiments of considerable temperature range, which up to the last few years were our most reliable data on the question. In a first series of researches he determined the specific heat of platinum by direct comparison

with the air thermometer between the temperatures of 500° and 1200°. He made use indirectly of the relation thus established between specific heat and temperature to determine by comparison with platinum the points of fusion of gold and silver; then, by extrapolation of this same relation, the points of fusion of palladium and of platinum.

Fusion.....	{	Ag*	Au	Pd	Pt
		954°	1045°	1500°	1779°

Finally, in a second series of experiments, he determined by direct comparison with the air thermometer the boiling point of zinc.

Boiling point.....	{	Zn
		929.6

Barus, when physicist of the United States Geological Survey, determined the boiling points of several metals by means of thermoelectric couples standardized against the air thermometer.

Boiling point.....	{	Cd	Zn
		772° and 784°	926° and 931°
Mean.....		778°	928.5°

Callendar and Griffiths, by means of a platinum resistance thermometer calibrated up to 500° by comparison with the air thermometer, have determined the following points of fusion and ebullition:

Fusion.....	{	Sn	Bi	Cd	Pb	Zn
		232°	270°	321°	328°	419°
Boiling point under 760 mm.....	{	Aniline	Naphthaline	Benzophenone	Mercury	Sulphur
		184.1°	217.8°	305.8°	356.7°	444.5°

These last figures may be compared with Regnault's, and Crafts' previous determinations with the gas thermometer:

Naphthaline	Benzophenone	Mercury	Sulphur
218°	306.1°	357°	445°

Heycock and Neville, employing the same method, but with extrapolation of the law of resistance for platinum established at that time only up to 450°, determined the following points of fusion:

Sn	Zn	Mg (99.5%)	Sb	Al (99%)	Ag	Au	Cu
232°	419°	633°	629.5°	654.5°	960.5°	1062°	1080.5°

\* We shall use figures in italics for all fixed points determined in terms of the gas thermometer without extrapolation.

Also using the platinum thermometer calibrated at 0, 100, and 444.7° C. (the sulphur boiling point), Waidner and Burgess more recently at the Bureau of Standards find the following:

## FREEZING POINTS

Sn	Cd	Pb	Zn	Sb	Al	Ag-Cu <sub>2</sub>	Ag	Cu-Cu <sub>2</sub> O	Cu
231.9	321.0	327.4	419.4	630.7	658.0	779.2	960.9	1063.2	1083.0

## BOILING POINTS

Naphthaline.....	218.0°	Benzophenone.....	306.0°
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Jaquerod and Wassmer, using a hydrogen thermometer of 66 c.c. bulb, find:

Boiling.....	Naphthaline....	217.7°	Benzophenone...	305.4°
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One of the most important standardizing temperatures is the boiling point of sulphur to which the value 444.6° C. should be assigned from the work of some half-dozen investigators.

At the Physikalisch-Technische Reichsanstalt the question of establishing a temperature scale has received deserved attention. In the early nineties Holborn and Wien, using a thermocouple calibrated in terms of a porcelain-bulb nitrogen thermometer as far as 1400°, found the fusing points:

Fusion.....	{	Ag	Au	Pd	Pt
		970°	1072°	1580°	1780°

These results for Ag and Au were subsequently found to be high by Holborn and Day, who, after trying porcelain, worked with a platinum-iridium-bulb nitrogen thermometer and thermocouple, employing electric heating, two improvements that greatly increased the accuracy. In fact, the return to metal bulbs in place of porcelain, and the introduction of electric heating in place of gas, may be considered the inauguration of modern gas pyrometry. Holborn and Day determined the following on the constant-volume gas scale:

Fusion.....	{	Cd	Zn	Sb	Al	Ag	Au	Cu
		321.7°	419°	630.5°	657.5°	961.5°	1064°	1084°

This scale, commonly known as the Reichsanstalt scale, was extended to 1600° by Holborn and Valentiner, who, using extrap-



it unsuitable for ordinary measurements; it serves only to give the definition of temperature and should only be used to standardize other pyrometers.

*Calorimetric Pyrometer* (Regnault, Violle, Le Chatelier, Siemens).— Utilizes the total heat of metals, platinum in the laboratory and nickel in industrial works. Is to be recommended for intermittent researches in industrial establishments because its employment demands almost no apprenticeship and because the cost of installation is not great.

*Radiation Pyrometer* (Rosetti, Langley, Boys, Féry).— Utilizes the total heat radiated by warm bodies. Its indications are influenced by the variable emissive power of the different substances. Convenient for the evaluation of very high temperatures which no thermometric substance can withstand (electric arc, sun, very hot furnaces), or when it is not convenient to approach the body whose temperature is wanted. Can be made self-registering.

*Optical Pyrometer* (Becquerel, Le Chatelier, Wanner, Holborn-Kurlbaum, Morse).— Utilizes either the photometric measurement of radiation of a given wave length of a definite portion of the visible spectrum, or the disappearance of a bright filament against an incandescent background. Its indications, as in the preceding case but to a much less degree, are influenced by variations in emissive power. The intervention of the eye aids greatly the observations, but diminishes notably their precision. This method is mainly employed in industrial works for the determination of the temperatures of bodies difficult of access — for example, of bodies in movement (the casting of a metal, the hot metal passing to the rolling mill). Can be used to estimate the highest temperatures and is the best method for use above  $1700^{\circ}$  C. in laboratory and works.

*Electric Resistance Pyrometer* (Siemens, Callendar, Waidner and Burgess).— Utilizes the variations of electric resistance of metals (platinum) with the temperature. This method permits of very precise measurements to  $1000^{\circ}$  C., but requires the employment of fragile apparatus. It merits the preference for very

precise investigations in laboratories. As a secondary instrument for the reproduction of a uniform temperature scale throughout the range in which the platinum resistance thermometer can be used, to  $1000^{\circ}$  except in very heavy wire, it is unsurpassed in precision and sensibility. It is also now constructed in convenient form for industrial use.

*Thermoelectric Pyrometer* (Becquerel, Barus, Le Chatelier).— Utilizes the measure of electromotive forces developed by the difference in temperature of two similar thermoelectric junctions opposed one to the other. In employing for this measurement a Deprez-d'Arsonval galvanometer with movable coil, one has an apparatus easy to handle and of a precision amply sufficient for industrial and many scientific uses. With a potentiometer, an instrument is obtained of the most considerable precision, available for use to  $1600^{\circ}$  C., or even to  $1750^{\circ}$  with proper precautions. This pyrometer was used for a good many years in scientific laboratories, before it spread into general industrial use, where it also renders most valuable service.

*Contraction Pyrometer* (Wedgwood).— Utilizes the permanent contraction that clayey materials take up when submitted to temperatures more or less high. It is employed to-day only in a few pottery works.

*Fusible Cones* (Seger).— Utilize the unequal fusibility of earthenware blocks of varied composition. Give only discontinuous indications. Such blocks studied by Seger are spaced so as to have fusing points distant about  $20^{\circ}$ . In general use in pottery works and in some similar industries.

There are a number of other pyrometers which have been found suitable in special cases or which for one reason or another have been found convenient in some particular line of work. Some of these we shall mention, among them being the mel-dometer (Joly), interesting to the chemist or mineralogist for determining fusing temperatures of minute specimens; the various industrial instruments based on the relative expansion of metals or of a metal and graphite used in air blasts and metal baths; and, finally, pyrometers based on the flow or

on the pressure of air or vapor (Hobson, Uhling-Steinbart, Job, Fournier).

*Recording Pyrometers* (Sir Roberts-Austen, Callendar, Le Chatelier, Siemens and Halske). — Finally, we shall describe in some detail the application of registering methods to pyrometry both for technical and laboratory installations, — a field that has been cultivated very intensively in recent years.

## CHAPTER I.

### STANDARD SCALE OF TEMPERATURES.

WE have seen that temperature is not a measurable quantity: it is merely comparable with respect to a scale arbitrarily chosen. The normal or ideal standard scale is the *thermodynamic scale*; but as it is impossible to realize rigorously this scale, it is necessary to have a practical one. In the same way that, besides the theoretical definition of the meter, there is a practical standard, a certain meter kept at the Bureau International des Poids et Mesures, there exists, besides the ideal scale of temperatures, a practical scale, which is that of a certain gas thermometer which we are going to study. We shall first discuss the gas laws in so far as is necessary for our purpose, and then show how exactly these laws are obeyed by the actual gases that may be used in defining the temperature scale in the several possible ways.

**Laws of Mariotte and Gay-Lussac.** — The laws of Mariotte (or Boyle) and of Gay-Lussac are the basis for the use of the dilatation of gases for the determination of temperatures. These two laws may be written

$$\frac{p_1 v_1}{p_0 v_0} = \frac{1 + \alpha t_1}{1 + \alpha t_0}, \dots \dots \dots (1)$$

in which we may assume for the present that the temperatures are being measured with the mercury thermometer from 0° C.  $\alpha$  is a numerical coefficient, the same for all gases, at least to a first approximation, and its value is about

$$\alpha = 0.00366 = \frac{1}{273}$$

when it is agreed that the interval between the temperatures of melting ice and boiling water is 100°.

But instead of considering the formula (1) as the expression of