The calorimetric or specific heat pyrometer is to be recommended for certain operations below 1000° C. in technical works where it is required to make only occasional measurements of moderate precision; in cases where there is not the personnel sufficiently skillful to use the more precise or delicate methods; and finally, where the importance of the measurements is not such as to justify the buying of more costly instruments.

CHAPTER IV.

THERMOELECTRIC PYROMETER.

Principle. — The junction of two metals heated to a given temperature is the seat of an electromotive force which is a function of the temperature only, at least under certain conditions which we shall define further on. In a circuit including several different junctions at different temperatures, the total electromotive force is equal to their algebraic sum. In a closed circuit there is produced a current equal to the quotient of this resultant electromotive force and the total resistance.

Experiments of Becquerel, Pouillet, and Regnault. — It was Becquerel who first had the idea to profit from the discovery of Seebeck to measure high temperatures (1830). He used a platinum-palladium couple, and estimated the temperature of the flame of an alcohol lamp, finding it equal to 135°. In reality the temperature of a wire heated in a flame is not that of the gases in combustion; it is inferior to this.

The method was studied and used for the first time in a systematic manner by Pouillet; he employed an iron-platinum couple which he compared with the air thermometer previously described (page 61). In order to protect the platinum from the action of the furnace gases, he inclosed it in an iron gun barrel which constituted the second metal of the junction. Pouillet does not seem to have made applications of this method, which must have given him very discordant results.

Edm. Becquerel resumed the study of his father's couple (platinum-palladium). He was the first to remark the great importance of using in these measurements a galvanometer of high resistance. It is the electromotive force which is a function of the temperature, and it is the current strength that is measured. Ohm's law gives

$$E = RI.$$

In order to have proportionality between these quantities, E and I, it is necessary that the resistance of the circuit be invariable. That of the couple necessarily changes when it is heated; this change must then be negligible in comparison with the total resistance of the circuit.

Edm. Becquerel studied the platinum-palladium couple and made use of it as intermediary in all his measurements on fusing points, but he did not use it, properly speaking, as a pyrometer; he compared it, at the instant of observation, with an air thermometer heated to a temperature near to that which he wished to measure. He also tried to make a complete calibration of this couple, but this attempt was not successful; he did not take into account the irregularities due to the use of palladium; besides, he made use successively for this graduation of a mercury thermometer and of an air thermometer which did not agree with each other. He was led to assume for the relation between the temperature and the electromotive force a very complex expression; the formulæ which he gives contain together twelve parameters, while with the parabolic formula of Tait and Avénarius two suffice; thus

$$e = a + b\,(t - t_0) + c\,(t^2 - t_0^2),$$

which well represents the phenomenon for the couple in question to 1500°.

Regnault took up the study of Pouillet's couple, and he observed such irregularities that he condemned unreservedly the thermoelectric method. But these experiments were hardly conclusive, for he does not seem to have considered the necessity of using a high-resistance galvanometer.

Experiments of Le Chatelier and of Barus. — The thermoelectric method possesses, nevertheless, very considerable practical advantages for use in the laboratory as well as industrially, such as:

Smallness of thermoelectric substance;

Rapidity of indications;

Possibility of placing at any distance the measuring apparatus.

Le Chatelier decided to take up the study of this method, intending at the outset not to make disappear the irregularities which seemed inherent in the phenomena in question, but to study the law of these irregularities, so as to determine corrections which would permit of making use of this method, at least industrially, for approximate measurements. These investigations showed in their turn that the sources of error observed could be suppressed; the principal one, and the only serious one, came from lack of homogeneity of the metals up to that time employed.

Barus, whose work in this field dates from 1881, studied in great detail the thermoelectric measurement of high temperatures as well as the advantages and limitations of the various pyrometric methods. He was led from his researches to prefer the couple Pt, 90 Pt–10 Ir.

Iron, nickel, palladium, and their alloys were found to be unsuited for the exact measurement of high temperatures, because, heated in certain of their points, they give birth to parasite currents, sometimes relatively intense. D. Berthelot and others, however, have since used successfully in oxidizing atmospheres, thermocouples with palladium as one element.

As an example of inhomogeneity, consider the electromotive forces observed by Le Chatelier in carrying a Bunsen flame along beneath a wire of ferronickel of 1 mm. diameter and 50 cm. long; the electromotive forces are expressed in microvolts (millionths of a volt):

Distance........	0.05	0.10	0.15	0.20	0.30	0.35	0.40	0.50
E.M.F..........	−200	+250	−150	−1000	−500	−200	−50	−200

An electromotive force of 1000 microvolts is that given by the usual couples that we are going to study for a heating of 100°. With such anomalies as above there could hardly be any measurements possible.

These anomalies may sometimes be due to accidental variations in the composition of the wires, but in general there is no preëxisting heterogeneity; a physical heterogeneity due to the heating is produced. Iron and nickel, heated respectively to 750° and 380°, undergo an allotropic transformation, incompletely reversible by rapid cooling.

In the case of palladium, there may be produced, in a reducing atmosphere, phenomena of hydrogenation which change completely the nature of the metal, so that a metal initially homogeneous may become by simple heating quite heterogeneous and form a couple.

Certain metals and alloys are quite free from these faults, notably platinum and its alloys with iridium and rhodium. The irregularities previously observed are thus due to the employment of iron and palladium in all the couples tried.

A second source of error, less important, comes from the annealing. In heating a wire at the dividing point between the hardened part and the annealed part, there is developed a current whose strength varies with the kind of wire and the degree of hardness. The twisting that a wire has undergone at a point suffices to produce a hardening. A couple whose wires are hard drawn throughout a certain length will give different indications according to the point of the wire where the heating ceases. Here are results in microvolts obtained by Le Chatelier with a platinum, platinum-iridium (20 per cent Ir) couple (platinum-iridium alloy is very easily annealed):

	100°	445°
Before annealing	1100	7200
After annealing	1300	7800
Difference	200	600

We shall now study successively:

1. The choice of the couple;
2. Thermoelectric formulæ;
3. The methods of measurement;
4. The sources of error;
5. The standardization.

Choice of the Couple. — We shall first reproduce the evidence and arguments which led Le Chatelier to prefer and introduce the thermocouple of composition platinum against its alloy with 10 per cent rhodium for temperature measurements in those cases for which the thermoelectric method is preferable or convenient. We shall then give account of some of the later work of others in this domain.

In the choice of the couple, account must be taken of the electromotive force, the absence of parasite currents, and the inalterability of the metals used.

Electromotive Force. — This varies enormously from one couple to another. Below are several such electromotive forces given between 0° and 100° by metals that can be drawn into wires and opposed to pure platinum.

	Microvolts.
Iron	2100
Hard steel	1800
Silver	900
Cu + 10% Al	700
Gold	600
Pt + 10% Rh Pt + 10% Ir	500
Cu + Ag	500
Ferronickel	100
Nickel steel (5% Ni)	0
Manganese steel (13% Mn)	− 300
Cu + 20% Ni	− 600
Cu + Fe + Ni	−1200
German silver (15% Ni)	−1200
German silver (25% Ni)	−2200
Nickel	−2200
Nickel steel (35% Ni)	−2700
Nickel steel (75% Ni)	−3700

Barus studied certain alloys between 0° and 920°; he obtained the following results against platinum:

	Microvolts.
Iridium (2%)	791
Iridium (5%)	2830
Iridium (10%)	5700
Iridium (15%)	7900
Iridium (20%)	9300
Palladium (3%)	982
Palladium (10%)	9300
Nickel (2%)	3744
Nickel (5%)	7121

Here is another series made by Barus at the boiling point of sulphur with alloys of platinum containing 2, 5, and 10 per cent of another metal:

Metals.	Au	Ag	Pd	Ir	Cu	
2%	− 242	− 18	+ 711	+1384	+410	
5	− 832	−105	+ 869	+2035	+392	
10	−1225	−158	+1127	+3228	+257	
	Ni	Co	Fe	Cr	Sn	Zn
2%	+2166	+ 26	+3020	+2239	+261	+396
5	+3990	−170	+3313	+3123	+199	+ 24
10	+5095	− 41	+3962	+3583	+151	
	Al	Mn	Mo	Pb	Sb	Bi
2%	+779	+ 758	+ 263	−268	+1155	+245
5	+938	+2206	+1673	+338		
10	....	....	+ 766			

Of all these metals, the only ones to keep by reason of their high electromotive force are the alloys of platinum with iron, nickel, chromium, iridium, and rhodium. The following table gives, in microvolts, the electromotive forces of the 10 per cent alloys of these five metals up to the temperature of 1500°:

Temperatures.	Fe	Ni	Cr	Ir	Rh
100°	438	646	405	995	640
445	3,962	4,095	3,583	6,390	3,690
920	9,200	9,100	....	14,670	8,660
1500	19,900	20,200	....	26,010	15,550

Absence of Parasite Currents. — The alloy with nickel gives parasite currents of great intensity, as do all the alloys of this metal. It is the same with iron. Chromium does not seem to present the same inconvenience: it forms an alloy difficult to fuse and, for this reason, difficult to prepare. With the alloys of iridium and of rhodium there is no considerable production of parasite currents if the metals are pure and the alloys homogeneous.

There remain, then, but three metals to consider: iridium, rhodium, and chromium. Of the alloys of these metals with platinum, that of iridium is the one which hardens the most easily.

Chemical Changes. — All the alloys of platinum are slightly alterable. Those of nickel and of iron, at high temperatures, assume a slight superficial brownish tint caused by oxidation of the metal. No test has been made to see if, after a long time, this attack would reach even to the interior of the wires.

According to Le Chatelier the alloys of platinum, and platinum itself, become brittle by simply heating them long enough, especially between 1000° and 1200°; this is due without doubt to crystallization. The platinum-iridium alloy undergoes this change much more rapidly than the platinum-rhodium, and this latter more rapidly than pure platinum. It is questionable, however, if this effect, other than a slight crystallization, occurs in a strictly oxidizing atmosphere with couples containing only Pt, Rh, or Ir.

But a much more grave cause of the alteration of platinum and its alloys is the heating to high temperatures in a *reducing atmosphere.*

All the volatile metals attack platinum very rapidly, and a great number of metals are volatile. Copper, zinc, silver, antimony, nickel, cobalt, and palladium, at their points of fusion, already emit a sufficient quantity of vapor to alter rapidly the platinum wires placed in the neighborhood. These metallic vapors, that of silver and palladium excepted, can only exist in a reducing atmosphere. Among the metalloids, the vapors of phosphorus and of certain compounds of silicon are particularly dangerous. It is true that one is rarely concerned with these uncombined true metalloids, but their oxides in the presence of a reducing atmosphere are more or less completely reduced. In the case of phosphorus, it is not only necessary to shun phosphoric acid, but also acid phosphates of all the metals and the basic phosphates of the reducible oxides; thus silicon, silica, and almost all the silicates, clay included, must be avoided if a reducing atmosphere is employed.

The reducing flames in a fire-clay furnace lead little by little to the destruction of the platinum wires. It is thus indispensable to protect the couples against any reducing atmosphere by methods which will be indicated further on.

In taking account of these different considerations, — electromotive force, homogeneity, hardness, alterability by fire, — Le Chatelier was led to give the preference to the couple Pt − Pt + 10% Rh, with the possibility of replacing the rhodium by iridium and perhaps by chromium. In all cases the wires should be annealed electrically to 1400° before using.

The usual diameter of wire employed is 0.6 mm., but one of 0.4 mm. contains only half as much metal, and even for most industrial purposes is of sufficient robustness. In the laboratory there is advantage, especially on account of heat conduction, to still further reduce this diameter.

Thermoelectric Formulæ. — In spite of numerous attempts to solve the problem, it has thus far been impossible to deduce from purely theoretical grounds a satisfactory equation connecting the temperature and electromotive force of any thermoelectric couple. As we shall see, it is necessary to set up, for each type of couple, an empirical equation or a series of such equations which, sometimes within rather restricted temperature limits, represents well enough the desired relation. There is a great diversity of such formulæ, and there has been in the past a considerable amount of indiscriminate and unwarranted extrapolation of such empirical relations to temperature regions both high and low, in which the assumed formulæ do not hold. From the very common use of the thermocouple as a temperature-indicating device, this practice has caused considerable confusion in the values to be assigned to high temperatures. We shall call attention to some of the formulæ that have been used and

point out their limitations both for interpolation and extrapolation.

In the construction of thermoelectric formulæ it is customary to assume a constant temperature, usually 0° C., for the cold junctions, and to further assume that the only source of E.M.F. is the hot junction. The complete expression, however, for the total E.M.F. developed in a thermoelectric circuit requires account to be taken also of (1) the Thomson effect, or the E.M.F.'s generated due to differences in temperature along a homogeneous wire; (2) the Peltier effect due to the heating of the junction of two dissimilar metals anywhere in the circuit; (3) the Becquerel effect, or the E.M.F.'s developed by physical or chemical inhomogeneity in a single wire.

The E.M.F. actually measured is the algebraic sum of all these quantities. Practically, the Thomson effect need not be taken account of separately in constructing a formula, as it is a function only of the temperature difference along the wires and of their nature.

The undesirable Peltier and Becquerel effects, the former occurring often in the measuring apparatus, and the latter mainly in the thermocouple wires, cannot be taken care of numerically in any useful thermoelectric formula, and must therefore be eliminated by the use of materials and methods free from these effects.

The following formulæ, therefore, all assume thermoelectric circuits in which the only sources of E.M.F. are due to the difference in temperature between the hot and cold junctions of the couple.

Thermoelectric Power. — By differentiating with respect to temperature the expression for the E.M.F.-temperature relation $E = f(t)$ for any couple, we get a quantity known as its thermoelectric power, $\frac{dE}{dt}$, which we may designate by H. This quantity is a convenient one with which to compare the numerical behavior at any temperature of two or more couples, or of one couple at different temperatures, as it gives the E.M.F. per de-