L being the length of the cold tube, and l the displacement of the warm tube.

$$k\,(d_1 - d_0)\,L = k\,(d' - d_0)\,l,$$

$$L\left(\frac{d_1}{d_0} - 1\right) = l\left(\frac{d'}{d_0} - 1\right),$$

$$L\left(\frac{p}{p_0} - 1\right) = l\left(\frac{T_0}{T} - 1\right),$$

an expression which gives a relation between the pressures and the temperatures.

This method, employed for the control of the boiling points, has given the following results:

	Pressure.	Temperature observed.	Temperature calculated.
Alcohol	741.5 mm.	77.69°	77.64°
Water	740.1	99.2	99.20
Water	761.04	100.01	100.01
Aniline	746.48	183.62	183.54
Aniline	760.91	184.5	184.28

Berthelot has standardized by the same method thermocouples which he used to determine the fusing points of silver and gold, and the boiling points of zinc and cadmium:

Silver, freezing	962° C.
Gold, freezing	1064
Zinc, boiling	920
Cadmium, boiling	778

The numbers found are nearly identical with those which result from the best determinations made by other methods.

We shall discuss further the determinations of fixed points in pyrometry in Chapter XI.

CHAPTER III.

CALORIMETRIC PYROMETRY.

Principle. — A mass m of a body, brought to a temperature T, is dropped into a calorimeter containing water at a temperature t_0. Let t_1 be the final temperature of water and substance. M being the water equivalent of the substances in contact (water, calorimetric vessel, thermometer, etc.) which are raised from t_0 to t_1, L_t^T the heat required to warm unit mass of the body from t_1 to T, we have

$$L_t^T \times m = M\,(t_1 - t_0).$$

Taking as origin of temperatures the zero of the centigrade thermometer, the heat required to warm unit mass of the body to the temperature T will be

$$L_t^T = L_{t_1}^T + L_0^t.$$

The quantity L_0^t is easy to calculate, because the specific heats at low temperatures are sufficiently well known:

$$L_0^t = ct_1.$$

The expression for the total heat becomes

$$L_0^T = \frac{M\,(t_1 - t_0)}{m} + ct_1.$$

t_1 and t_0 are the temperatures given by the direct readings of the thermometer.

The value of the second member is thus wholly known, and consequently that of the first member which is equal to it. If previous experiments have made known the value of the total heat L_0^T for different temperatures, one may from the knowledge of L_0^T determine the value of T. It will be sufficient to trace a curve on a large scale whose ordinates are temperatures, and

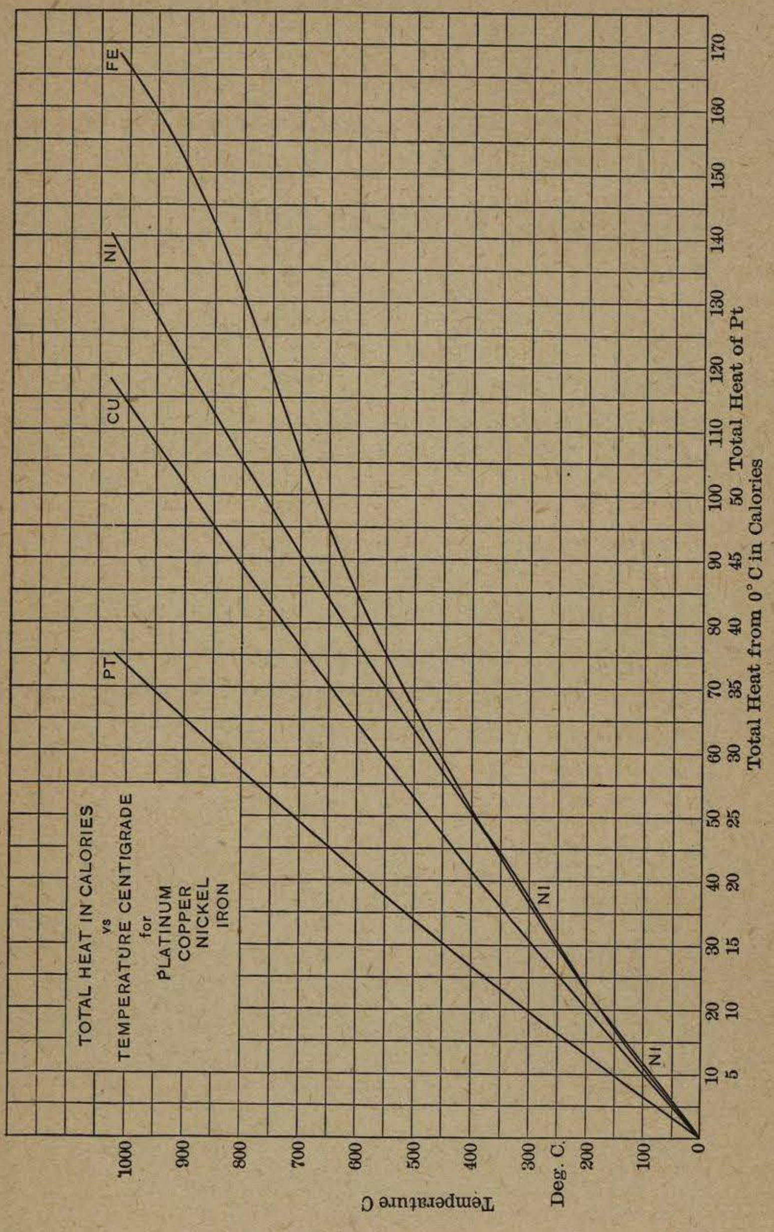

Fig. 17. Total Heat of Metals from 0° C.

abscissas total heats, and to find upon this curve the point whose abscissa has the value given by the calorimetric experiment.

In Fig. 17 are given curves of temperature in terms of total heat from 0° C. for the several metals used in specific heat pyrometry. The values of the total heats are the means, for each metal, of the experimental results cited in the several tables which follow.

Choice of Metal. — Four metals have been proposed: *platinum*, *iron*, *nickel*, and *copper*.

Platinum. — This metal was first proposed by Pouillet, and taken up again by Violle. It is much to be preferred to the other metals; its total heat has been compared directly with the indications of the gas thermometer. This metal can also be reproduced identical with itself. Iridium, which commercial platinum often carries, has about the same specific heat. The high price of these substances is an obstacle to their use extensively in works; for a calorimeter of a liter it is necessary to have at least 100 grm. of platinum, — or $100 in a volume of 5 c.c., — easily lost or made away with.

Violle determined the total heat of platinum from 0° to 1200°, and computed it by extrapolation to 1800°.

W. P. White has determined the specific heat of platinum to 1500°, obtaining somewhat lower values than Violle. The differences cannot be accounted for by differences in temperature scales. A few measurements by Tilden to 600° give values between the others, and Plato at 600° and 750° finds values agreeing closely with White's.

TOTAL HEAT OF PLATINUM FROM 0° C. IN CALORIES.

Temperature.	Violle.	White.	Temperature.	Violle.	White.
100	3.23	....	1000	37.70	35.45
200	6.58	....	1100	42.13	39.32
300	9.95	9.49	1200	46.65	43.28
400	13.64	13.09	1300	(51.35)	47.26
500	17.35	16.75	1400	(56.14)	49.22
600	21.18	20.44	1500	(61.05)	55.20
700	25.13	24.15	1600	(66.08)	(59.26)
800	29.20	27.88	1700	(71.23)	(63.45)
900	33.39	31.63	1800	(76.50)	.....

White's measurements on mean specific heat satisfy the equation $0.0319_8 + 3.4 \cdot 10^{-6}t$.

Iron. — Regnault, in an investigation made for the Paris Gas Company, had proposed, and caused to be adopted, iron, in attributing to it a specific heat of 0.126, instead of 0.106 at 0°. He used a cube of 7 cm. sides which was thrust into the furnaces by means of long iron bars. The calorimeter was of wood and had a capacity of 4 liters.

Various observers have determined the total heat of iron; at high temperatures the accord is not perfect among the results, as shown in the following table:

TOTAL HEAT OF IRON FROM 0° C. IN CALORIES.

Temperature.	Pionchon.	Euchène.	Harker.	Oberhoffer.	Weiss and Beck.
100	11.0	11.0	....	....	....
200	22.5	23.0	23.0	23.4	23.1
300	36.8	37.0	37.0	37.5	36.1
400	51.6	52.0	51.3	52.4	49.5
500	68.2	69.5	66.9	66.0	64.4
600	87.0	84.0	83.8	84.6	81.2
700	108.4	106.0	104.1	113.4	101.0
800	135.4	131.0	127.8	135.2	124.2
900	157.2	151.5	148.0	152.1	148.5
1000	170.9	173.0	155.7	167.0	.....
1100	.....	.....	168.8	182.6	.....
1200	.....	.....	.....	199.2	.....
1300	.....	.....	.....	215.8	.....
1400	.....	.....	.....	232.4	.....
1500	.....	.....	.....	250.5	.....

The determinations of Pionchon and of Euchène are in terms of incorrect temperature scales, at least above 800° C., and although those of the other observers are in terms of approximately the same scale, the one ordinarily used to-day, this agreement is far from satisfactory. Oberhoffer's results show an abrupt change in specific heat beginning at 650°, and changes in specific heat corresponding to the allotropic forms of iron. The results of Weiss and Beck show an abrupt change in specific heat at 750°, corresponding to the magnetic transformation point. According to Oberhoffer and Meuthen, the addition of carbon to iron increases the specific heat in the proportion of 0.0011 per each 0.5 per cent carbon added, at least for the temperature range 0° to 650° C.

In spite of its common use for this purpose, this metal is not at all suitable for calorimetric use, by reason in the first place of its great oxidability. There is formed at each heating a coating of oxide which breaks off upon immersion in water, so that the mass of the metal varies from one observation to the next. Besides, iron, especially when it contains carbon, possesses changes of state accompanied during the heating by a marked absorption of heat. By cooling in water, hardening takes place, which may irregularly prevent the inverse transformations. The use of electrolytic iron is therefore preferable, since the most marked transformation and the one at the lowest temperature is thus avoided, and the oxidation is less.

Nickel. — At the Industrial Gas Congress in 1889 Le Chatelier proposed nickel, which is but slightly oxidizable up to 1000°, and which above 400° does not possess changes of state as does iron.

The total heat of nickel has been determined by Pionchon, by Euchène, and by Weiss and Beck.

The differences are due very probably in part to impurities that the nickel may contain, as well as to experimental and temperature-scale uncertainties.

TOTAL HEAT OF NICKEL FROM 0° C. IN CALORIES.

Temperature.	Pionchon.	Euchène.	Weiss and Beck.
100	11.0	12.0	....
200	22.5	24.0	23.1
300	42.0	37.0	36.2
400	52.0	50.0	50.0
500	65.5	63.5	63.2
600	78.5	75.0	76.6
700	92.5	90.0	90.0
800	107.0	103.0	104.9
900	123.0	117.5	.....
1000	138.5	134.0	.....

Copper is sometimes used, and although when pure it appears to possess no transformation regions, it oxidizes and scales very readily and cannot be used to as high temperatures as any of the other metals proposed. In the following table are given values of the total heat of copper as computed from the experiments of Le Verrier and of Frazier and Richards.

TOTAL HEAT OF COPPER FROM 0° C. IN CALORIES.

Temperature.	Le Verrier.	Frazier and J. W. Richards.
100	10.4	9.6
200	20.8	19.5
300	31.2	29.8
400	42.2	40.4
500	54.7	51.4
600	66.5	62.8
700	77.8	74.4
800	91.0	86.5
900	103.8	99.0
1000	115.6	111.7

Calorimeters. — In laboratories a platinum mass is often employed with Berthelot's calorimeter, a description of which is given in various publications on calorimetry (Fig. 18). The thermometer used for the measurement of the rise in temperature should be very sensitive, so that a rise of from 2° to 4° be sufficient in order to render negligible the cooling correction. If use is made, for instance, of a thermometer giving the hundredth of a degree, the mass of platinum should be about one-twentieth the mass of the water in the calorimeter.

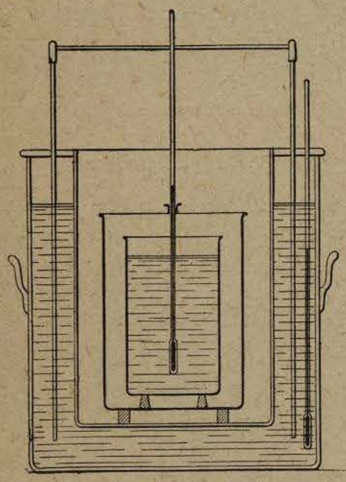

Fig. 18. Berthelot's Calorimeter.

A form of water-inclosed calorimeter, with furnace, such as used by White in specific heat determinations, is shown diagrammatically in Fig. 19. This method of operation is also applicable to temperature estimations. The water cover is swung aside when the platinum mass is dropped into the calorimeter.

This type of calorimeter is to be preferred in exact calorimetric work where high temperatures are involved, as the uncertainties of radiation and evaporation are reduced to a minimum. The usual mercury thermometer may be replaced to advantage by some form of electric thermometer.

Industrial Calorimeters (Fig. 20). — In the arts, where the measurements are made with less precision, and where it is necessary to consider the cost of installation of the apparatus, nickel may be made use of, a thermometer giving tenths of a degree, and zinc calorimeter, which may be home-made. Such an installation may cost as little as $5. A mass of nickel should be used equal to one-twentieth of the mass of water of the calorimeter.

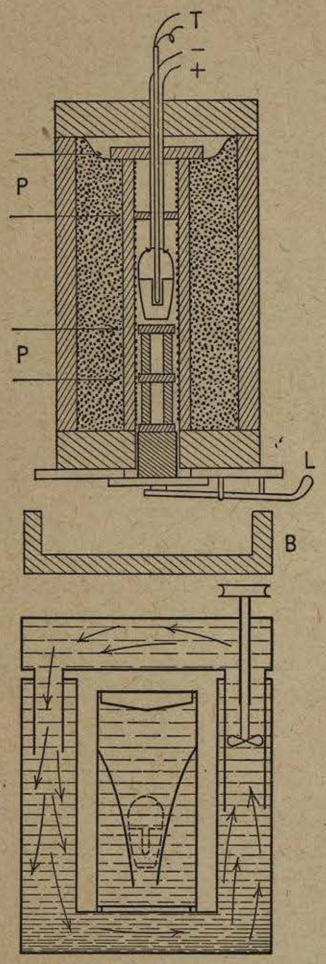

Fig. 19. White's Calorimeter.

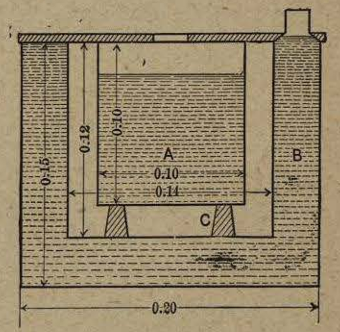

Fig. 20. Industrial Calorimeter.

The calorimeters used by the Paris Gas Company are after the Berthelot pattern; they are also water-jacketed.

Such an apparatus may consist of a cylindrical calorimeter A of two liters capacity, of zinc or of copper; a double cylindrical jacket B of the same metal, containing water, and which may be surrounded by felt on the outside. The calorimeter rests on this

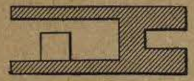

Fig. 21. Metal Carrier.

jacket by means of a wooden support C. There is preferably a metallic cover in good contact with the outside vessel. A thermometer graduated to fifths of a degree, having a small but quite long bulb, serves as stirrer. The thermometric substance is a piece of nickel of mass equal to one-tenth that of the water, or 200 grm., so as to have considerable rise of temperature easy to read by the workmen who make the measurements.

As a general rule, one must avoid placing the thermometric substance upon the floor of the furnace. The piece of nickel, which is made in the form of small cylinders having from 15 to 25 mm. diameter and from 10 to 30 mm. length, rests so as to be insulated from the floor in a nickel crucible provided with a foot and with two arms attached somewhat above the center of gravity. When it has been heated for a half-hour, an observer takes out the crucible with a forked rod, and another seizes this crucible with tongs to empty it into the calorimeter.

Use is not made of an iron crucible because this metal oxidizes and lets drop scales, which falling into the calorimeter would vitiate the experiment. Fig. 21 shows a suitable arrangement for containing a nickel cylinder.

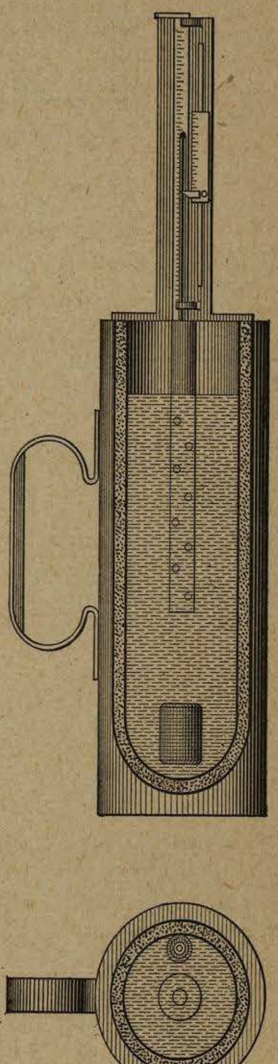

Fig. 22. Siemens Calorimeter.

Siemens Calorimeter. — A convenient form of direct-reading calorimeter due to Siemens is shown in Fig. 22. Using always the same mass of water and a ball of given mass and kind, the thermometer or an auxiliary scale may be graduated to read directly the temperature attained by the heated ball. Hollow copper cylinders are usually furnished with this apparatus.

Precision of Measurements. — Biju-Duval made a series of experiments to study the sources of error arising from the use of the industrial calorimeter by comparing its indications to those of the thermoelectric pyrometer of Le Chatelier. The observations were taken by varying the following conditions:

Use of thermometer graduated to $\frac{1}{5}°$ or to $\frac{1}{50}°$.

Use of the old wooden gas-works calorimeter or of the water-jacketed calorimeter.

Use of iron or nickel.

I. *Experiment.* — Old wooden gas-works calorimeter. Iron. Thermometer in fifths.

$$P = 10{,}000 \text{ grm.}$$
$$p = 1031 \text{ grm.}$$
$$t_0 = 20.8°$$
$$t_1 = 36.2°$$
$$Q_0^t = 153.5 \text{ cal.}$$

Computed temperature:

Mean specific heat of iron = 0.108	$t = 1420°$
Mean specific heat of iron = 0.126	$t = 1210$
Total heat according to Biju-Duval	$t = 915$
Thermoelectric pyrometer	$t = 970$

It is thus evident that the mean specific heats even with the correction suggested by Regnault give temperatures much too high. With the curve of total heats the temperature found is much too low on account of the following losses of heat:

1. Absorption of heat by the wooden walls;
2. Radiation from the iron cube during transfer;
3. Cooling of the water in the calorimeter, whose temperature exceeded by 16° the temperature of the surroundings.

The following experiments were made with the thermometer reading to $\frac{1}{50}^\circ$; the piece of nickel was protected against radiation by a crucible. The two calorimeters were compared.

II. *Trial with the Wooden Calorimeter.* —

$T = 975^\circ$ by the thermoelectric pyrometer
$P = 10{,}000$ grm.
$p = 145$ grm.
$t_0 = 20.21^\circ$
$t_1 = 21.99^\circ$
$L_0^T = 125$ cal.
$L_0^T = 131.5$ cal. from the curve at 975°.

The difference is 6.5 calories, or 5 per cent loss due to the jacket.

III. *Trial with the Water-jacketed Calorimeter.* —

$T = 985^\circ$
$P = 2000$ grm.
$p = 48.4$ grm.
$t_0 = 18.86^\circ$
$t_1 = 21.95^\circ$
$L_0^T = 130$ cal.
$L_0^T = 133$ cal. from the curve at 985°.

The difference is 3 calories, or a loss of about 2 per cent only when use is made of a carefully made calorimeter and of a thermometer giving $\frac{1}{50}^\circ$. This corresponds to an uncertainty of less than 20° in the temperatures sought. Some of this uncertainty may be due to the temperature assumed as correct in these measurements and to loss of heat during transfer. It is possible to work to better than 5° by the most refined methods, using a platinum mass. With the $\frac{1}{10}^\circ$ thermometers, necessitating a much greater rise of temperature of the water in the calorimeter, an uncertainty of 25° or more may exist. The relatively small mass of water used with a less sensitive thermometer is not necessarily a disadvantage, however, if the calorimeter is properly protected against heat loss and evaporation due to the greater temperature rise.

Conditions of Use. — The advantages of the calorimetric pyrometer are:

1. Its low net cost;
2. The ease of its use, which allows of putting it in the hands of a workman.

Its inconveniencies are:

1. The time necessary to take an observation, about a half-hour, except with the Siemens form;
2. The impossibility of taking continuous observations;
3. The impossibility of exceeding 1000° by the use of the piece of nickel;
4. The deterioration of the balls used due to oxidation.

Its use does not seem to be recommendable for laboratories, as there are continuous methods of greater accuracy readily available for such uses. In the laboratory, the calorimetric method is used ordinarily for the determination of specific heats at high temperatures rather than of these temperatures. In recent years, there have been introduced many refinements into calorimetric measurements, such as vacuum-jacketed calorimeters which nearly eliminate heat losses during the rise in temperature within the vessel; resistance thermometers and thermoelements of great sensitiveness and precision which give the rise in temperature within the calorimeter more accurately than does a mercury thermometer; electric heating and vacuum furnaces for the preheating of the sample without contamination to the desired high temperature; and many other details of manipulation and construction, for descriptions of which the reader should consult the writings of Berthelot, Louginine and Schukarew, Dickinson, Richards, White, Oberhoffer, and others.

It is possible, for instance, to keep the total error due to the calorimeter to within 1 in 10,000. These improvements are of the greatest importance for the exact determination of specific and latent heats and similar constants at high temperatures, but have little interest from the purely pyrometric point of view, since much more delicate and accurate temperature-measuring methods exist which do not involve the transfer of heat.

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