sistance of the selenium varies, and the indications of the ammeter may be empirically calibrated in terms of temperature. As selenium is quite insensible to the invisible heat waves, the lower limit of this method is above incandescence. Selenium also requires some time to recover its original resistance after being acted upon by light, and this lag might prove troublesome. As a dial instrument is used, the method could readily be made recording.

CHAPTER IX.

VARIOUS PYROMETRIC METHODS.

WHILE some of the several types of pyrometer which we have described in the preceding chapters have, by a process of elimination, become generally recognized as meeting most requirements for high-temperature measurements, scientific and industrial, there nevertheless remain several methods, some of which are useful in special fields of investigation or practice, and others mark some important development in the history of pyrometry. We shall mention briefly a few of these methods.

Wedgwood's contraction pyroscope, the oldest among such instruments, presents to-day hardly more than an historic interest, for its use has been almost entirely abandoned. It utilizes the permanent contraction assumed by clayey matters under the influence of high temperature. This contraction is variable with the chemical nature of the paste, the size of the grains, the compactness of the wet paste, the time of heating, etc. In order to have comparable results, it would be necessary to prepare *simultaneously, under the same conditions*, a great quantity of cylinders, whose calibration would be made in terms of the gas thermometer. Wedgwood employed cylinders of fire clay, baked until dehydrated, or to 600°; this preliminary baking is indispensable, if one wishes to avoid their flying to pieces when suddenly submitted to the action of fire. These cylinders have a plane face on which they rest in the measuring apparatus, so as always to face the same way (see the frontispiece). The contraction is measured by means of a gauge formed by two inclined edges; two similar gauges of 6 inches in length, one an extension of the other, are placed side by side; at one end they have a maximum separation of 0.5 inch, and at the other a minimum separation of 0.3 inch. Longitudinally the divisions are of 0.05 inch; each

division equals $\frac{1}{240}$ of $\frac{2}{10}$ of an inch, or $\frac{1}{1200}$ inch, which corresponds to a relative contraction of $\frac{1}{1200} \div \frac{5}{10} = \frac{1}{600}$ in terms of the initial dimensions.

We then have the following relation between the Wedgwood degrees and the linear contraction per unit of length:

Wedgwood	0	30	60	90	120	150	180	210	240
Contraction	0	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40

Le Chatelier has made experiments to determine the degrees of the Wedgwood pyrometer in terms of the scale of the air thermometer by making use of clayey substances of different kinds, and in the first place of the cylinders from an old Wedgwood pyrometer of the École des Mines. The contraction which accompanies the dehydration is quite variable with the nature of the pastes. In these experiments the time of heating was half an hour.

Centigrade temperature	600°	800°	1000°	1200°	1400°	1550°
Wedgwood	0	4	15	36	90	132
Argile de Mussidan	0	2	14	36	78	120
Limoges porcelain	0	0	2	21	88	91
Faïence de Choisy-le-Roi	0	2	5	12	48	75
Faïence de Nevers	0	0	0	32	Melted	Melted
Kaolin	0	4	12	15	55	118
Clay 25 / Titanic acid 75	0	4	9	19	123	160

This table shows how variable are the observations; it is impossible, consequently, to compare the old measurements of Wedgwood and of his successors, because the manufacture of the cylinders has varied with the course of time.

Wedgwood had given a graduation made by a process of extrapolation which he has not explained, — a graduation according to which he attributed 10,000° C. to 130° of his pyrometer, which corresponds to about 1550°. One might still seek to reëstablish the graduation by utilizing the determinations of the fusing points of the metals made by Wedgwood, but the results are too discordant to warrant any definite conclusion. According to Wedgwood, copper would be more fusible than silver, iron would not be far removed from silver; it is probable that these observations were made with very impure metals, or at any rate were

made with metals much oxidized before their fusion. In any case the cylinders which he made use of in his first experiments assume a much greater contraction than those of the pyrometer of the School of Mines whose graduation was given above. One might with considerable reserve indicate the following graduation for measurements made with the first cylinders employed about the year 1780:

Wedgwood degrees	0	15	30	100	140
Centigrade degrees	600	800	1000	1200	1400

The preparation of the cylinders was a most care-taking operation. Molded in soft paste, they were necessarily somewhat irregular. After the first baking they had to be trimmed to bring them to a uniform size. To-day, in several pottery works where the method is still employed, a much greater regularity is obtained by using a very dry paste, 5 per cent of water for example, molding it under great pressure, about 100 kg. per square centimeter, in molds of turned steel. The precision of the measurements is increased by augmenting the diameter, to 50 mm. for example. It is necessary at the same time to reduce the thickness to about 5 mm., in order that the compression be uniform throughout the mass.

This apparatus cannot be recommended in any instance as a true pyrometer, serving indirectly to evaluate temperatures in terms of the air-thermometer scale. The graduation is laborious and can only be made by means of the intermediary of another pyrometer; the use of fixed points is not adapted for this graduation because the curve of contraction of clay in function of the temperature is too irregular for two or three points to determine it; in no case do the indications of this instrument possess any considerable precision.

But as simple pyroscope, that is to say, as an apparatus to indicate merely the equality or inequality of two temperatures, the Wedgwood pyrometer is very convenient. It has the advantage of costing almost nothing and it is easy to use and within the comprehension of any workman. It seems to be particularly recommendable for certain ceramic industries, in which the ordi-

nary pastes found there may be used to make the contraction cylinders. It is necessary for this that the normal baking of these pastes be stopped at a temperature comprised within the period of rapid contraction. This is the case with fine faïence and with ordinary earthenware. That would not be the case, however, for stanniferous faïence nor for porcelain, because the baking of the first is stopped before the beginning of the contraction, and that of the second after its finish.

Expansion of Solids.—Some of the earliest forms of indicating pyrometers were based on the relative expansion of two metals, or of a metal and graphite or fire clay. Some of these instruments have had and still enjoy a very wide use both in Europe and America, often under the name *mechanical thermometers* for the lower-range instruments, and some of them are suitable for certain industrial processes not requiring exact temperature determination or control. A common form of dial instrument is shown in Fig. 127. A tube of iron incloses a rod of graphite, and their differential expansion with change in temperature is communicated by levers to a pointer turning over a dial graduated in degrees. The upper limit of these instruments is about 800° C. (1500° F.), but they deteriorate rapidly when used at the higher temperatures. Their indications change with time, due to changes produced in the materials by continued heatings. Correcting the zero of such an instrument, which should be done frequently, does not completely correct the rest of the scale, as the expansion properties of the two materials change differently with heating. Varying depths of immersion will also change the readings.

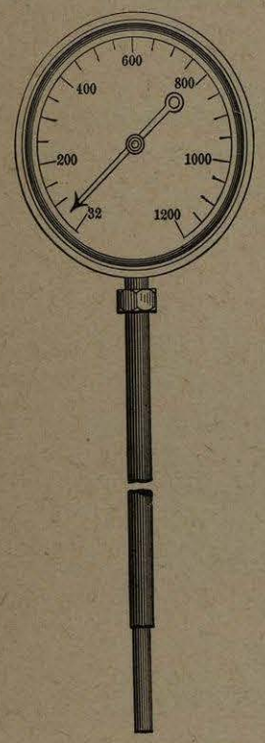

Fig. 127. Expansion Pyrometer.

The Joly Meldometer.—A modified form of this instrument was previously mentioned (page 271). As in its usual form it may be of great service to chemists, mineralogists, and others in determining the melting points and identification of minute specimens of minerals, salts, metals, and alloys, a further description may be of interest.

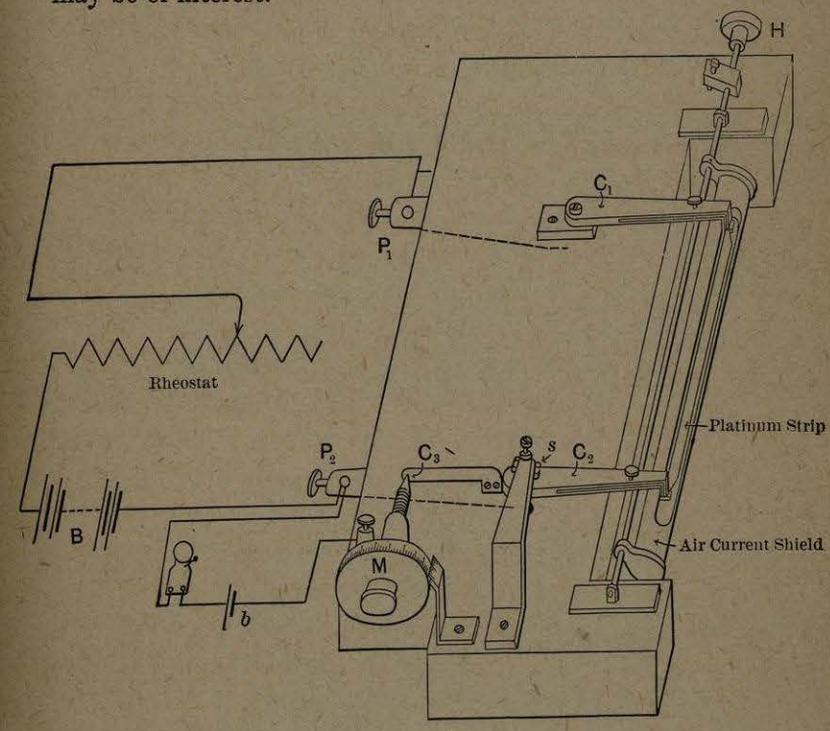

Fig. 128. Joly's Meldometer.

A platinum strip (Fig. 128) 10 cm. long, 4 mm. wide, and 0.02 mm. thick is held between two clamps *C*, *C*, and kept under a slight tension by the spring *s*. A storage-battery current controlled by a small step rheostat *R* is sent through the platinum strip whose length at any instant is given by the micrometer screw *M*, whose contact is made appreciable by the closing of the circuit of an electric bell. The platinum strip is calibrated preferably by means of salts of known melting points, as KNO_3 (399° C.), KBr (730°), NaCl (800°), and K_2SO_4 (1060°). Metals

may also be used, but they tend to deteriorate the platinum. The upper limit of the instrument is about 1500° C., the Pd point being obtainable with difficulty. Permanent elongation sets in somewhat before this point is reached. The gold point (1063° C.) can be determined to 2° C., and only a few moments are required for an observation.

To take an observation, a speck of the specimen whose melting point is sought is placed on the middle of the strip under a low-power microscope magnifying about twenty-five times. The current is increased and at the instant of melting, as observed with the microscope, the micrometer is set to make contact and read; when by interpolation, most conveniently made graphically, the temperature is found corresponding to the length of strip observed. This instrument gives a nearly but not quite linear relation between length of strip and temperature.

High-range Mercury Thermometers. — Although mercury boils normally at about 356° C., yet this liquid subjected to high pressure may be kept from boiling and, suitably inclosed, may be used as thermometric substance to much higher temperatures. Compressed under an atmosphere of some inert gas, as nitrogen or carbonic acid, and inclosed in a very hard glass, the mercury thermometer can be used up to 550° C. (1000° F.). When a thermometer designed for only moderate temperatures, 200° C. or less, is sealed off gas free, there will be distillation of the mercury into the colder parts of the bore unless the column projects sufficiently above the heated region or the whole thermometer is immersed.

There are two methods of producing the necessary pressure within the bore to prevent distillation and boiling of the mercury. In the one, there is a small bulb at the top of the bore, and the thermometer is sealed off at atmospheric pressure with the mercury at ordinary temperature; in the other, there is a large upper bulb, and the sealing off is done at increased pressure, making use of an auxiliary bulb. The second construction is preferable, as the internal-pressure change with rise of temperature, and consequent deformation of the main bulb containing mercury, is much less than with the first.

Due to deformations in the glass, and consequent changes in readings, all high-range mercury thermometers should be furnished with some fixed point, preferably the ice point. This permits controlling conveniently the behavior of the thermometer due to changes in the volume of the bulb after the instrument has been calibrated. The bulbs of such thermometers should be carefully annealed, before filling, at a temperature higher than the instrument is to be used, and the thermometer should also be annealed after it is made and allowed to cool slowly, otherwise considerable and irregular changes in its indications will occur, amounting to several degrees. It is also advantageous to heat and cool slowly the thermometer a great many times before testing and using it. The zero reading of such a thermometer should be taken after every observation in work of precision. If a considerable length of stem emerges into the air when taking a reading, a very considerable error, 25° C. or so, may be introduced at high temperatures due to the difference in temperature of the bulb and stem. This "stem correction" varies slightly from one kind of glass to another and is very nearly:

$$\text{Stem correction} = 0.00016 \cdot n \cdot (T - t)^\circ \text{C.},$$
$$= 0.000088 \cdot n \cdot (T - t)^\circ \text{F.},$$

where n = number of degrees emergent from bath;
T = temperature of bath;
t = mean temperature of the emergent mercury column determined by some auxiliary means, as the *faden* thermometer of Mahlke.

Among the thermometric glasses for the construction of high-range instruments, and the upper limits to which they may be used safely, are: Jena 16^{III} normal, Corning normal, and the French *verre dur*, which reach 450° C. or somewhat higher; Jena 59^{III}, a borosilicate glass, although sometimes graduated to 550° C., should not be used over 520° C.; with special grades of combustion tubing 570° C. may be reached. If after proper annealing and preliminary heat treatment the zero of a thermometer falls, it is being used at too high temperatures.

Thermometers which are to be used as high-temperature primary standards, or instruments which reproduce in themselves the temperature scale, should have both the ice and steam points, which permits calibrating the instrument in terms of the fundamental interval 0° to 100° C. Due to the fact that the mercury-in-glass expansion varies from glass to glass, and is also different for all of them from the gas expansion on which the temperature scale is based, it is necessary to apply a correction to reduce the readings of a mercury-in-glass thermometer to the gas scale, unless the thermometer was originally "pointed" in terms of this scale. The relation between the scales given by Jena glasses and the gas scale is shown in the following table:

VARIATION FROM GAS SCALE OF JENA-GLASS THERMOMETERS.

Gas scale.	Jena 16^{III}	Gas scale.	Jena 59^{III}
0	0	0	0
100	100.00	100	100.0
150	149.90	200	200.7
200	200.04	300	304.1
220	220.21	325	330.9
240	240.46	350	358.1
260	260.83	375	385.4
280	281.33	400	412.3
300	301.96	425	440.7
		450	469.1
		475	498.0
		500	527.8

If the bore of the thermometer is irregular, it should be calibrated by the use of a 50-degree or 100-degree thread.

Ordinary high-temperature thermometers are tested most conveniently by comparison with a standard, or by taking readings at a series of known temperatures. High-temperature thermometers for a given limited range are kept of a reasonable length of stem and at the same time with an open scale by the insertion of intermediary bulbs which eliminate the undesired portions of the scale.*

* Thermometric glasses and high-temperature thermometers are discussed in Hovestadt's "Jaener Glas" (in German and English), Mathias' "Les Modifications Permanentes du Verre," and in the publications of the Bureau of Standards. Guillaume's "Thermométrie de Précision" describes details of calibration and manipulation.

The glass of mercury thermometers has been successfully replaced by quartz, which is almost an ideal thermometric envelope, possessing an insignificant expansion and no appreciable zero lag, and capable of being used at very high temperatures. Such mercury-in-quartz thermometers are now constructed by Siebert and Kühn, and are graduated to about 700° C.

Dufour has tried to substitute tin for mercury-in-quartz thermometers, thereby attaining a temperature of over 1000° C. Such thermometers have not yet, however, come into use. It is a difficult matter, not yet satisfactorily solved, to find a substance suitable to use as thermometric fluid in quartz at high temperatures.

Fusing-point Pyrometry. — As long ago as 1827, Prinsep proposed to compare temperatures by means of the fusing points of certain metals and alloys. But the nonoxidizable metals are not numerous and all are relatively very costly: silver, gold, palladium, platinum. Use has, however, been made sometimes of these metals and their alloys, in admitting that the fusing point of a mixture of two substances is the arithmetical mean of the points of fusion of the components, which is not quite exact. The use of these alloys is entirely abandoned to-day, and with reason.

In a sense, this method of pyrometry may be said to be still in use, since the temperature scales of the several standardizing laboratories are practically defined by the freezing temperatures of pure metals.

By making use of *metallic salts*, among which a great number may be heated without alteration, one might construct a scale of fusing points whose use would be often very convenient; but this work is not yet done, at least not in a sufficiently precise manner. To the separate salts may be added their definite combinations and their eutectic mixtures which have perfectly definite fusing points. But any mixture whatever of two salts cannot be taken, because in general the solidification takes place throughout a large interval of temperature and in a progressive manner.

In some metallurgical operations, it is often necessary to be certain that objects are heated above some definite temperature. Salt baths of known freezing points, and of materials not attacking the metals used, serve excellently both for heating such objects and automatically giving the minimum temperature allowable.

We may cite in this connection the investigations of Brearley and Morewood and of Grenet on pure salts and eutectic and isomorphous mixtures suitable for this purpose. For the heat treatment of steels, Grenet recommends the following series of salts:

GRENET'S SERIES OF SALTS FOR HEAT TREATMENT OF STEELS.

	Melting point.		Melting point.
K_2SO_4	1070° C.	KCl	775° C.
$BaCl_2$	955	KBr	730
Na_2SO_4	865	KI	682
$5\,K_2SO_4+5\,Na_2SO_4$	850	$5.8\,KCl+4.2\,NaCl$	655
$3\,K_2SO_4+7\,Na_2SO_4$	830	$3\,NaCl+7\,KBr$	625
$2\,K_2SO_4+8\,Na_2SO_4$	825	$Ba(NO_3)_2$	600
Na_2CO_3	810	$Ca(NO_3)_2$	550
NaCl	800		

The uncertainty of our knowledge of the numerical values of the melting points of some of the salts is illustrated in the table on next page and in Chapter XI.

It would be worth while to carry out a careful series of determinations of the melting points of these and other salts, using the care and refinements of method that have been employed in recent work on metals, and employing large quantities of salt, 300 to 1000 grms.

"*Sentinel pyrometers*" and pastes, such as those of Brearley (The Amalgams Company, Sheffield), are also useful in certain operations. The former are cast in the form of small cylinders from molecular mixtures of salts. For temperatures below 500° C. they are inclosed in glass tubes and therefore last indefinitely, and for higher temperatures are placed in saucers (Fig. 129). Two such "sentinels" may be used, for example, to control a furnace within any given temperature range, the one being liquid and the other solid. The paste, made from salts mixed with

MELTING POINTS OF SALTS.

Date.	1896.	1894.	1903.	1905.
Authors.	Ramsay and Eumorfopoulos.	McCrae.	Ruff and Plato.	Hüttner and Tammann.
Method.	Meldometer.	Thermoelectric.	Thermoelectric.	Thermoelectric.
Calibration data.	KNO_3=339 K_2SO_4=Au+7° =1052.	Diphenylamine =304 SBP=445 Au=1072.	Reichsanstalt scale.	Sb=630.6 Au=1064.
Quantity in grms.	0.001.	Small.	20.	25–40.
Na_2SO_4	884	883	880	897
Na_2CO_3	851	861	...	853
NaCl	792	813	820	810
NaBr	733	761	765	748
NaI	603	695	650	...
K_2SO_4	1052	1059	1050	1074
K_2CO_3	880	893	880	894
KCl	762	800	790	778
KBr	733	746	750	740
KI	614	723	705	680
Li_2SO_4	815	...	...	859
Li_2CO_3	618	...	...	734
$CaCl_2$	710	802	780	...
$SrCl_2$	796	854	...	...
$BaCl_2$	844	916	960	...

paraffin, is smeared onto the metal to be heated, and melting of the paste is readily recognized. The range covered by the sentinels and pastes is to 1070° C.

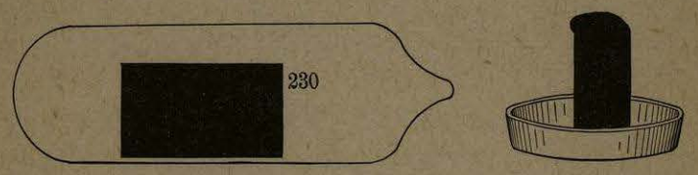

Fig. 129. Sentinel Pyrometers.

Any method based on the use of fusing points alone, whether metals, alloys, or salts, is evidently a discontinuous one, and has its main usefulness in processes where only a maximum or minimum temperature is required.