In admitting that the measurements of volume be made to 0.1 c.c., one should have a precision of only 10° in 1000° on account of the insufficient volume of the thermometric reservoir.

Barus. — This American physicist devised a rotating apparatus, remarkable for its uniformity of temperature, but he applied it directly only to the standardization of thermoelectric couples. He worked at constant pressure. By means of couples graduated in this way, he determined the boiling points of zinc (926° to 931°) and of cadmium (773° to 784°); the boiling point of bismuth was

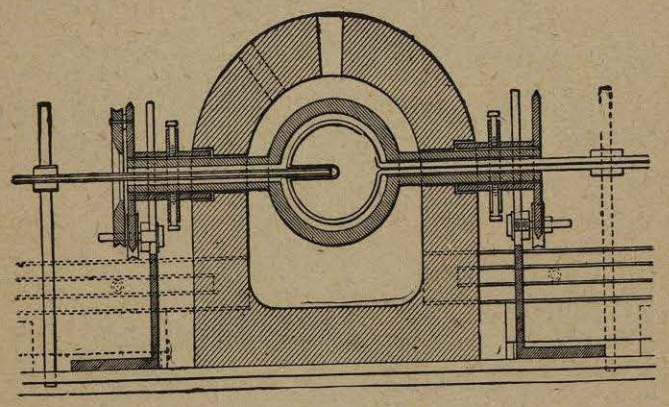

Fig. 7. Apparatus of Barus.

found equal to 1200° under a reduced pressure of 150 mm., which would give under atmospheric pressure by extrapolation 1500°.

Fig. 7 represents the longitudinal section of Barus' apparatus. It is composed essentially of a porcelain pyrometer containing an interior tube in which is placed the couple. The pyrometer fixed at a point of its stem is held stationary. It is surrounded by a muffle of casting whose general shape is that of revolution about the axis of the pyrometer; this muffle is composed of two similar halves held by means of iron collars, and can be given a motion of rotation about its axis of figure, in such a manner as to assure uniformity of heating. It is heated by gas burners placed below. An outer covering of fire clay keeps in the heat about the iron muffle.

Holborn and Wien. — Holborn and Wien made a very complete standardization of the thermoelectric couple Pt, 90 Pt–10 Rh proposed by Le Chatelier. They made use of a porcelain reservoir of about 100 c.c. capacity, terminating at its two ends in capillary porcelain tubes. The thermoelectric junction is placed inside the bulb, and each of its wires is led out by one of the lateral tubes; this arrangement allows of determining at various points the real temperature of the dead space whose volume is 1.5 c.c.

They worked at constant volume, with a very low initial pressure so as always to have depression; they were able to reach 1430°. Above 1200° they could make but a single observation with one pyrometer; below this, about ten observations.

They determined very approximately the coefficient of expansion of their porcelain, a product of the Berlin works, and found it equal to 0.0000045, the identical number given by Le Chatelier for the Bayeux porcelain.

They made use of this pyrometer, employing as intermediary a couple, to fix the fusing points of certain metals:

Silver	*970°*
Gold	*1072*
Palladium	1580
Platinum	1780

These figures, at the time they were obtained, were counted among those which seemed to merit the most confidence; however, it is necessary to note that the volume of the bulb was too small to assure a very great accuracy, and its expansion coefficient not well known.

We shall return to these experiments when treating of electric pyrometers.

Recent Experimental Investigations. — Modern gas thermometry of precision may be said to begin with the introduction of electric furnaces, and the discarding of porcelain bulbs, both of which were effected by Holborn and Day. The constant-volume thermometer is the one almost universally used in the more recent gas thermometer researches at temperatures above 500° C., and

the inclosed gas is usually nitrogen. There have been further experiments at the Reichsanstalt, where the work to 1100° C. was first repeated by Holborn and Day and then carried to 1600° C. by Holborn and Valentiner. At the Geophysical Laboratory in Washington, also, Day, Clement, and Sosman have determined a series of fixed points from zinc to palladium, using greatly improved methods for the exact determination of the higher temperatures. Jaquerod and Perrot have used several gases in quartz glass to the temperature of fusion of gold; and the hydrogen thermometer has been used by Jaquerod and Wassmer for the determination of the boiling points of naphthaline and benzophenone. The scale of the platinum-resistance thermometer has been compared with that of nitrogen to 500° C., at constant pressure by Callendar, and at constant volume by Chappuis and Harker, and by Holborn and Henning; and from these series of measurements the boiling point of sulphur has been determined by these observers and also by Eumorfopoulos, using Callendar's form of the constant-pressure thermometer.

We shall discuss in some detail most of these recent researches, in part here, and in part in the chapter on standardization.

Holborn and Day. — Their preliminary work was done with porcelain bulbs at temperatures above 500° C., using nitrogen and hydrogen and with a bulb of Jéna borosilicate glass No. 59^{III} filled with hydrogen, for temperatures below 500°. Porcelain bulbs glazed outside and also inglazed bulbs were used. Errors due to changes in the bulbs were detected by taking "zero" readings and also by the simultaneous use of thermocouples. Salt baths were used up to 700° at first, but later electric heating in air was employed in all the high-temperature work.

The hard glass bulbs of about 167 cm. capacity showed less changes, after annealing, than the irregularities in the thermocouple measurements, due to the lack of sensitiveness of the latter at low temperatures; and these glass bulbs were found preferable to those of porcelain up to 500° C. The precision attainable with thermocouple control was about 0.6° C.

Porcelain bulbs of 100 c.c. capacity, glazed inside and out, filled

with hydrogen, and heated to only 700°, gave very discordant results due apparently to chemical action between the hydrogen and the walls of the bulb and to water vapor generated. Used with nitrogen and heated electrically to about 1100° C., the mean difference between the observed and calculated values was ± 1.5° C. Far less satisfactory results were obtained with porcelain glazed only on the outside.

A first series of experiments with a metal bulb were made with a 20 per cent iridium alloy of platinum, the bulbs being cylindrical, of 208 c.c. volume and 0.5 mm. wall, and the dead space was considerably reduced over that of the porcelain bulbs. The electric heating oven was also improved by winding it logarithmically so that at 1150° the temperature distribution was constant to 3° over that portion of the oven containing the bulb. This was still further equalized by the presence of the metallic bulb; also at very high temperatures the tendency to equilibrium through radiation balances more nearly the losses by end conduction. Temperature control to 0.1° C. at 1000° C. may be realized electrically with care. A precision of better than 1° C. was then obtained, and the conclusion seemed warranted that the metallic bulbs in an electrically heated furnace, where no gases or other materials acting upon platinum were in contact with it, were superior to any form of porcelain bulb.

Their later work consisted in a determination of fixed points, using the thermocouple as intermediary, after having found the coefficient of expansion of the material of their bulb and shown that the bulb underwent no deformation after heating. The correction for expansion amounts to 30° at 1000° and 40° at 1150°. The expansion was determined for a 50 cm. bar in a comparator which could be heated electrically to 1000° C.

Although no change in volume of the thin-walled bulb could be detected on cooling, a temporary yielding of the glowing walls under the comparatively high pressure might have taken place, so a bulb having walls 1 mm. thick was substituted, the composition being 90 Pt–10 Ir. This bulb was as satisfactory as the first.

The results obtained by Holborn and Day for the fixed points, as well as their work with thermoelements, will be discussed later.

Jaquerod and Perrot. — Using a quartz bulb filled at constant volume successively with nitrogen, air, oxygen, carbon monoxide, and carbonic acid, and employing an electric resistance furnace, results agreeing to 0.3° were obtained for the fusing point of gold with the first four gases, using a common coefficient of expansion based on Chappuis' limiting value and using varying initial pressures. The use of quartz reduces the correction for the expansion of the bulb to 2° at 1000°.

This work shows that in the range 0° to 1100° C. the coefficients of expansion of these gases are practically identical (see page 26).

Callendar's Constant-pressure Thermometer. — For the calibration of the platinum-resistance thermometer Callendar has studied an arrangement of the constant-pressure gas thermometer in which the dead space is reduced to a minimum by an ingenious device which consists in interposing in the capillary tube a column of sulphuric acid which is always brought to the same position (Fig. 8). It is then permissible to leave vacant spaces in the manometer of any volume, and this simplifies the measurements.

The *bulb* is of glass, and its capacity is 77.01 c.c. The capillary tube has a diameter of 0.3 mm. It is attached to a small U tube of 2 mm. diameter which contains the sulphuric acid. The total value of the waste space is thus reduced to 0.84 c.c.

The sulphuric acid before each measurement is brought up to a reference mark. The density of this liquid being one-seventh that of mercury, the errors made in determining its level should be divided by seven to express them in heights of mercury. The use of this column of sulphuric acid has the inconvenience to oblige the experimenter to watch constantly the apparatus during the whole time of heating and cooling in order to maintain the pressure equilibrium in the two parts of this column; otherwise the liquid would be driven into the manometer or absorbed into the bulb.

The *manometer* is one open to the air and is read conjointly with the height of the barometer.

The *coefficient of expansion* of the hard glass used in the construction of the thermometer was measured for a tube of same make by means of two microscopes carried upon a micrometer screw but sighted on the cold ends of the tube. A cold comparison tube could be placed under the microscopes to verify the invariability of their distance apart.

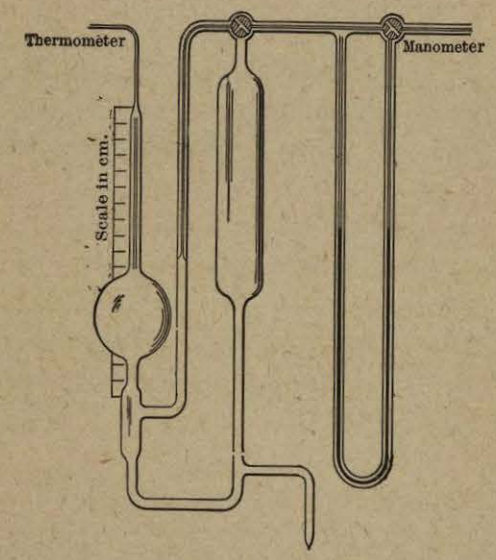

Fig. 8. Callendar's Differential Manometer.

MEAN COEFFICIENT OF EXPANSION.

t	α
17°	0.00000685
102	706
222	740
330	769
481	810

After heating to 400° there were permanent changes amounting to from 0.02 to 0.05 per 100.

If the zero is taken at intervals of time of varying length,

permanent displacements are noted in the bulb. The following table gives some examples:

Date.	Oxygen Thermometer.	Nitrogen Thermometer.	Remarks
	mm.	mm.	
Jan. 21, 1886....	693.1	695.4	Filled at 300°; measurement taken 4 days later.
Jan. 22, 1886....	692.9	695.1	
Jan. 23, 1886....	692.9	694.9	After heating to 100°.
Jan. 25, 1886....	692.0	693.8	
Jan. 25, 1886....	692.0	694.1	After heating to 100°.

This change of zero has been attributed to a partial absorption of the air by the glass. Glass, an amorphous body resembling liquids somewhat, may dissolve gases, especially at high temperatures, although this is not borne out by Holborn and Day's work on nitrogen.

For temperatures higher than 300° this source of error becomes very serious, especially if the gas is hydrogen. This gas disappears progressively by solution in the glass or by oxidation, replacing elements of the glass. It is necessary to revert to nitrogen. This fact was observed by Chappuis and Harker in the course of a study of the platinum-resistance pyrometer when the temperatures measured reached as high as 600°.

One of the more recent forms of this thermometer in which there is complete compensation of the dead space is shown in Fig. 9, where *A* is the thermometer bulb connected by a capillary *a* to an overflow bulb, or, as here shown, to a burette *B*. The compensating capillary *b* is also connected to a bulb *C*, and across the two capillaries *a* and *b* is inserted the differentia manometer *D*. The bulbs *C* and *B* for most exact work should be inclosed in a bath at constant temperature, as an ice bath. The relative sizes of the bulbs for the greatest accuracy will depend upon the temperature range to be studied. When equilibrium and compensation are established at any temperature, the mass of the gas in the two parts of the apparatus will be the same if the pressures are adjusted to equality as shown by the sensitive manometer *D*, this supposing that *C* and *B* are at exactly the

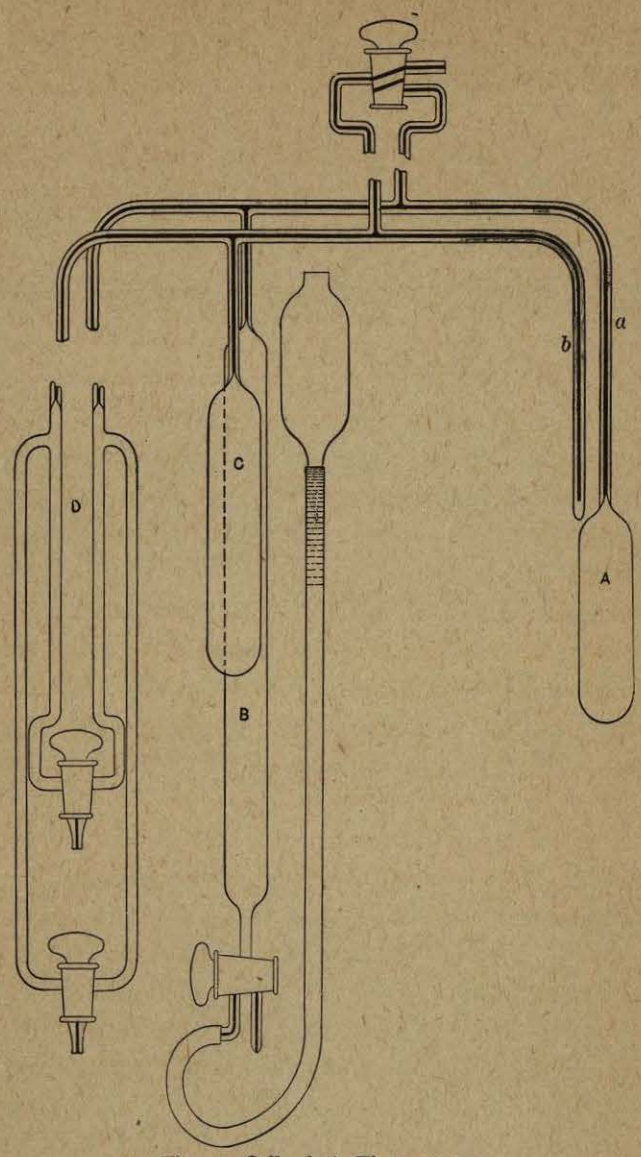

Fig. 9. Callendar's Thermometer.

same temperature. For a change in temperature the volume change of the gas in *B*, i.e., forced over from *A*, may be made by reading this volume on the burette, or better by weighing the displaced mercury. The upper stopcock serves to exhaust and fill the apparatus.

A determination of temperature, making no allowance for correction terms, is made as follows: For the compensating side of the apparatus we have

V_0 = volume of gas in C;
m_0 = mass of gas in C;
θ_0 = temperature of gas in C on gas scale;
p_0 = pressure of gas in C;
v = volume of capillaries;
θ = average temperature of capillaries.

Then

$$p_0\left(\frac{V_0}{\theta_0}+\frac{v}{\theta}\right)=mk,$$

where k is a constant.

For the thermometer proper we have, using a similar notation,

$$p_t\left(\frac{V_t}{\theta_t}+\frac{V_m}{\theta_m}+\frac{v}{\theta}\right)=m_1k,$$

the subscript $_t$ referring to A, and $_m$ to B.

But $m_1 = m$ and $p_t = p_0$ as conditions of compensation; therefore

$$\frac{V_t}{\theta_t}+\frac{V_m}{\theta_m}=\frac{V_0}{\theta_0}.$$

But C and B are at the same temperature, θ_0, or $\theta_m = \theta_0$. Finally

$$\theta_t=\frac{V_t\times\theta_0}{V_0-V_m}.$$

This type of thermometer with an air-filled porcelain bulb was used by Callendar and Griffiths to determine the boiling point of sulphur, for which temperature, after correcting for the expansion of porcelain, they obtained *444.53°* C. on the constant-pressure air scale. Eumorfopoulos, using air in a bulb of Jéna 16^{III} glass, has obtained very recently with the same type of thermometer *444.55°*, with a range in eleven experiments of 0.37° C., the thermometer bulb of 90 c.c., properly screened, being put into the sulphur vapor. A preliminary publication gave 443.58°,

but this was in terms of an uncertain extrapolation of the absolute expansion of mercury from 100°, which was used to obtain the coefficient of expansion of the glass bulb to the S.B.P. The correction of +0.97° was computed by Callendar and Moss in terms of their very recent measurements of the absolute expansion of mercury to 300° C.

Eumorfopoulos gives also the exact formulæ for the use of such a thermometer. He found Jéna 16^{III} to give very troublesome changes of zero, the bulb changing in volume by about 1 per cent during the course of his experiments.

Used with a quartz-glass or platinum-alloy bulb, such a gas thermometer may become an instrument of the greatest accuracy for the experimental extension of the gas scale at constant pressure.

Holborn and Valentiner. — The need of extending the gas scale to as high temperatures as possible with modern appliances was appreciated at the Reichsanstalt, and this difficult task was first undertaken in 1906 by Holborn and Valentiner, who compared the constant-volume nitrogen scale to 1600° C. with that of the platinum-rhodium thermocouple and the optical pyrometer.

The experiments were executed with two bulbs, one of a 20 per cent iridium alloy of platinum of 208 c.c. capacity, heated in an Heræus platinum-foil resistance furnace, and one of iridium, 54 c.c. capacity, heated in an Heræus iridium-tube furnace. Initial pressures of 136 to 250 mm. were used. To avoid contamination of the wires of the single thermocouple used, they were inclosed in quartz-glass tubes. In spite of very considerable lack of uniformity of temperature within the furnace along the thermometer bulb, — as much as 60° C. in some cases, — and very considerable corrections for the dead space, — 125° to 150° at 1600° with the iridium bulb, — these observers consider their results accurate at 10° C. at the highest temperatures. We shall return to their thermoelectric and optical measurements in their respective chapters.

Day, Clement, and Sosman. — Not since the classic researches