

iridium and 20 per cent of rhodium, respectively, which they have used as gas-thermometer bulbs:

$$90 \text{ Pt} \cdot 10 \text{ Ir} : \lambda \cdot 10^9 = 8841 t + 1.306 t^2 \text{ from } 300^\circ \text{ to } 1000^\circ \text{ C.}$$

$$80 \text{ Pt} \cdot 20 \text{ Rh} : \lambda \cdot 10^9 = 8790 t + 1.610 t^2 \text{ from } 300 \text{ to } 1400$$

It is of interest to note that, according to these measurements, the coefficient of expansion of a platinum alloy of intermediate composition cannot be predicted by simple interpolation; therefore in any new work the actual coefficient should be determined. Holborn and Valentiner find, by a less rigorous method, however, that the expansion formula above given for 80 Pt · 20 Rh may be used to 1600° without serious error. The rhodium alloy of platinum was substituted for that of iridium at the Geophysical Laboratory for the gas-thermometer bulb material because the evaporation of iridium out of the alloy was found to be very troublesome by contaminating the thermocouple wires, in their colder parts particularly, and so changing the E.M.F. readings. The rhodium alloy is less objectionable in this respect.

Iridium. — Only one series of measurements has been made with a bulb of iridium, that of Holborn and Valentiner, and while it appeared to give results comparable with an alloy bulb, it is probably better to use the 80 Pt · 20 Rh bulb for the reason above given. Also, iridium, besides evaporating rapidly at high temperatures, is very brittle. They find for iridium to 1600° the expansion coefficient

$$\lambda \cdot 10^9 = 6697 t + 1.158 t^2.$$

Iron has but one apparent advantage, its cheapness; it is as permeable to hydrogen as is platinum; it is not merely oxidizable in the air, but is besides attacked by carbonic acid and water vapor. Thus the only gas that can be used with iron is pure nitrogen, and even this is questionable. The coefficient of expansion of iron is greater and increases more rapidly than that of platinum:

	Between 0° and 100°.	Between 0° and 1000°.
Mean linear coefficient.....	0.000012	0.000015

Also, this increase is not regular; there is produced at 850°, at

the instant of the allotropic transformation, a sudden change of length, a contraction of 0.25 per cent.

It is very difficult to obtain pure iron; very small quantities of carbon modify somewhat the value of the coefficient of expansion. Besides, the change of state of steel at 700°, corresponding to recalescence, is accompanied in the heating by a linear contraction, varying with the amount of carbon present, from 0.05 to 0.15 per cent.

Iron, therefore, cannot be considered seriously for work of any precision, and as the only excuse for working with the gas thermometer at all is to obtain the highest possible accuracy, no substance should be used for a bulb which presents any serious defects.

Porcelain was adopted as a result of the discussion between H. Sainte-Claire-Deville and Becquerel; it was considered as absolutely impermeable, but without decisive tests.

Even well-baked porcelain consists of a paste somewhat porous and permeable; it is only the glazing that assures its impermeability. But this covering may sometimes not be whole; as it softens above 1000°, it is susceptible of cracking if left for a considerable time with an excess of pressure on the interior of the apparatus. According to Holborn and Wien, the glazing is broken after reaching 1100°, when a considerable difference of pressure is established in the direction of the lifting up of this glazing.

Finally, like all verres, porcelain dissolves gases, and in particular water vapor, which passes through it quite readily. A pyrometer left a long time in the flame at about 1200° becomes filled with water vapor, which can be seen to condense in the manometer after a few weeks.

The experiments of Crafts have shown that the rapidity of the passage of water vapor through porcelain, in a pyrometer of from 60 to 70 c.c. capacity at the temperature of 1350°, was 0.002 grm. of water vapor per hour.

It is thus not safe to employ porcelain at temperatures higher than 1000°, at least not in the thermometric processes which suppose the invariability of the gaseous mass.

The expansion of porcelain has been the object of a great number of measurements which, for porcelains of very different make, give values near to one another; the mean linear coefficient between 0° and 1000° varies between 0.000045 and 0.00005 for hard porcelain — that is to say, baked for a long time at a temperature in the neighborhood of 1400°.

Here are the results of experiments made by Le Chatelier and by Coupeaux; the experiments were made with porcelain rods 100 mm. in length, and the numbers express the elongation of these rods in millimeters:

Porcelain.	Temperatures.					
	0°	200°	400°	600°	800°	1000°
Bayeux.....	0.075	0.166	0.266	0.367	0.466	
Sèvres dure (cuite à 1400°).....	.078	.170	.270	.378	.470	
Limoges.....	.076	.168	.268	.360	.465	
Sèvres nouvelle (cuite à 1400°).....	.090	.188	.290	.390	.490	

These numbers should be multiplied by three to give the cubical expansion.

Porcelain has still another inconvenience; the glazing is usually put on the outside only of vessels, so that the porosity of the paste gives an uncertainty due to the unequal absorption of gases at increasing temperatures.

According to Barus, it is impossible to fill with dry air a pyrometer, not glazed inside, at ordinary temperatures. The water is not driven out by pumping out several times and letting in dry air. An apparatus filled in this way will indicate between melting ice and boiling water from 150° to 200°. Nor is filling the apparatus at 100° satisfactory: it will indicate 115° for this same interval of 100°. Barus thinks that at 400°, by repeating the operation several times, one can consider the apparatus as filled with dry air.

The use of porcelain bulbs in several recent pyrometric researches of great importance has been a cause of outstanding differences in the determination of fixed points in pyrometry as

the sulphur boiling point, differences that are due mainly to the uncertainties in the expansion coefficient of the particular samples of porcelain used.

The work of Chappuis, Tutton, Bedford, and of Holborn, Day, and Grüneisen has shown the expansion of porcelain to be anomalous, and that therefore extrapolation for the coefficient cannot be made safely even over a hundred degrees for the most exact work. There is always a deformation of the bulbs of uncertain and irregular amounts in a constant-volume thermometer sufficient to render results doubtful at temperatures as low as 500° C., and Holborn and Day were unable with porcelain bulbs to get any considerable precision at 1000° C., and finally discarded them entirely.

They found for the expansion of Berlin porcelain

$$\lambda \cdot 10^9 = \{2954t + 1.125t^2\} \text{ from } 0^\circ \text{ to } 1000^\circ,$$

but this value is too high for temperatures below 250° as indicated by Chappuis; and Holborn and Grüneisen have shown that at about 700° C. a considerable change in the coefficient takes place, the expansion becoming more rapid at higher temperatures.

It would probably not be worth while to make further pyrometric studies with porcelain bulbs, when possible to avoid their use.

Glass cannot be used above 550° C., but to 500° C. it may replace porcelain to advantage if Jéna borosilicate 59^m is used, as the deformation after heating is somewhat less and more uniform. The coefficient of expansion of this glass as measured in the form of capillary tubes by Holborn and Grüneisen is

$$\lambda \cdot 10^9 = 5833t + 0.882t^2.$$

This glass was used by Holborn and Henning in 1911 to 450° with the gases nitrogen, hydrogen, and helium, to the last of which it is slightly permeable.

Jéna 16^m glass was used by Eumorfopoulos to 445° C. Its coefficient of expansion in terms of the value of Callendar and Moss for the absolute expansion of mercury to 300° is

$$\{2385 + 1.31(t - 100)\} 10^{-8},$$

obtained by using the thermometer bulb as a mercury-weight thermometer at 0° , 100° , and 184° . This glass has a troublesome zero lag.

Several investigations, using both constant-pressure and constant-volume thermometers, have been carried out with glass bulbs to 500°C .

Quartz glass, in the amorphous or fused form, can now be obtained in vessels of several hundred cubic centimeters capacity, thanks to many attempts culminating successfully in the effects of Heraeus, and Siebert and Kühn. The chemical and physical properties in view of its pyrometric use have been studied by many investigators, Shenstone being a pioneer in advocating its use in thermometer bulbs. Vitrified quartz vessels seem to resist deformation to fairly high temperatures, the upper limit when the interior is a vacuum being not far from 1300°C .; the substance is appreciably plastic at 1500° .

Fused quartz or silica glass is attacked by alkalis, and the slightest trace of such, as from handling, may do damage when the heating is carried very high. Weak acids and neutral salts are without effect as shown by Mylius, but at high temperatures all oxides attack it. Heated with a porcelain tube, or even alone, to temperatures above 1100°C ., the quartz tends to lose its transparency, cracking and changing over into a crystalline structure which readily crumbles to the touch on cooling. Water vapor even in traces hastens this process. Moissan has shown that it is slightly soluble in a lead bath above 1100°C ., and very much more so in zinc. Villard showed that it is permeable to hydrogen but less so than platinum, nor does it seem to occlude other gases. It is also quite permeable to helium. Travers and Jaquerod find also that silica is reduced by hydrogen at high temperatures.

Its great advantage in gas thermometry is its lack of deformation and its extremely small coefficient of expansion, about $\frac{1}{17}$ that of platinum, or, more exactly, as determined by Holborn and Henning with a comparator,

$$\lambda \cdot 10^9 = 540t \text{ from } 0^\circ \text{ to } 1000^\circ.$$

Scheel, using a Fizeau apparatus, finds

$$\lambda \cdot 10^9 = 322t + 1.47t^2 \text{ between } 0^\circ \text{ and } 100^\circ,$$

where the curvature is of the same order as for metals. There is some question, however, as to the constancy of this coefficient.

In work at 1000°C . the expansion correction is reduced from over 20° with porcelain or platinum to about 1° , and its uncertainties become, therefore, negligible, permitting a great increase in accuracy. Silica glass has been used successfully by Jaquerod and Perrot as a thermometer bulb to the melting point of gold with several gases. It cannot be used continuously as an envelope, however, at temperatures much over 1100°C ., for the reasons stated above.

Early Experimenters. — We shall study now the experiments made by various investigators, and we shall see in what degree the conditions of precision indicated in the course of this account have been realized.

Pouillet. — Pouillet was the first to make use of the air thermometer for the measurement of high temperatures; he obtained very good values for the epoch at which he worked.

His pyrometer was made of a platinum bulb, of ovoid form, of 60 c.c. capacity, to which was gold-soldered a platinum capillary

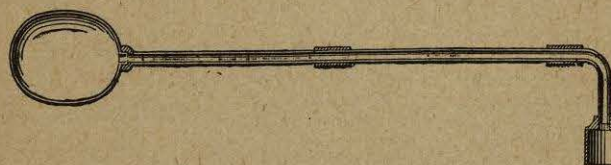


Fig. 5. Pouillet's Thermometer.

tube of 25 cm. in length; continuous with this tube was another of silver of the same length fastened to the manometer. The joining of the platinum and silver tubes was made by means of a metal collar (Fig. 5). The dead space had thus a volume of 2 c.c.

The manometer was made up of three glass tubes embedded at their lower ends in a metallic piece; the first tube serving as a measurer was graduated in cubic centimeters, the second con-

stituted the manometer properly speaking, and the third served to fill the apparatus.

A cock conveniently placed permitted variation of the quantity of mercury contained in the apparatus (Fig. 6). The principle of this apparatus is the same as that of the more recent Regnault manometer; this latter differs from the manometer of Pouillet only in the suppression of the third tube, which is replaced by a bottle joined to the emptying cock by a rubber tube.

Pouillet's determinations of fusing points follow:

Gold.....	1180° (too high by 115°)
Silver.....	1000 (too high by 40°)
Antimony.....	432 (too low by 200°)
Zinc.....	423 (good)

Ed. Becquerel. — This savant took up and continued the work of Pouillet with the same apparatus. But at the close of a discussion with H. Sainte-Claire-Deville on the question of the permeability of platinum, he made use successively of pyrometers of iron and of porcelain. The results obtained with platinum seem, however, to be far the best.

	Pyr. of Pt.	Pyr. of Porcelain
Boiling point of zinc.....	930° (good)	890°
Fusing point of silver.....	960 (good)	916
Fusing point of gold.....	1092	1037

The figures for gold differ among themselves by about 25°.

Experiments of H. Sainte-Claire-Deville and Troost. — They, after their discussion with Becquerel, made numerous experiments with the porcelain air thermometer; they obtained very discordant results, which they did not publish at the time.

They placed the most confidence in the determinations made by the aid of the vapor of iodine (we shall speak of this later); but when the inaccuracy of this method was pointed out, they made known the results that they had obtained for the boiling point of zinc.

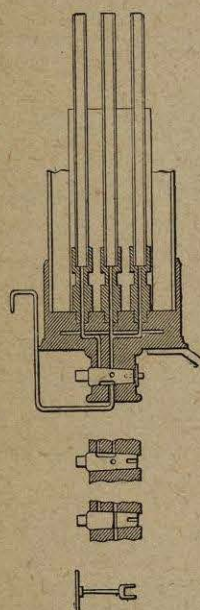


Fig. 6. Pouillet's Manometer.

They employed a crucible of plumbago having a capacity of 15 gm. of zinc; the metal was added anew as fast as it evaporated.

The crucible was placed in a furnace filled with coal. Around the pyrometer was arranged a covering of fire clay; but this arrangement was quite insufficient to eliminate errors due to radiation. The same measurements were repeated with different gases. The figures obtained for the boiling point of zinc range from 916° to 1079° and seem to be a function of the nature of the gas, which is inexplicable.

Violle. — Guided by H. Sainte-Claire-Deville, whom his successive failures had instructed in the difficulties of the problem, Violle made a series of measurements which were among the best for a long time. He made use of a porcelain thermometer, and he worked simultaneously at constant pressure and constant volume. The agreement of the two numbers shows if the mass has remained constant; this is the equivalent of the volumetric method of Becquerel.

The most serious objection that can be made to these observations concerns the uncertainty of the equality of temperatures of the pyrometer and of the substance studied placed beside the former; from this point of view, however, these experiments, made in the Perrot furnace, were much more satisfactory than those made in coal furnaces previously employed.

1. A first series of determinations was of the specific heat of *platinum*. A platinum mass of 423 gm. was put into a Perrot muffle alongside the pyrometer, and when the mass was in a state of temperature equilibrium it was immersed, either directly in water or in a platinum eprouvette placed, opening upward, in the midst of the calorimeter water. In the first case the experiment was made in a few seconds; in the second it lasted fifteen minutes, and the correction was as high as 0.3° per 10°; the results, however, were concordant. At 787° two experiments gave 0.0364 and 0.0366; mean, 0.0365.

At 1000° twelve experiments were made employing the method of immersion; the numbers found vary from 0.0375 to 0.0379; mean, 0.0377.

Near 1200° the measurements were made at constant pressure and at constant volume.

Temperature at Constant Volume.	Temperature at Constant Pressure.	Mean.	Specific Heat of Platinum.
1171°	1165°	1168°	0.0388
1169	1166	1168	.0388
1195	1192	1193	.0389

The mean specific heat from his observations may be represented by the formula

$$C_0^t = 0.0317 + 0.000006 \cdot t,$$

and true specific heat by

$$\frac{dq}{dt} = 0.0317 + 0.000012 \cdot t.$$

Violle used these determinations to fix, by extrapolation, the fusing point of platinum, which he found equal to 1779°. He measured for that the quantity of heat given out by 1 gm. of solid platinum from its fusing point to 0°. For this purpose a certain quantity of platinum is melted, into which is plunged a spiral wire of the same metal, and, at the instant that the surface of the bath solidifies, by aid of this wire a cake of solid platinum is lifted out and immersed in the water calorimeter.

The latent heat of fusion of platinum is equal to 74.73 c. \pm 1.5; this number results from five determinations.

2. A second series of experiments was on the specific heat of *palladium*; the determinations were made, in part by comparison with platinum, in part by the air thermometer. The results obtained by the two methods are concordant.

The mean specific heat is given by the formula

$$C_0^t = 0.0582 + 0.000010 \cdot t.$$

The true specific heat is equal to

$$\frac{dq}{dt} = 0.0582 + 0.000020 \cdot t.$$

The fusing point of palladium was found equal to 1500°. The

latent heat of fusion of palladium, measured by the same experiments, was found to be 36.3 calories.

3. In another series of experiments Violle determined the boiling point of zinc. He employed an apparatus of enameled casting, heated in a triple envelope of metallic vapor; the top was covered with clay and cow-hair to prevent superheating of the coverings. The measurements were made with pressure and volume simultaneously variable. He found about 930°.

4. A last series is relative to the fusing points of metals, which were determined by comparison with the total heat of platinum:

Silver.....	954° (too low by 7°)
Gold.....	1045 (too low by 18°)
Copper (probably saturated with Cu ₂ O) ..	1050 (too low by 13°)

Mallard and Le Chatelier. — In their investigations on the temperatures of ignition of gaseous mixtures, Mallard and Le Chatelier made use of a porcelain pyrometer, which was exhausted; then air was let in and the gaseous volume thus absorbed was measured. It is possible to reach 1200° without noticing any breaking down of the porcelain; but this giving way is complete at 1300° under the action of the vacuum.

This method was used in the following way to measure the temperatures of ignition of gaseous mixtures: The air was exhausted from the apparatus, and the temperature was measured by the air volume which filled it; the air was again exhausted and the apparatus was filled with the gaseous mixture. Whether or not there was ignition was known by the comparison of the volume of the mixture with that of the air introduced under the same conditions of temperature, at least in the cases of mixtures burning with contraction.

The pyrometer used had a capacity of 62 c.c., after deduction of the dead space (1 c.c.); the following table gives the volumes of air corresponding to different temperatures:

400°.....	26.7 c.c.
600.....	20.6
800.....	16.7
1000.....	14.1
1200.....	12.2