

Then determine the values of the different terms; let t_1 and t_2 be the absolute temperatures of the surroundings when the bulb is at the temperatures T' and T_0 .

$$\begin{aligned} 1. \quad \frac{d\Delta}{\Delta_0} &= \frac{\Delta - \Delta_0}{\Delta_0}, \\ \Delta &= \Delta_0 \cdot [1 - k(t_2 - t_1)], \\ k &= 0.00018(t_2 - t_1), \\ \frac{d\Delta}{\Delta_0} &= -0.00018(t_2 - t_1). \\ 2. \quad \frac{dV}{V_0} &= \frac{V - V_0}{V_0}, \\ V &= V_0[1 + k'(T' - T_0)], \\ k'(\text{porcelain}) &= 0.0000135, \\ \frac{dV}{V_0} &= 0.0000135(T' - T_0), \end{aligned}$$

by neglecting the variations of volume of the bulb due to changes of pressure.

$$3. \quad -\frac{dn}{n_0} = \frac{x_2 - x_1}{n_0},$$

in calling x_2 and x_1 the number of molecules contained in the dead space ϵ at the temperatures t_2 and t_1 . We have, in fact, N being the total mass contained in the apparatus,

$$\begin{aligned} n &= N - x_2, \\ n_0 &= N - x_1, \\ n - n_0 &= -(x_2 - x_1). \end{aligned}$$

To determine x_1 and x_2 :

$$\begin{aligned} P_0\epsilon &= x_1 R t_1, \\ P\epsilon &= x_2 R t_2, \\ -\frac{dn}{n_0} &= \frac{\epsilon}{V_0} \left(\frac{P}{t_2} - \frac{P_0}{t_1} \right) \cdot \frac{T_0}{P_0}. \end{aligned}$$

In noting that

$$\frac{P}{P_0} = \frac{T'}{T_0},$$

we have

$$-\frac{dn}{n_0} = \frac{\epsilon}{V_0} \left(\frac{T'}{t_2} - \frac{T_0}{t_1} \right).$$

Put

$$\begin{aligned} t &= \frac{t_1 + t_2}{2}, \\ \theta &= \frac{t_2 - t_1}{2}. \end{aligned}$$

After substitution we have

$$\frac{dn}{n_0} = -\frac{\epsilon}{V_0} \cdot \left(\frac{T' - T_0}{t} - \frac{\theta}{t} \cdot \frac{T' + T_0}{t} \right).$$

These successive transformations are for the purpose of making evident from the formula:

1. The ratio of the dead space to the total volume: $\frac{\epsilon}{V_0}$;
2. The temperature measured: $T' - T_0$;
3. The variation of the surrounding temperature θ ;

which are the three essential factors on which depends the correction in question.

Formula (6) then becomes:

$$\begin{aligned} \frac{dT}{T'} &= -0.00018(t_2 - t_1) + 0.0000135(T' - T_0) \\ &\quad - \frac{\epsilon}{V_0} \cdot \left(\frac{T' - T_0}{t} - \frac{\theta}{t} \cdot \frac{T' - T_0}{t} \right). \end{aligned}$$

Let us take a numerical example in order to show the importance of these correction terms in the three following cases:

$$\begin{aligned} T' - T_0 &= 500^\circ, \\ T' - T_0 &= 1000^\circ, \\ T' - T_0 &= 1500^\circ. \end{aligned}$$

In taking

$$\frac{\epsilon}{V_0} = 0.01,$$

$$t = 27^\circ + 273^\circ = 300^\circ,$$

$$2\theta = 10^\circ,$$

we have

$$dT_{500} = -1.4^\circ + 5.15^\circ + 13.1^\circ = 16.85^\circ,$$

$$dT_{1000} = -2.3^\circ + 17.0^\circ + 38.2^\circ = 52.9^\circ,$$

$$dT_{1500} = -30.7^\circ + 35.7^\circ + 90.0^\circ = 122.5^\circ.$$

These figures show the very great importance of the dead space, whose exact volume it is very difficult to determine. This method of computation of the corrections by logarithmic differentials is only approximate, and is not sufficient for real measurements, but it renders more clear the general discussion of the causes of error.

Let us see what uncertainty in the temperature may result from the uncertainty which there may be in the volume of the dead space. In reality there is a continuous passage from the high temperature of the pyrometer to the surrounding temperature on a length which may vary from 10 to 30 centimeters, according to the thickness of the walls of the furnace. The volumes of the bulb and of the dead space which should be taken in order that the above formulas be exact should be such that the real pressure is equal to the pressure that would exist in supposing that a complete and sudden change of temperature took place at a definite fictitious point, separating the heated part from the cold part of the apparatus. The probable position of this point is estimated, and if the estimation is poorly made, two errors are committed, one on the real volume heated and the other on the dead space, errors equal and of opposite sign so far as the volume is concerned.

To calculate this *error*, as in the case of the corrections, we may employ the method of logarithmic differentials.

Applying the same formula as before, we find for the relative error $\frac{dT}{T}$:

$$\frac{dT}{T} = -\frac{dV}{V_0} \left(\frac{T' - T_0}{t} - \frac{\theta}{t} \cdot \frac{T' - T_0}{t} \right);$$

and neglecting the second term of the parenthesis, which is relatively very small,

$$\frac{dT}{T} = -\frac{dV}{V_0} \left(\frac{T' - T_0}{t} \right).$$

Letting the section of the capillary tube be equal to 1 sq. mm., the volume of the bulb 100 c.c., and assuming an uncertainty of 100 mm. in the position of the transition point, a value often not exaggerated, we find the following errors in the temperatures:

$$dT_{500} = 1.7^\circ,$$

$$dT_{1000} = 3.9^\circ,$$

$$dT_{1500} = 8.5^\circ.$$

We thus see that at 1000° the error resulting from the uncertainty in the origin of the dead space may reach several degrees for a bulb of 100 c.c.

A second cause of error results from the changes of mass following the ingoings and outgoings of gas. As before, we have

$$\frac{dT}{T} = -\frac{dn}{n_0}.$$

Consider the experiments of Crafts. There enters per hour at 1350° in a bulb of porcelain of 100 c.c., 0.002 gm. of water vapor, or 0.225 milligram molecules; the initial volume inclosed at the start is 4.5 milligram molecules:

$$\frac{dT}{T} = \frac{0.225}{4.5} = 0.05,$$

which leads to an error of

$$dT_{1350^\circ} = 70^\circ \text{ (about)}$$

for an experiment lasting one hour.

This computation demonstrates clearly the enormous errors which may result from the penetration of an outside gas during the time of one hour, a length of time much less than that of an ordinary experiment. It is true that this error decreases rapidly with rise of temperature, and it is very probably zero at 1000° , if there is no break in the glazing.

2. *Constant-pressure Thermometer.* — We still employ the same formula (4):

$$\frac{H\Delta V}{H_0\Delta_0 V_0} = \frac{nRT}{n_0 R_0 T_0},$$

which gives for a first approximation

$$\frac{T'}{T_0} = \frac{n_0}{n}.$$

Calling t_1 and t_2 the surrounding absolute temperatures corresponding to T_0 and T_1 , u_1 and u_2 , the corresponding volumes of the dead space and of the reservoir, we have, for the determination of n and n_0 , the relations:

$$n_0 = N - x_1 = \frac{H_0\Delta_0 V_0}{t_2 \cdot t_1},$$

$$n = N - x_2 = n_0 - (x_2 - x_1),$$

$$x_2 = \frac{H\Delta u_2}{Rt_2},$$

$$x_1 = \frac{H_0\Delta_0 u_1}{Rt_1}.$$

As before, there is a correction to be applied to the approximate temperature T' thus obtained:

$$\frac{dT}{T'} = \frac{dH}{H_0} + \frac{d\Delta}{\Delta_0} + \frac{dV}{V_0},$$

an expression the values of whose terms are known.

Let us see now the causes of error and discuss their importance.

The error resulting from the uncertainty in the boundary of the hot and cold volumes is

$$\frac{dT}{T'} = \frac{dn_0}{n_0} - \frac{dn}{n} = \frac{dn}{n_0} \left(1 - \frac{T'}{T_0} \right) = - \frac{dn_0}{n_0} \left(\frac{T' - T_0}{T_0} \right).$$

As before, let

$$\frac{dn}{n_0} = \frac{1}{1000}.$$

Then we find

$$dT_{500} = 1.5^\circ,$$

$$dT_{1000} = 5.0^\circ,$$

$$dT_{1500} = 9.3^\circ.$$

Thus the errors due to this cause are still greater than by the method of constant volume.

In order to make exactly the correction for the dead space, the method of Regnault's compensator may be employed, as in the work of Sainte-Claire-Deville and Troost; this allows of placing the measuring apparatus at a considerable distance from the fire, which makes the experiments much easier.

Let us now examine the error resulting from the entrance of exterior gases:

$$\frac{dT}{T'} = \frac{dn}{n} = \frac{dn_0}{n_0} \cdot \frac{T}{T_0}.$$

For the experiment of Crafts, the error would be 413° instead of 70° , the bulb being filled at the start at atmospheric pressure.

It is thus evident that, from all points of view, the method of constant volume is more precise than that of constant pressure; the lack of impermeability of the coverings was the only hindrance preventing the use of the former in early practice.

3. *Volumetric Thermometer.* — The volumetric thermometer of Becquerel does not require the invariability of the gaseous mass throughout the duration of the experiment. The method consists in measuring the changes of pressure resulting from a given variation of the gaseous mass contained in the bulb. Becquerel employed very slight changes of mass; the changes of pressure are then equally slight, which diminishes the precision of the measurements.

There is no theoretical inconvenience in reaching an absolute vacuum, or, what is practically more simple, using the exhaustion given by a water pump, as was done by Mallard and Le Chate-

lier; this considerably increases the precision. If the exhaustion is complete, we have the relation

$$\frac{PV}{RT'} = n = \frac{P_0 u_0}{RT_0},$$

u_0 being the volume of the reservoir corresponding to the surrounding temperature T_0 . If the two volumes are filled under atmospheric pressure, $P = P_0$, and then

$$\frac{T'}{T_0} = \frac{u}{V}.$$

There are two corrections to make: the first relative to the expansion of the envelope, the second to the difference between P and P_0 when the exhaustion is produced by a water pump:

$$\frac{dT}{T'} = \frac{dP}{P} + \frac{dV}{V}.$$

In general dP is in the neighborhood of 15 mm. of mercury, which gives

$$\frac{dP}{P} = 0.02.$$

Also,

$$\frac{dV}{V} = 0.0000135(T' - T_0),$$

$$\frac{dT}{T'} = -0.02 + 0.0000135(T' - T_0).$$

Calculating this correction for different temperatures, we have

$$dT_{500} = -10.4^\circ,$$

$$dT_{1000} = -8.5,$$

$$dT_{1500} = -0.35.$$

Let us compute now the error which comes from the uncertainty in the position of the line of separation of the warm part and the cold part of the apparatus; it is, besides, the only remaining one:

$$\frac{dT}{T'} = \frac{dV}{V}.$$

As before, assuming the higher limit to be $\frac{1}{1000}$,

$$\frac{dT}{T'} = \frac{1}{1000},$$

which leads to

$$dT_{500} = 0.77^\circ,$$

$$dT_{1000} = 1.27,$$

$$dT_{1500} = 2.77.$$

From the point of view of the reduction of these errors, this method is preferable to the others, but it appears to have the theoretical disadvantage of not being reducible to the thermodynamic scale.

This whole discussion of the sources of error in the measurement of temperatures aims merely to obtain a determination of the temperature of the pyrometer employed. But this temperature is in itself not the real object of the measurements; it is but an intermediary to arrive at a knowledge of the temperature of certain other bodies supposed to be in thermal equilibrium with the pyrometer. Now this equilibrium is extremely difficult to realize, and it is more often the case that there is no way of being sure of the exactitude with which it has been obtained. Here is then a source of error very important in the measurement of temperatures, especially of high temperatures, at which radiation becomes an important consideration. Within an inclosure whose temperature is not uniform, which is true for the majority of furnaces, there may exist enormous differences of temperatures between neighboring parts. One cannot too strongly insist upon the presence of this source of error, with whose existence too many investigators have not sufficiently occupied themselves.

Substance of the Bulb. — One of the most important points to consider is the choice of the substance which constitutes the bulb; it is necessary to know its expansion to account for the variation of its volume under the action of heat; and one must be sure of its impermeability to gases under pressure.

The following substances have been used up to the present time to make these bulbs: platinum and its alloys, iridium, iron, porcelain, glass, and fused quartz.

Platinum, in spite of its high price, was employed by Pouillet and Becquerel; it has the advantage over iron in not being oxidizable, over porcelain in not being fragile. Its coefficient of expansion increases in a regular manner with temperature:

	Between 0° and 100°.	Between 0° and 1000°.
Mean linear coefficient.....	0.000007	0.000009

In the course of a noted controversy between H. Sainte-Claire-Deville and E. Becquerel, the former of those savants discovered that platinum was very permeable to hydrogen, a gas whose presence is frequent in flames at points where the combustion is not complete. Unfortunately, platinum was accordingly completely abandoned. It is possible, in very many cases, to be sure of the absence of hydrogen, and the very precise experiments of Randall showed that red-hot platinum was quite impermeable to all gases other than hydrogen, even with a vacuum inside the apparatus. With electric heating there is no danger of attack of metal bulbs by furnace gases, as was feared by the early observers using other heating methods.

Alloying platinum with iridium or rhodium greatly stiffens the bulb, and Chappuis used a platinum-iridium bulb of a liter capacity in his researches on the normal gas scale; and in the later investigations of Holborn and Day at the Reichanstalt in their comparison of thermocouple indications with the nitrogen scale up to 1150° C., bulbs of this material replaced porcelain to great advantage. Alloys of 10 and 20 per cent of iridium were used, giving an extremely rigid bulb and with the walls only 0.5 mm. thick, one which undergoes no appreciable deformation after being subjected to the considerable pressures required in the constant-volume gas thermometer at high temperatures. This alloy is also impermeable to nitrogen, but must be guarded against reducing gases and silicates at high temperatures.

Holborn and Day also determined the coefficients of expansion of platinum, as well as other metals, alloys, and porcelain.

For platinum and platinum-iridium they found:

$$\text{Platinum} : \lambda \cdot 10^9 = 8868 t + 1.324 t^2 \text{ from } 0^\circ \text{ to } 1000^\circ;$$

$$80 \text{ Pt} \cdot 20 \text{ Ir} : \lambda \cdot 10^9 = 8198 t + 1.418 t^2 \text{ from } 0^\circ \text{ to } 1000^\circ.$$

These determinations were made on bars nearly 50 cm. long in a most carefully constructed comparator heated electrically. The uniformity of the expansion of platinum is shown by the fact that Benoît's determination by Fizeau's method in the interval 0° to 80° C. gave

$$\lambda \cdot 10^9 = 8901 t + 1.21 t^2.$$

So that in this case extrapolation of over 900° C. led to no serious error.

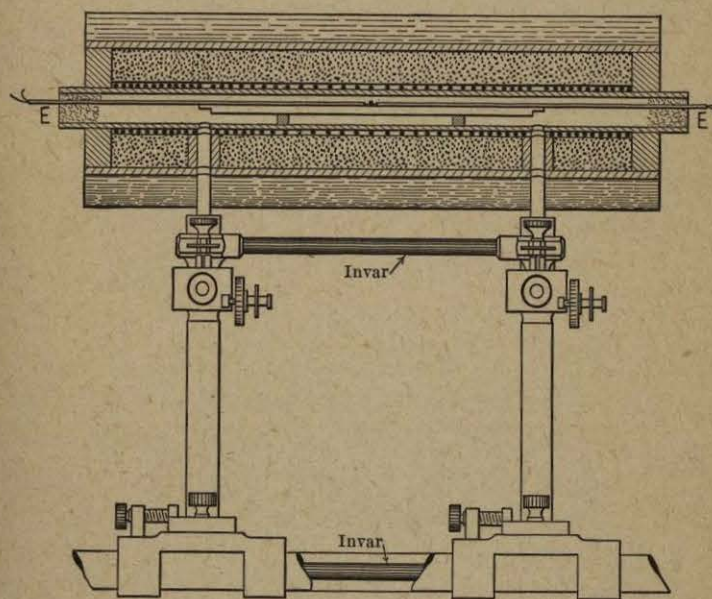


Fig. 4. Apparatus for Linear Expansion.

Day and Sosman, at the Geophysical Laboratory of the Carnegie Institution, have measured, with an improved apparatus (Fig. 4) similar to that of Holborn and Day, the expansion of the platinum alloys containing 10 per cent (10.6 by analysis) of