

on the pressure of air or vapor (Hobson, Uhling-Steinbart, Job, Fournier).

*Recording Pyrometers* (Sir Roberts-Austen, Callendar, Le Chatelier, Siemens and Halske). — Finally, we shall describe in some detail the application of registering methods to pyrometry both for technical and laboratory installations, — a field that has been cultivated very intensively in recent years.

## CHAPTER I.

### STANDARD SCALE OF TEMPERATURES.

WE have seen that temperature is not a measurable quantity: it is merely comparable with respect to a scale arbitrarily chosen. The normal or ideal standard scale is the *thermodynamic scale*; but as it is impossible to realize rigorously this scale, it is necessary to have a practical one. In the same way that, besides the theoretical definition of the meter, there is a practical standard, a certain meter kept at the Bureau International des Poids et Mesures, there exists, besides the ideal scale of temperatures, a practical scale, which is that of a certain gas thermometer which we are going to study. We shall first discuss the gas laws in so far as is necessary for our purpose, and then show how exactly these laws are obeyed by the actual gases that may be used in defining the temperature scale in the several possible ways.

**Laws of Mariotte and Gay-Lussac.** — The laws of Mariotte (or Boyle) and of Gay-Lussac are the basis for the use of the dilatation of gases for the determination of temperatures. These two laws may be written

$$\frac{p_1 v_1}{p_0 v_0} = \frac{1 + \alpha t_1}{1 + \alpha t_0}, \dots \dots \dots (1)$$

in which we may assume for the present that the temperatures are being measured with the mercury thermometer from 0° C.  $\alpha$  is a numerical coefficient, the same for all gases, at least to a first approximation, and its value is about

$$\alpha = 0.00366 = \frac{1}{273}$$

when it is agreed that the interval between the temperatures of melting ice and boiling water is 100°.

But instead of considering the formula (1) as the expression of

an experimental law joining the product  $pv$  to the temperature defined by the mercury thermometer, we may require of experiment merely the law of Mariotte and write *à priori* the formula in question, giving a new definition of temperature approximating that of the mercury thermometer. This new scale has the advantage that it adapts itself to the study of very much higher temperatures. The use of this process suggested by Pouillet was carefully studied by Regnault and has since become the most common method of defining temperatures practically.

The expression for the laws of Mariotte and Gay-Lussac can be put in the form

$$pv = nR \left( \frac{1}{\alpha} + t \right) \dots \dots \dots (2)$$

by calling  $n$  the number of units of quantity (this unit may be either the molecular weight or the gram);  $R$  the value of the expression

$$\frac{p_0 v_0}{\frac{1}{\alpha} + t_0}$$

for unit quantity of matter taken at the temperature of melting ice and under atmospheric pressure.

**Gas Thermometers.** — The equivalent expressions (1) and (2), which arbitrarily by convention give the definition of temperature in terms of the elastic properties of a gas, may be utilized, from the experimental point of view, in various ways for the realization of the standard thermometer.

1. *Constant-volume Thermometer.* — In the thermometer designated by this name, the volume and the mass are kept invariable.

The expression (2) then gives between the two temperatures  $t$  and  $t_0$  the relation

$$\frac{p}{p_0} = \frac{1}{\alpha} + t_0,$$

from which

$$t - t_0 = p - p_0 \left( \frac{1}{\alpha} + t_0 \right) \dots \dots \dots (3)$$

2. *Constant-pressure Thermometer.* — In this case the pressure and the volume of the heated mass remain constant, but the mass is variable; a part of the gas leaves the reservoir. The expression (2) then gives

$$1 = \frac{n}{n_0} \cdot \frac{\frac{1}{\alpha} + t}{\frac{1}{\alpha} + t_0},$$

from which

$$t - t_0 = \frac{n_0 - n}{n} \left( \frac{1}{\alpha} + t \right) \dots \dots \dots (4)$$

It would be much more logical, instead of the classic expressions constant-volume thermometer or constant-pressure thermometer, to say *thermometer of variable pressure, thermometer of variable mass*, which describe much more exactly the manner of their action.

3. *Thermometer of Variable Pressure and Mass.* — The action of this apparatus combines those of the two preceding types. A part of the gas leaves the reservoir, and the pressure is not kept constant. The expression (2) gives

$$\frac{p}{p_0} = \frac{n}{n_0} \cdot \frac{\frac{1}{\alpha} + t}{\frac{1}{\alpha} + t_0},$$

from which

$$t - t_0 = \frac{pn_0 - p_0n}{p_0n} \cdot \left( \frac{1}{\alpha} + t_0 \right) \dots \dots \dots (5)$$

4. *Volumetric Thermometer.* — There exists a fourth method of the use of the gas thermometer which was suggested by Ed. Becquerel, and presents, as we shall see later, a particular interest for the evaluation of high temperatures. We keep the name for it given by its inventor. The determination of the temperature is obtained by two measurements made at the same temperature, and not as in the preceding methods by two measurements made at two different temperatures one of which is supposed known.

The mass contained in the reservoir is varied, and the ensuing change of pressure is observed. The expression (2) gives

$$pv = nR\left(\frac{1}{\alpha} + t\right),$$

$$p'v = n'R\left(\frac{1}{\alpha} + t\right),$$

from which

$$(p - p')v = (n - n')R\left(\frac{1}{\alpha} + t\right),$$

or

$$t = -\frac{1}{\alpha} + \frac{p - p'}{n - n'} \cdot \frac{v}{R} \dots \dots \dots (6)$$

This necessitates a preliminary determination of the constant  $R$ .

In the particular case in which  $p' = 0$ , which supposes that a complete vacuum is obtained, the preceding relation becomes simpler and is

$$t = -\frac{1}{\alpha} + \frac{p}{n} \cdot \frac{v}{R} \dots \dots \dots (7)$$

The definitions of temperature given by these different thermometers would be equivalent among themselves and with that of the mercury thermometer if the laws of Mariotte and Gay-Lussac were rigorously exact, as used to be held, and if the expansion of mercury in glass were linear. The only advantage of the gas thermometer then would be to extend to high temperatures the scale of the mercury thermometer. In this way it was employed by Pouillet, Becquerel, and Sainte-Claire-Deville.

**Experiments of Regnault.** — The very precise experiments of Regnault caused a modification in the then admitted ideas concerning the mercury thermometer as well as the gas thermometer, and led to the definite adoption of the gas thermometer as standard.

In the first place these experiments established that different mercury thermometers are not comparable among themselves on account of the unequal dilatation of the differing glass employed

in their construction. Thus they cannot give an invariable scale for the determination of temperature. In comparing them from 0° to 100° they do not present between these extreme temperatures very great differences, 0.30° as a maximum, but at temperatures above 100° these differences may become considerable and reach 10° to 20° or more. (See also Chap. IX.)

Constant-vol. air thermometer, $p_0=760$ .	Mercury thermometer in			
	Crystal.	White glass.	Green glass.	Bohemian glass.
100°	+ 0.00°	+ 0.00°	+ 0.00°	+ 0.00°
150	+ 0.40	- 0.20	+ 0.30	+ 0.15
200	+ 1.25	- 0.30	+ 0.80	+ 0.50
250	+ 3.00	+ 0.05	+ 1.85	+ 1.44
300	+ 5.72	+ 1.08	+ 3.50	
350	+ 10.50	+ 4.00		

The numbers figuring in this table indicate the quantities by which it is necessary to increase or diminish the temperatures given by the air thermometer in order to have them correspond with those which were observed with the different mercury thermometers.

It was thus impossible to define the practical scale of temperatures in terms of the mercury thermometer. The use of the gas thermometer became necessary. But Regnault recognized that it was not possible to take a *single coefficient of dilatation*  $\alpha$  independent of the *nature* of the gas, of its *pressure*, and of the *mode of dilatation* utilized. The coefficient of expansion at constant volume ( $\beta$ ) and the coefficient of expansion at constant pressure ( $\alpha$ ) are not identical. This follows from the fact that the law of Mariotte is not rigorously exact; we have in reality

$$pv = p_0v_0 + \epsilon,$$

$\epsilon$  being a very small quantity, but not zero.

The experiments of Regnault permitted him not only to detect but to measure this variation of the coefficient of expansion. Here are, for example, the results which he found for air between 0° and 100°.

Volume constant.			Pressure constant.		
Pressure	$\beta$	$\frac{1}{\beta}$	Pressure	$\alpha$	$\frac{1}{\alpha}$
266	0.003656	273.6	760	0.003671	272.4
760	3655	272.8	2525	3694	270.7
1692	3689	271	2620	3696	270.4
3655	3709	269.5			

For air at 4.5° Rankine obtained, from the experiments of Regnault, the formula

$$pv = p_0v_0 + 0.008163 \frac{p - p_0}{\omega} \cdot pv$$

$\omega$  being the atmospheric pressure.

These coefficients vary also from one gas to another, as is shown by the following table, taken also from Regnault's experiments:

MEAN COEFFICIENT BETWEEN 0° AND 100°.

Volume constant.			Pressure constant.		
Pressure. mm.	$\beta$	$\frac{1}{\alpha}$	Pressure mm.	$\alpha$	$\frac{1}{\beta}$
<i>Air.</i>					
760	0.003665	272.8	760	0.003671	272.4
3655	3709	269.5	2620	3696	270.4
<i>Hydrogen.</i>					
760	3667	272.7	760	36613	273.1
			2545	36616	273.2
<i>Carbon Monoxide.</i>					
760	3667	272.7	760	3669	272.5
<i>Nitrogen.</i>					
760	3668	272.6			
<i>Carbonic acid.</i>					
760	3688	271.2	760	3710	269.5
3589	3860	259	2520	3845	259.5
<i>Sulphurous acid.</i>					
760	3845	259.5	760	3902	253.0
			980	3980	251.3

These experiments show that the easily liquefiable gases have coefficients quite different from those of the permanent gases.

For the permanent gases the coefficients for constant volume differ much less among themselves than those for constant

pressure; for the former the extreme deviation does not exceed  $\frac{1}{1000}$ ; for the latter it is three times as great. Setting aside air, which is a mixture and which contains more easily liquefiable oxygen, the coefficients for constant volume of H<sub>2</sub>, N<sub>2</sub>, and CO are identical.

Finally, for hydrogen the coefficient of expansion does not vary appreciably with the pressure.

The inequality of the coefficients of expansion, however, does not prevent us from taking any gas whatever to define the scale of temperature, provided we apply to it the proper coefficient determined by experiment between 0° and 100°. The scales are identical, if the coefficients of expansion do not vary with the temperature. This is the conclusion to which Regnault came from a comparison of thermometers at constant volume, differing by their initial pressure or the nature of the gas. Here are the results obtained, starting from the fixed points 0° and 100°, by the aid of the following formulæ:

$$pv = nRT,$$

$$p_0v = nRT_0,$$

$$p_{100}v = nRT_{100},$$

$$\frac{p - p_0}{p_{100} - p_0} = \frac{T - T_0}{T_{100} - T_0} = \frac{t}{100}.$$

AIR THERMOMETER.

$p^0 = 751$ mm.	$p^0 = 1486$ mm.
Degrees.	Degrees.
156.18	156.19
259.50	259.41
324.33	324.20

PRESSURE = 760 MILLIMETERS.

Air thermometer.	Hydrogen thermometer.	Air thermometer.	CO <sub>2</sub> thermometer.
Degrees.	Degrees.	Degrees.	Degrees.
141.75	141.91	159.78	160.00
228.87	228.88	267.35	267.45
325.40	325.21	322.8	322.9

The deviations do not exceed  $0.2^\circ$ , a value that Regnault estimated not to exceed the limits of error of his experiments; he concluded from this that one gas may be used as well as another, and he took air for the normal thermometer.

Nevertheless his experiments on sulphurous acid had shown a very marked variation of the coefficient of expansion of this gas with the temperature. The following table gives the mean coefficient at constant volume between  $0^\circ$  and  $t^\circ$  for this case:

	$\beta$
98.0.....	0.0038251
102.45.....	38225
185.42.....	37999
257.17.....	37923
299.90.....	37913
310.31.....	37893

By analogy it is permissible to suppose that a similar effect should take place with the other gases; but the differences were then too small, and the degree of precision of the methods of Regnault insufficient to detect it.

**Results Obtained by Chappuis.** — This effect has been demonstrated by experiments of very great precision made at the Bureau International des Poids et Mesures, at Sèvres. Chappuis has found, between  $0^\circ$  and  $100^\circ$ , systematic deviations between thermometers of hydrogen, nitrogen, and carbonic acid, filled at  $0^\circ$  under a pressure of 1000 mm. of mercury.

Hydrogen ther.	N ther.-H ther.	N ther.-CO <sub>2</sub> ther.
- 15°	- 0.016°	- 0.094°
0	0	0
+ 25	+ 0.011	+ 0.050
+ 50	+ 0.009	+ 0.059
+ 75	+ 0.011	+ 0.038
+ 100	0	0

In this table, taking as definition of the temperature the hydrogen thermometer at constant volume, the numbers in the last two columns indicate the deviations observed with the thermometers of nitrogen and carbonic acid; it is certain that these deviations are systematic. These results allow of the determination of the mean coefficients of expansion:

$t$	$\beta$ (hydrogen)	$\beta$ (nitrogen)	$\beta$ (carbonic acid)
$0^\circ$	.....	0.00367698	0.00373538
100	0.00366254	367466	372477

Thus the coefficients decrease with rise of temperature, while remaining higher than that of hydrogen, to which they tend to approach. The more recent work of Chappuis and Harker and others in the establishment of a normal scale of temperatures for high temperatures will be discussed in the following sections.

In the interval  $0^\circ$  to  $100^\circ$ , the values given above, calculated from Chappuis' data of 1888, may not be absolutely exact, but they are probably very nearly correct. Some of the later results are given below; those marked Callendar are calculated by him from the data of Kelvin and Joule, using a modified formula; Chappuis' results are from his latest determinations (1902), while those of Lehrfeldt and Rose-Innes are calculations involving special thermodynamical assumptions.

#### DIFFERENCE BETWEEN SCALES OF NITROGEN AND HYDROGEN THERMOMETERS.

$$t_n - t_h, \text{ vol.} = \text{const.}, P_0 = 100 \text{ cms.}$$

Temp. Cent.	Callendar. 1903.	Chappuis. 1902.	Rose-Innes. 1901.	Lehrfeldt. 1898.
+20	+ .006	+ .005	+ .002	+ .011
+40	+ .009	+ .008	+ .002	+ .017
+50	+ .009	+ .010	+ .002	+ .019
+60	+ .008	+ .009	+ .002	+ .019
+80	+ .005	+ .004	+ .001	+ .015

**Normal Scale of Temperatures.** — It results from these experiments that the different scales furnished by the various gas thermometers are not rigorously identical; the deviations between  $0^\circ$  and  $100^\circ$  are very small, but their existence is certain. It becomes necessary, therefore, in order to have a *scale of temperature rigorously defined*, to make a choice of the *nature* of the gas, of its *manner of dilatation*, and of its initial *pressure*.

The *normal thermometer* selected by the Bureau International des Poids et Mesures to define the practical scale of temperatures, and everywhere adopted to-day, is the *hydrogen thermometer*, operated at constant volume and filled with gas at 1000 millimeters of mercury at the temperature of melting ice.

For high temperatures this definition is inadmissible, because we would reach such pressures that the apparatus could not withstand. The use of the method at constant volume, that is to say, at invariable mass, is besides bad on account of the permeability of the coverings at high temperatures. It would be of great advantage to be able to employ a gas other than hydrogen and operate the thermometer at variable mass. Practically, it has been the custom, in most of the recent work at high temperatures, to use nitrogen gas at reduced pressure, 150 to 300 mm. of Hg at 0° C., although there has been, as yet, no formal agreement as to the gas or type of thermometer to use in defining the high temperature scale.

In the actual state of experimentation at high temperatures, it has been impossible as yet to obtain results exact to better than 1°, and indeed, practically, we are far from arriving at this accuracy for the highest temperatures measurable. It is very likely that we can, under these conditions, employ indifferently for the construction of the normal thermometer any permanent gas whatsoever that does not diffuse into or through the containing bulb. According to the preceding experiments, all the gases would have a dilatation slightly greater than that for hydrogen, and their coefficient of expansion, which decreases with rise of temperature, would approach that for hydrogen. For determining experimentally the error possible with a normal thermometer thus modified, we possess the following experimental data.

Crafts compared in the neighborhood of 1500° the expansion at constant pressure of nitrogen and carbonic acid, and found for this latter the mean coefficient 0.00368 in assuming 0.00367 for nitrogen.

The experiments were made by displacing in a Meyer's tube nitrogen by carbonic acid, or carbonic acid by nitrogen.

10 cc. N <sub>2</sub> displace	10 cc. CO <sub>2</sub> displace
10.03 of CO <sub>2</sub>	9.95 of N <sub>2</sub>
10.01	9.91
10.00	9.98
10.03	9.93
9.95	
10.09	Mean 9.94
Mean 10.02	

The two measurements give positive and negative differences of the same order of magnitude; but it should be noticed that the observed deviation ( $\frac{4}{1000}$  on an average) hardly exceeds the possible error of observation. However it may be, carbonic acid, which differs much from the permanent gases at ordinary temperatures, no longer so differs in an appreciable degree at 1500°.

Violle made some comparative measurements on the air pyrometer used at constant pressure and constant volume in his determinations of the specific heat of platinum.

Volume constant.	Press. constant.	Difference.
1171°	1165°	6°
1169	1166	3
1195	1192	3

There was on an average a deviation of only 4° between the two modes of observation, and the greater part of this deviation should be laid to accidental variations of the gaseous mass resulting from the permeability of the coverings.

Chappuis has made an exhaustive experimental study of the divergences of gases from the normal scale at comparatively low temperatures and he finds that the coefficient of nitrogen (at constant volume) gradually diminishes as above stated (p. 21), but that at about 75° C. it reaches a limiting value equal to

$$\beta_{\text{lim}} = 0.00367330,$$

and it may be assumed that above this temperature the gas is in a perfect state.

The mean coefficient at constant volume for this gas between 0° and 100° is

$$\beta_{0-100} = 0.00367466$$