

and the limiting value for an initial pressure $P_0 = 0$ is

$$\beta_{P_0=0} = 0.0036617.$$

This follows from the divergence that Chappuis and Harker found for the constant-volume nitrogen-thermometer from the normal scale of temperatures, in terms of the initial pressure; their experiments gave

$$\frac{\delta\beta}{\delta p} = 1.28 \cdot 10^{-8} \text{ per mm. change in pressure.}$$

It is to be remembered that when the volume or pressure coefficient is found for any pressure, that value is, by definition, the one to use in computing the normal scale of temperatures.

The experiments of Chappuis and Harker were carried out at the International Bureau of Weights and Measures and included also a comparison of the platinum-resistance and nitrogen thermometers up to 500°C. and a determination of the sulphur boiling point, to which questions we shall return.

Such a normal scale of temperature for the nitrogen thermometer is given by finding the coefficient β , at 0°C. for a pressure P_0' which the gas would have, supposing it to remain perfect in the range 0° to 100° . If $P_0 = 100 \text{ cm.}$, $P_{100} = 136.7466 \text{ cm.}$;

whence $P_0' = 100.0086$ and $\beta = \frac{P_{100} - P_0'}{100 P_0'} = 0.00367348$, if

$\beta_{\text{lim}} = 0.00367330$ as stated above.

Nitrogen at constant pressure gives, according to Chappuis,

$$\frac{\delta\alpha}{\delta p} = 1.19 \cdot 10^{-8} \text{ per mm.}$$

and

$$\alpha_{p=0} = 0.0036612.$$

The divergences from the normal scale for this gas are about double those at constant volume, and the divergences between the uncorrected scale and the theoretical scale of the constant-volume thermometer, whose constants are given above and which represents the normal scale of temperatures, are proportional to the temperature measured from 100° and have the following values:

At 100°	0.000°
200.....	.023
300.....	.047
400.....	.070

These deviations are evidently very slight and are entirely negligible within this range for practically all pyrometric uses. We shall see, however, that at 1000° this correction may assume a certain importance.

For hydrogen, the limiting values given by D. Berthelot are:

$$\beta_{p=0} = 0.0036625,$$

$$\alpha_{p=0} = 0.0036624,$$

and the deviations of this gas from the normal scale are immaterial.

The latest results of Chappuis on the elastic properties of the various thermometric gases are given in the following table:

EXPANSION COEFFICIENTS OF THERMOMETRIC GASES ACCORDING TO CHAPPUIS.

$10^4 \times$	Hydrogen.	Nitrogen.	Air.	CO ₂ .
β_{0-20}		3675.9		3733.5
β_{0-40}		3675.4		3729.9
β_{0-100}	3662.56	3674.6	3674.41	3726.2
$\beta_{p=0}$	3662.56	3661.7		3670
$\delta\beta/\delta P_0$	0	0.0128		
α_{0-20}		3677.0		3760.2
α_{0-40}		3674.97		3753.6
α_{0-100}	3660.04	3673.15	3672.82	3741.0
$\alpha_{p=0}$	3662.49	3661.2		3671
$\delta\alpha/\delta P_0$	0.0186	0.0119		

Where $\alpha = \frac{1}{V} \cdot \frac{dV}{dT}$ and $\beta = \frac{1}{P_0} \cdot \frac{dP}{dT}$ and $P_0 = 1000 \text{ mm. Hg.}$

Jaquero and Perrot have compared the coefficients of expansion β of several gases in a silica bulb between 0°C. and the melting point of gold and at initial pressures from 170 to 230 mm. of Hg, with the following results:

EXPANSION COEFFICIENTS AT HIGH TEMPERATURES.

Gas.	β .	Melting point of Au.	Pressure at 0° C. mm.
Nitrogen.....	0.0036643	1067.2	200-230
Oxygen.....	0.0036652	1067.5	180-230
Air.....	0.0036663	1067.2	230
CO.....	0.0036638	1067.05	240
CO ₂ {	$p = 240$	1066.5	170
	$p = 170$		

We can then affirm that, in employing any permanent gas with any mode of dilatation, we shall not differ certainly by more than 1° at 1000° from the temperature of the normal scale, and that, with the exception of CO₂, all the permanent gases have very nearly the same expansion coefficient.

Theoretically it would be preferable to use hydrogen under reduced pressure, which would certainly not give deviations of 1° from the normal scale; but there is always the danger of the passage of this gas through the coverings and of its combustion by oxygen or oxides.

Practically it would be better to take nitrogen, whose expansion deviates little from that of hydrogen, less than the deviation of air. Callendar has suggested the use of helium or one of the other newly discovered inert, monatomic gases, such as argon, as they diverge less than nitrogen from the hydrogen scale, cannot dissociate and do not pass through metals, at least in the case of argon.

For high temperatures the normal thermometer will be, then, one of nitrogen or other inert gas.

Thermodynamic Scale. — It is defined, in terms of Carnot's principle applied to a reversible cycle working between two sources at constant temperatures, by the relation

$$\frac{Q_1}{Q_0} = \frac{T_1}{T_0} \dots \dots \dots (1)$$

1. *Approximate Expression.* — Consider Carnot's cycle formed, as is well known, of two isotherms and two adiabatics, and let us seek the quantity of heat absorbed following the isotherm T_1 .

From Joule's experiments we have approximately

$$Q_1 = A \int p \, dv.$$

The laws of Mariotte and Gay-Lussac give

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

where t is the temperature of the gas thermometer; then,

$$dv = -R \frac{dp}{p^2} \left(\frac{1}{\alpha} + t \right);$$

$$\text{and } Q_1 = -AR \left(\frac{1}{\alpha} + t_1 \right) \cdot \int_{p_1}^{p_1'} \frac{dp}{p} = AR \left(\frac{1}{\alpha} + t \right) \log \frac{p_1'}{p_1''}$$

Similarly,

$$Q_0 = AR \left(\frac{1}{\alpha} + t_0 \right) \log \frac{p_0'}{p_0''}$$

Equation (1) becomes

$$\frac{T_1}{T_0} = \frac{Q_1}{Q_0} = \frac{\frac{1}{\alpha} + t_1}{\frac{1}{\alpha} + t_0} \left(\log \frac{p_1'}{p_1''} - \log \frac{p_0'}{p_0''} \right) \dots \dots (2)$$

But the experiments on adiabatic expansion give

$$pv^\gamma = \text{const.},$$

where γ is the ratio of the specific heats at constant pressure and volume, and combining with the laws of Mariotte and Gay-Lussac,

$$p^{\gamma-1} \cdot t^{-\gamma} = \text{const.}$$

Consequently $\frac{p_1}{p_0}$ depends only on the ratio $\frac{t_1}{t_0}$, which is the same the whole length of the two isotherms. Thus

$$\frac{p_1'}{p_0'} = \frac{p_1''}{p_0''},$$

or

$$\frac{p_1'}{p_1''} = \frac{p_0'}{p_0''}.$$

Equation (2) then takes the very simple form

$$\frac{T_1}{T_0} = \frac{\frac{1}{\alpha} + t_1}{\frac{1}{\alpha} + t_0};$$

that is to say, the *ratio of the absolute thermodynamic temperatures is equal to the ratio of the absolute temperatures of the gas thermometer*; and if on the two scales it is agreed to take equal to 100 the interval comprised between the temperatures of melting ice and the vapor of boiling water, we have, at any temperature, the equality

$$T = \frac{1}{\alpha} + t.$$

But this is only a first approximation, for we have employed relations that are but roughly so: the laws of Joule, Mariotte, and Gay-Lussac.

2. *Second Approximation.* — Reconsider the problem by a more exact method. Since T differs very little from $\frac{1}{\alpha} + t$, and since the laws of Mariotte and Gay-Lussac are nearly true, we write, following a method of calculation indicated by Callendar,

$$pv = RT(1 - \phi),$$

ϕ being a very small function of p and of T (thermodynamic temperature).

We have, then, between the temperature of the gas thermometer and the thermodynamic temperature, the relation

$$\frac{\frac{1}{\alpha} + t_1}{\frac{1}{\alpha} + t_0} = \frac{T_1(1 - \phi_1)}{T_0(1 - \phi_0)},$$

which will permit of passing from one scale of temperature to the other if we know the corresponding value of ϕ .

Consider, as before, Carnot's cycle, and let us determine the heat of isothermal expansion in a more exact manner, by utilizing

the experiments of Joule and Thomson on the expansion through a porous plug, and those of Regnault on the deviations from Mariotte's law.

We write for this that the changes in energy between two given isothermal states are the same, either for the reversible expansion or for the expansion of Joule and Thomson.

$$Q_1 - A \int_{v_1'}^{v_1''} p dv = -A(p_1''v_1'' - p_1'v_1') + \int_{p_0'}^{p_1''} \frac{d\epsilon_1}{dp} dp,$$

ϵ being the very feeble change in heat of the gas accompanying its passage through the porous plug, in the experiment of Joule and Thomson. We get from this

$$Q_1 = A \int_{v_1'}^{v_1''} v dp + \int \frac{d\epsilon_1}{dp} dp \text{ (at constant temperature),} \quad (3)$$

for

$$d(pv) = p dv + v dp.$$

The relation

$$pv = RT(1 - \phi)$$

gives for the value of v

$$v = \frac{RT}{p}(1 - \phi),$$

which, substituted in equation (3), leads to

$$Q_1 = ART_1 \cdot \int_{p_1'}^{p_1''} \frac{dp}{p} - ART_1 \cdot \int_{\phi_1} \frac{d\phi}{p} + \int \frac{d\epsilon_1}{dp} dp. \quad (4)$$

Similarly, we have

$$Q_0 = ART_0 \cdot \int_{p_0'}^{p_0''} \frac{dp}{p} - ART_0 \cdot \int_{\phi_0} \frac{d\phi}{p} + \int \frac{d\epsilon_0}{dp} dp. \quad (5)$$

If we introduce these values in the expression for Carnot's cycle, after division by T_1 and T_0 we should find an identity:

$$\begin{aligned} \frac{Q_1}{T_1} - \frac{Q_0}{T_0} = AR \log_e \frac{p_1'' p_0'}{p_1' p_0''} - \int_{p_1'}^{p_1''} \left(AR \frac{\phi_1}{p} - \frac{1}{T_1} \cdot \frac{d\epsilon_1}{dp} \right) dp \\ + \int_{p_0'}^{p_0''} \left(AR \frac{\phi_0}{p} - \frac{1}{T_0} \cdot \frac{d\epsilon_0}{dp} \right) dp = 0. \end{aligned}$$

The law of adiabatic expansion gives

$$\frac{p_1'' p_0'}{p_1' p_0''} = 1, \quad \log_e \frac{p_1'' p_0'}{p_1' p_0''} = 0.$$

In order, then, that the expression reduce to an identity it is necessary that

$$\frac{1}{T} \cdot \frac{d\epsilon}{dp} = AR \frac{\phi}{p}, \quad \text{or} \quad \phi = \frac{d\epsilon}{dp} \cdot p \cdot \frac{1}{AR} \cdot \frac{1}{T}.$$

Referring to the experiments on air of Joule and Thomson, we have

$$\phi = 0.001173 \cdot \frac{p_1}{p_0} \cdot \left(\frac{T_0}{T_1}\right)^3,$$

p_0 being the atmospheric pressure, and T_0 the temperature of melting ice.

This is still an approximate result, for we have depended upon the experiments of Joule and Thomson and on the law of adiabatic expansion; however, the approximation is more close. If it seems sufficient for air, it is certainly not so for carbonic acid. Neither is the formula rigorously exact for air.

Gas Scale Corrections. — Callendar has calculated the correction to make to the air thermometer readings by extrapolation up to 1000° , and he found the following results:

Readings of centigrade thermometer.	Volume constant.		Pressure constant.	
	ϕ	Δt	ϕ	Δt
0°	0.001173	0	0.001173	0
100	0.000627	0	0.000457	0
200	393	0.04	225	0.084
300	267	0.09	127	0.20
500	147	0.23	52	0.47
1000	54	0.62	12	1.19

The deviations of the air thermometer at high temperatures are thus very slight if concordance is established at 0° and 100° , and we have seen that in the case of nitrogen the experiments of Chappuis and Harker have shown the same to be true for this gas.

Callendar, in a more recent computation based upon the work of Kelvin and Joule and the experiments of Chappuis and others, arrives at the following values for the scale corrections for the best thermometric gases:

SCALE CORRECTIONS FOR GASES, ASSUMING $\theta_0 = 273.10^\circ$.

Temperature centigrade.	Constant pressure, 76 cm.				Constant volume, $p_1 = 100$ cm.			
	Helium.	Hydrogen.	Nitrogen.	Air.	Helium.	Hydrogen.	Nitrogen.	Air.
- 150	+0.073	+0.084	+0.045	+0.001	-0.026	+0.013	+0.195	+0.186
- 100	+ .030	+ .022	+ .328	+ .314	- .012	+ .005	+ .080	+ .076
- 50	+ .009	+ .006	+ .090	+ .086	- .004	+ .002	+ .024	+ .023
- 20	+ .003	+ .002	+ .025	+ .024	- .001	+ .000	+ .007	+ .007
+ 20	- .0016	- .0009	- .0141	- .0134	+ .0008	- .0003	- .0043	+ .0041
+ 40	- .0022	- .0013	- .0195	- .0186	+ .0011	- .0004	- .0059	+ .0056
+ 50	- .0022	- .0013	- .0195	- .0186	+ .0011	- .0004	- .0059	+ .0056
+ 60	- .0021	- .0012	- .0180	- .0172	+ .0011	- .0004	- .0054	+ .0053
+ 80	- .0013	- .0008	- .0113	- .0108	+ .0007	- .0002	- .0038	+ .0034
+ 150	+ .0054	+ .0029	+ .043	+ .041	- .0031	+ .0010	+ .0143	+ .0136
+ 200	+ .0128	+ .0068	+ .101	+ .096	- .0076	+ .0024	+ .035	+ .033
+ 300	+ .0332	+ .0165	+ .243	+ .232	- .023	+ .0059	+ .088	+ .084
+ 450	+ .071	+ .034	+ .495	+ .472	- .047	+ .013	+ .189	+ .180
+ 1000	+ .243	+ .104	+ 1.53	+ 1.46	- .187	+ .044	+ .646	+ .616

The above table indicates that for the gases hydrogen and helium no attention need be paid to the thermodynamic correction, for it is quite negligible for the whole temperature range for these two gases. All the gases are also seen to have a greater correction at constant pressure than at constant volume. Again it is to be noted that at small initial pressures these corrections will be proportionally reduced, and finally that it is only in the most refined work that this correction need be applied, as in the establishment of a fixed point in pyrometry as the gold fusing-point.

D. Berthelot has indicated a simple method for calculating this thermodynamic correction for any gas.

For a constant-volume thermometer:

$$T - T_0 = t \left(1 - \frac{a}{373} \frac{100 - t}{273 + t} \right),$$

T_0 being the absolute temperature of melting ice (273.10°), T the absolute temperature sought corresponding to the centigrade temperature t given by the gas thermometer in question at an initial pressure of one atmosphere. For other pressures p the correction to t must be multiplied by $\frac{p}{76}$.

For the constant-pressure thermometer

$$T - T_0 = t \left[1 - \frac{a}{373} \frac{100 - t}{273 + t} \left(1 + \frac{273}{373} \frac{646 + t}{273 + t} \right) \right].$$

The value of a depends upon the critical constants of the gas and is

$$a = \frac{27}{64} R^2 \cdot \frac{T_c^3}{p_c},$$

where R is the gas constant (here $\frac{1}{273.1}$), T_c and p_c the critical pressure and temperature respectively.

TABLE OF CRITICAL CONSTANTS.

	p_c	t_c	a
Carbonic acid.....	72.9 atm.	+ 31.3	2.188
Oxygen.....	50.0	-118	0.422
Air.....	39.0	-140	.342
Carbon monoxide.....	35.9	-141	.363
Nitrogen.....	33.6	-146	.343
Hydrogen.....	13.0	-240	.016
Helium.....	3	-268	.009

The formulæ of Berthelot give practically identical values for the thermodynamic corrections as found by Callendar. Buckingham has discussed in detail the departures of the temperature scales, both constant volume and constant pressure, given by the several gases, from the thermodynamic scale by a method similar to that of Berthelot's, but using a somewhat simpler equation of state. The most interesting results relate to the behavior of nitrogen, which is now generally used as the thermometric gas in high temperature measurements, and in Fig. 1 are given the corrections of the nitrogen thermometer at $P_0 = 1000$ mm. of Hg taken from Buckingham's paper.

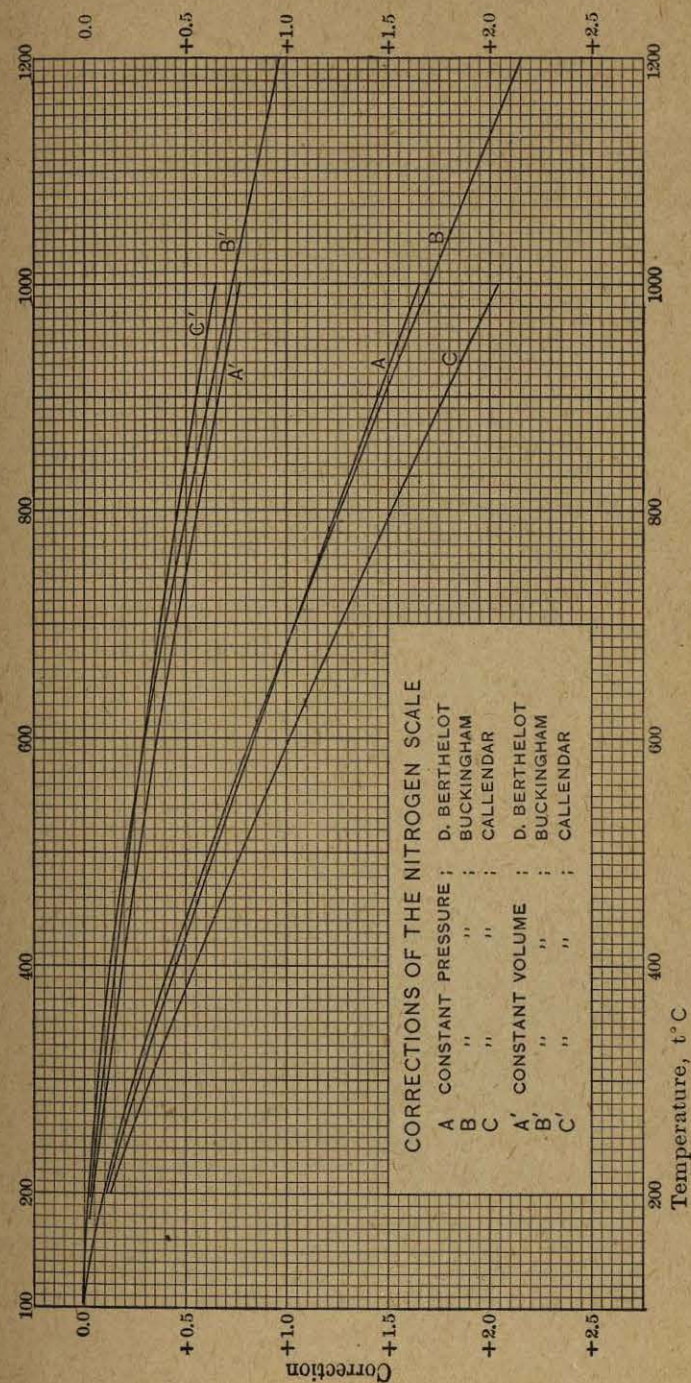


Fig. 1. Nitrogen Thermometer Corrections.

It should be noted that the calculated corrections to reduce the readings of any gas thermometer to the thermodynamic scale are extrapolations from data on the Joule-Thomson effect made at ordinary temperatures. This is probably not a serious source of concern, however, as both Buckingham and Berthelot show that the several gases, when treated by the method of corresponding states, that is reduced in pressure and temperature to the fractions of their critical constants, furnish data all lying on the same curve.

Experimental science has now reached such a development that as above stated these corrections to the thermodynamic scale cannot always be neglected.

The Ice Point. — The experiments of Kelvin and Joule may also be used to determine the absolute temperature of the point of fusion of ice on the thermodynamic scale. Below are the results of a computation by Lehrfeldt made several years ago.

	Gas-ther.	Thermodyn. ther.
Hydrogen.....	273.08°	272.8°
Air.....	272.43	273.27
Nitrogen.....	273.13	273.2
Carbonic acid.....	268.47	274.83 (Thomson) 273.48 (Natanson)

The thermodynamic temperature of melting ice should be in all cases the same; the deviations come mainly from the uncertainties in the measurements of the heat of expansion, indicating the desirability of repeating Joule and Thomson's work with modern appliances.

There have been several more recent computations of the temperature of fusion of ice on the thermodynamic scale ($= \frac{1}{\alpha} \equiv \frac{1}{\beta}$) based on the experimentally found deviations of several of the real gases from the ideal state, account being taken of the Joule-Thomson effect as measured by various observers, the thermal expansion and the compressibility as determined by Chappuis and by Amagat, the computations requiring the use of a modified form of Van der Waal's equation of state. Some of these calculations are as follows:

THERMODYNAMIC TEMPERATURE OF MELTING ICE (θ_0)

Author.	Gases used in computation.	θ
D. Berthelot (1903).....	H, CO ₂ , Air	273.11
Buckingham (1907).....	H, N, CO ₂ , Air	273.174
Rose-Innes (1908).....	H	273.131
	N	273.136

The following table gives Callendar's résumé of the expansive properties of the thermometric gases. In the table θ_0 is the thermodynamic temperature of the ice-point as determined from hydrogen, and T_0 this point on the various gas scales.

EXPANSION AND PRESSURE COEFFICIENTS FOR $\theta_0 = 273.10^\circ$.

Gas.	Constant pressure, 76 cm.			Constant volume, $p_0 = 100$ cm.		
	$\theta_0 - T_0$	T_0	$1/T_0$	$\theta_0 - T_0$	T_0	$1/T_0$
Helium.....	+0.10	273.00	.0036628	+0.19	272.91	.0036640
Hydrogen.....	-.135	273.235	.00365985	+.067	273.034	.00366254
Nitrogen.....	+.70	272.40	.0036708	+.99	272.11	.00367466
Air.....	+.71	272.39	.0036709	+.96	272.14	.00367425

Chappuis' latest values give in the case of hydrogen $\frac{1}{\alpha} = 273.038$

and $\frac{1}{\beta} = 273.033$ for zero pressure on the hydrogen scale, as computed by himself, showing no sensible difference in the two hydrogen scales in the range 0° to 100° C., and, taken with the preceding tables, that the hydrogen and thermodynamic scales differ by about 0.10° C. at 0° C. Our knowledge of the thermodynamic scale, as realized by correcting the several gas scales, may be said to be in a very satisfactory condition. As we shall see in the chapter on the laws of radiation, the normal or thermodynamic scale of temperatures may be extended to temperatures indefinitely high in terms of the intensity of radiation total or monochromatic, which proceeds from a small opening in any enclosure at constant temperature throughout. We shall have realized, therefore, a single standard or normal temperature scale

independent of the properties of any particular substance, continuous from the absolute zero to the highest temperatures that may be produced, and one that is practically reproducible for all technical and scientific purposes, by methods that are available in the several standardizing laboratories.

CHAPTER II.

GAS PYROMETER.

Introduction. — We have seen that the standard scale of temperatures adopted by the International Committee of Weights and Measures is given by a certain constant-volume hydrogen thermometer, namely that of the International Bureau at Sèvres, which instrument, however, has not been used to measure temperatures above 100° C. The type of gas thermometer which is to be considered standard for higher temperatures has not as yet been agreed upon by any authoritative body, but for reasons which we shall develop, the constant-volume nitrogen thermometer appears to have the preference, at least for temperatures above 200° C. From what we have seen in the preceding chapter, it is practically immaterial in the definition of the high temperature scale what form of thermometer is actually used, as the indications of any of the gas thermometers may readily be compared with those of another by well established methods of computation and reduced with great accuracy to a common theoretical basis, that of the thermodynamic scale.

It may be well to recall, at this point, in what consists the actual operation of the location of a temperature on the chosen gas scale, and point out, at the same time, some of the difficulties involved. The gas thermometer bulb must be brought throughout its volume to a sufficiently uniform temperature. To obtain a volume of 500 c.c. of gas, for example, constant in temperature to 1° at 1000° C. has not yet been attempted by any experimenter. Whatever the system of gas thermometry used, on account of the transient nature of the phenomenon measured, pressure on a manometer, a mass of displaced mercury, etc., it is also necessary, except in certain special cases as some boiling points, to bring to this same temperature some other body whose registra-