

of Barus in the early eighties have serious gas-thermometer investigations been carried out in America until these experimenters (1904-10) undertook the redetermination of a series of fixed points from zinc to palladium in terms of the constant-volume nitrogen thermometer. The preliminary work of Day and Clement was done with a platinum-iridium bulb, but on

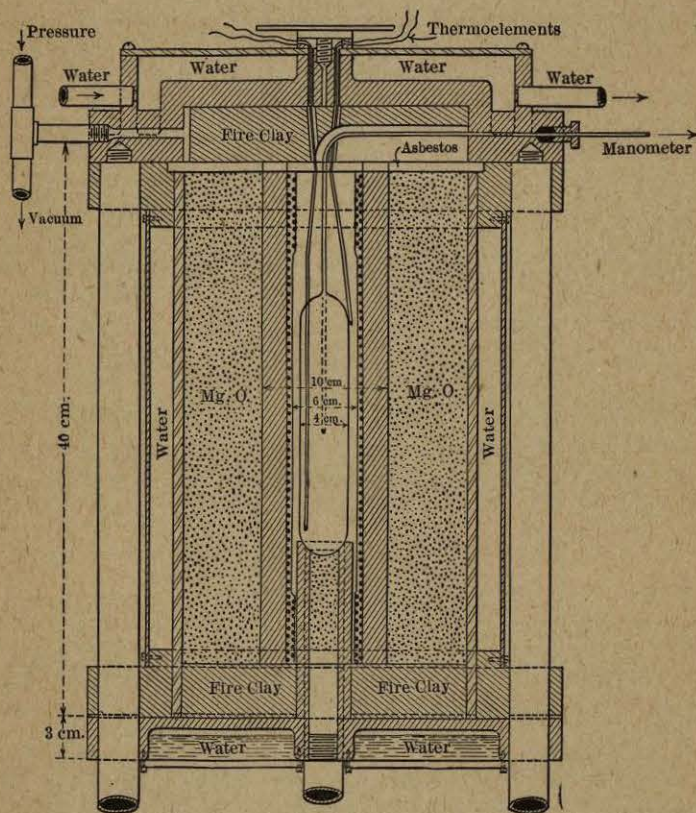
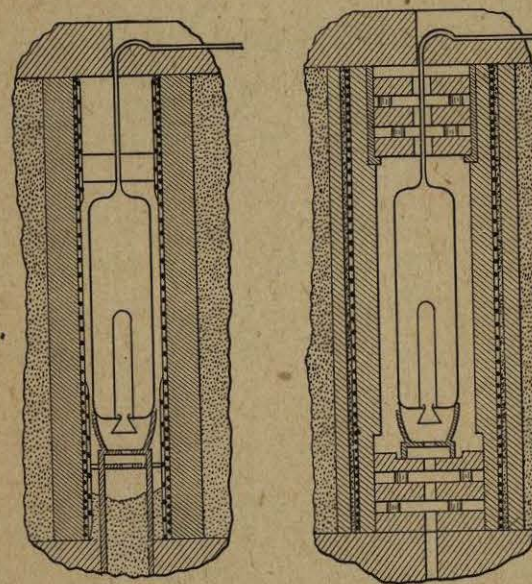


Fig. 10. Bomb Furnace and Gas Thermometer of Geophysical Laboratory.

account of the impossibility of completely eliminating the contaminating effects of evaporated iridium on the thermocouples, even when the latter were quartz inclosed, a bulb of 80 Pt-20 Rh was substituted in the later experiments, it having been shown by Holborn and Austin that rhodium distills from the alloy less readily in nitrogen than does iridium.

The greatest attention was given to the perfecting of experimental methods and details of measurement, such as (1) an absolutely gas-tight bulb of constant volume, secured by having the same gas and pressure outside as within the thermometer bulb, which necessitated the conversion of the furnace into a gas-tight bomb such as shown in Fig. 10; (2) uniform distribution of temperature over the bulb during the measurements, obtained by the use of conveniently spaced and independently controlled heating coils of platinum wire and suitably adjusted diaphragms, as shown in Figs. 11 and 12, the latter being improvements over



Figs. 11, 12. Forms of Bulbs and Methods of Winding and Diaphragming.

the earlier forms of furnace used at the Geophysical Laboratory; (3) the reduction to a minimum of the error due to the dead space in the capillary tube connecting the bulb and manometer, the details of which are shown in Fig. 13; (4) the exact determination of the coefficient of expansion of the bulb; and (5) the equalizing of the temperature of the manometer by air circulation. In the work of Day and Sosman, a return was made to the Barus form of reëntrant bulb (Figs. 11 and 12), and the temperature distribu-

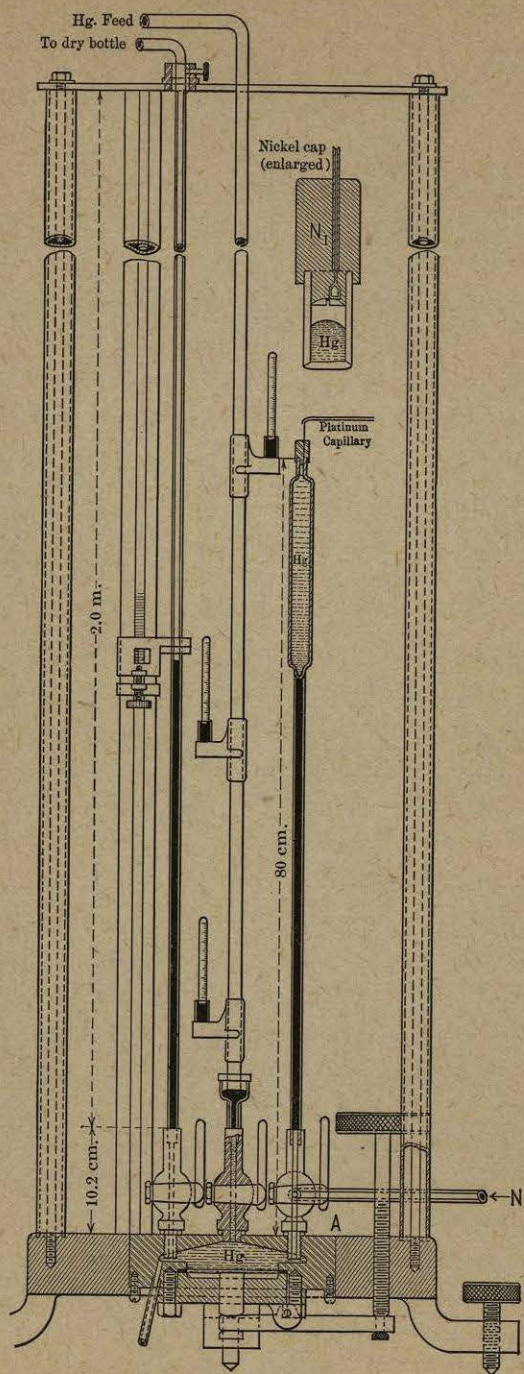


Fig. 13. Manometer of Geophysical Laboratory Thermometer.

tion over the bulb was studied by means of numerous attached platinum wires, which were used differentially, with the bulb itself as one element of a thermocouple, as well as by independent couples. The preliminary values of the silver, gold, and copper fixed points published by Day and Clement were later found by Day and Sosman to be low, mainly on account of incomplete temperature compensation along the bulb, especially at the ends.

Day and Sosman repeated the earlier work to 1100° and then determined several new fixed points, salts as well as metals, in the interval 1100° to 1600° , and consider their final results to be of great accuracy, -0.3° at the zinc and 2° at the palladium point, — after an exhaustive study of some twenty-five possible sources of error. For measurements at 1500° C., they found, for example, the errors in the effect of the dead space $\frac{v}{V}$ reduced to 0.5° , of

temperature integration over the bulb to 1.0° , and of the expansion coefficient of the bulb to 0.2° . It seems safe to say that their results are certain to 1.2° at 400° and to 10° at 1500° C.

It should be noted, however, that this gas thermometer was designed primarily for great accuracy at the highest temperatures, and as used lacks sensibility at the lower temperatures, so that the values obtained for the lower fixed points would seem to have less relative weight than for the higher ones. For example, the results of Day and Sosman, according to Waidner and Burgess, from interpolation with the resistance thermometer from the zinc point, would lead to a value of the sulphur point 1° C. lower than the value directly observed by several experimenters. The gas and resistance thermometer measurements of Holborn and Henning (1911) confirm those of Waidner and Burgess on these lower freezing points. We shall return to this question in the chapter on standardization. There is no doubt that this investigation of Day and Sosman, however, is the best that has yet been made in gas thermometry at the highest temperatures.

Comparison of Results. — It may be of interest at this point to compare some of the characteristic constants and numerical results obtained from the most recent observations, using the

constant-volume nitrogen thermometer at high temperatures. The errors are those assigned by the observers.

SOME CONSTANTS AND RESULTS WITH THE NITROGEN THERMOMETER.

Observers.	Initial Pressure in mm. of Hg.	Bulb Material.	Volume of Bulb.	v/V .	Corr. for v/V at 1100° C.	Correc. for Bulb Expansion at 1100° C.	Uniformity of Temperature over Bulb.	Freezing Points.				
								Zn	Au	Pd		
Holborn and Day	286 276	80 Pt · 20 Ir 90 Pt · 10 Ir	c.c. 208 .0042 196 .0046	20	20	43	3 to 10	{ 419.0 ±0.5	1064.0 ±1.0	}	
Jaquerod and Perrot	195 to 230	Quartz glass	43 .0180									70
Holborn and Valentiner	147 137	80 Pt · 20 Ir Iridium	208 .0042 54 .022	{ 20 90 to 110	20	35	3 to 60	}	}	1575 ±10	}
Day and Sosman	217 to 347	80 Pt · 20 Rh	206 .0015									

Suggestions for Future Experiments. — It is perhaps easier to criticize than execute experiments of precision, but from what has been said above it is evident that there is still need for more work with the gas thermometer before the high-temperature scale is established in an entirely conclusive manner. Thus, the outstanding uncertainty of nearly 0.5° at the sulphur boiling point should be eliminated; and while there is good agreement, better than 5° at 1100° C., a difference of 25° between observers exists at the palladium melting point (1550° to 1575°); and at temperatures to which it now seems hopeless to extend the gas scale directly, this range of uncertainty increases, becoming about 100° at 3000° C., or at the melting point of tungsten.

Methods. — The constant-volume method has been preferred by almost all experimenters who have worked at high temperatures, and the results by this method also have smaller corrections to reduce to the thermodynamic scale. For the lower range of temperatures at least, in view of the outstanding discrepancies, it would be well to adopt the same instrument for use both at constant pressure and constant volume. To as high tempera-

tures as possible, the bulb should be immersed in stirred liquid baths to insure uniformity of temperature; and in this range of temperatures, or to perhaps 900°, the transfer of the gas scale can probably be made with the greatest accuracy by means of platinum-resistance thermometers, the wires of which can be made to integrate very exactly the bulb temperature.* The volumetric method has not been used in any recent work, although it appears to possess the smallest instrumental corrections. It labors under the disadvantage of having an uncertain thermodynamic correction, but this largely disappears at high temperatures, where the outstanding uncertainties largely exceed this small correction. It would, therefore, be worth while carrying out new experiments by this method, especially at very high temperatures. The method of Crafts and Meier (p. 83) is also worthy of further study at high temperatures. The work of Day and Sosman shows that, for the constant-volume thermometer, the deformation of the bulb may be eliminated, and the error due to the dead space reduced to an almost negligible amount. Their work also shows the importance of an exact determination of the coefficient of expansion of the bulb and an exact adjustment of temperature over it by the use of properly designed electric furnaces. The uncertainty in the temperature of the manometric parts of the apparatus gives rise to an appreciable error which may be eliminated in future work by water-jacketing.

The Bulb. — All recent work has shown the superiority of the metal bulb when its coefficient of expansion is carefully determined. The alloy 80 Pt · 20 Rh is the material that has been used so far which best suits all the requirements for temperatures to 1600° C., namely, rigidity, impermeability, regular expansion, and small contaminations of the auxiliary temperature apparatus. The best form appears to be cylindrical with a reëntrant tube. It may be possible to find refractory earths which are sufficiently impermeable to use with some modification of the Crafts and

* Both of these improvements and others have been introduced by Holborn and Henning to 450° C. since the above was written.

Meier method at very high temperatures; or possibly metallic tungsten or one of its alloys may be adopted for use in a suitable atmosphere for pushing the gas scale to the highest limits. In all cases it is desirable to have the volume of the bulb as great as possible consistent with uniform temperature distribution. To 500°, there should be no difficulty in using a 500 c.c. bulb.

The Gas. — Nitrogen has proved satisfactory in every respect, and this gas will probably be continued in use, although there would be some theoretical advantage, at least for the higher temperatures, in substituting one of the monatomic inert gases, such as argon or helium.

It is questionable whether it is worth while to attempt to extend the use of the gas thermometer above 1600° C., as the constants of the laws of radiation can be exactly determined in this range, and the radiation laws are eminently suited for extrapolation, as they give the thermodynamic scale directly.

The Manometer. — It would be well to eliminate the somewhat troublesome and uncertain reference to a variable pressure, that of the atmosphere, by the entire elimination of the barometer. This can be done, whatever the type of gas thermometer used, by evacuating to zero pressure the space above the manometer column and sealing off the manometer tube provided with a suitable globe or bulb at the top.* Variations in the temperature of the mercury columns of the manometer may be completely eliminated by water-jacketing. The errors of the manometer are then easily made negligible compared with those of expansion of the bulb, the temperature distribution over it, and the transfer to the comparison thermometer.

In general, it may be stated that it is not worth while to carry out any further gas thermometer experiments unless the utmost precautions are taken to assure the highest accuracy possible with modern appliances.

Industrial Air Pyrometers. — There have been attempts to construct air thermometers suitable for industrial usage, the argument sometimes being advanced that a gas pyrometer is

* See note, p. 81.

per se better than any other. As we have seen, however, there is probably no physical instrument which is more difficult to employ satisfactorily, and any seeming gain in making direct use of an air thermometer for industrial use is wholly illusory. Other evident objections are fragility, uncertain correction due to the dead space, and the development of small and often unperceived leaks. Furthermore, an empirical calibration is necessary, so that such an instrument does not carry the gas scale about with itself.

Among the instruments that have been considerably used is Wiborgh's air pyrometer, shown in Fig. 14. A lens-shaped

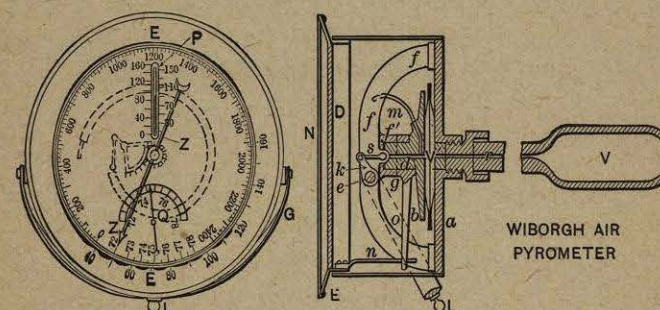


Fig. 14.

reservoir *V*' is open to the air before an observation is taken, but when a temperature is to be read this lens is closed to the outer air and collapsed by a lever *L*, thus adding a definite mass of air to the bulb *V* of the thermometer; the resulting pressure is transmitted to a dial as in an aneroid barometer; provision is made for automatically correcting for variations in the pressure and temperature of the atmosphere. The Bristol Company have also made industrial forms of gas pyrometer.

Indirect Processes. — We shall place in this list various experiments in which the laws of the expansion of gases have been used only in an indirect way, or have been extended to vapors.

Method of Crafts and Meier. — It is a variation of the method of H. Sainte-Claire-Deville and Troost, consisting in removing the gas by means of a vacuum. Crafts and Meier displaced the

gas of the pyrometer by carbonic acid or hydrochloric acid, gases easily absorbable by suitable reagents. Hydrochloric acid is the more convenient, for its absorption by water is immediate; but there is to be feared at high temperatures its action on the air with formation of chlorine; it is preferable to employ nitrogen in place of air.

The apparatus (Fig. 15) consists of a porcelain bulb, whose inlet is large enough to let pass the entrance tube of the gas, which reaches to the bottom of the bulb. This arrangement increases considerably the influence of the dead space and consequently diminishes the precision of the determinations.

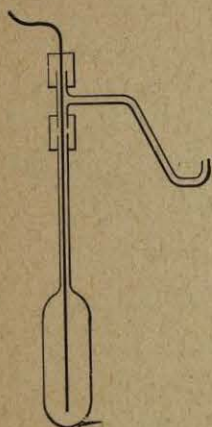


Fig. 15. Method of Crafts and Meier.

This method is especially convenient for observations on the densities of vapors which are made by the same apparatus; it then allows of having an approximate idea of the temperatures at which the experiments are made.

Crafts and Meier have in this way determined the variations in density of iodine vapor as a function of the temperature.

Regnault had previously proposed a similar method, without, however, making use of it.

1. One fills with hydrogen an iron vessel brought to the temperature that one desires to measure, and the hydrogen is driven out by a current of air; at the outlet of the metallic reservoir the hydrogen passes over a length of red-hot copper, and the water formed is absorbed in tubes of sulphuric acid in pumice stone and weighed. This method, very complicated, is bad on account of the permeability of the iron at high temperatures.

At the same time, he proposed the following method:

2. An iron bottle containing mercury is taken; the vessel, being incompletely closed, is heated to the desired temperature and then allowed to cool, and the remaining mercury is weighed.

This method is also defective on account of the permeability of iron at high temperatures; the hydrogen of the furnace gases can penetrate to the inside of the recipient and drive out an equivalent quantity of mercury vapor.

Methods of H. Sainte-Claire-Deville.—1. This savant tried in the first place to measure temperature by a process analogous to that of Dumas' determination of vapor densities. He took a porcelain bulb full of air, and heated it in the inclosure whose temperature was wanted, and sealed it off by the oxyhydrogen flame. He measured the air remaining by opening the bulb under water and weighing the water that entered, or else he determined merely the loss in weight of the bulb before and after heating. Observations taken on the boiling point of cadmium gave 860° .

2. In a second method, which has the advantage of replacing the air by a very heavy vapor, Deville returned to the idea of Regnault, consisting in utilizing the vapor of mercury; but he ran against a practical difficulty. He had replaced the permeable iron recipients by porcelain recipients; the mercury condensed in the neck of the pyrometer and fell back in cold drops which caused the bulb to break.

For this reason he abandoned mercury and replaced it with iodine; the return of a cold liquid was completely obviated by reason of the nearness of the boiling point of this substance (175°) and its fusing point (113°). A large number of observations were made by this method; the boiling point of zinc, for example, was found to be equal to 1039° .

This method is quite faulty, as the iodine does not obey the laws of Mariotte and Gay-Lussac. The vapor density of this substance decreases with rise of temperature, this effect being attributed to a doubling of the iodine molecule. This fact was established by Crafts and Meier and confirmed by Troost.

Method of D. Berthelot.—All the preceding methods are limited by the difficulty of realizing solid envelopes resisting temperatures higher than 1600° . D. Berthelot has devised a method which, at least in theory, may be applied to any temperatures, however high, because there is no envelope for the gas, or

at least no envelope at the same temperature. It is based on the variation of the index of refraction of gaseous mass heated at constant pressure; the velocity of light depends upon the chemical nature and the density of this medium, but is independent of its physical state. A gas, a liquid, or a solid of the same chemical nature produces a retardation of the light dependent only upon the quantity of matter traversed; this law, sensibly true for any bodies whatever, should be rigorously exact for substances approaching the condition of perfect gases. This retardation is measured by the displacement of interference fringes between two beams of parallel light, the one passing through the cold gas, the other through the hot gas. In reality, Berthelot employs a null method; he annuls the displacement of the fringes in changing at constant temperature the pressure of the cold gas until its density is equal to that of the gas in the warm arm which is at constant pressure.

There is a difficulty arising from the necessity of separating the light into two parallel beams, then reuniting them without imparting a difference of phase which renders the fringes invisible with white light. This is done in the following way (see Fig. 16):

A beam of light ab falls on a mirror MM' , which breaks it up into two parallel beams, bf and cd ; in order to separate the beams so as to be able to place apparatus conveniently with respect to them, a prism P gives to the beam bf the direction gh ; one can thus secure a separation of 92 mm. A second prism P_1 brings the beam cd into lm , and after reflection from a second mirror, $M_1M'_1$, the fringes are observed in a telescope focused for parallel rays. The tubes containing the gases are placed at T and T_1 .

It is evidently necessary that the prisms P and P_1 be perfectly made. A preliminary adjustment is made with yellow light, then it is perfected with white light.

The tube at variable pressure is closed by two pieces of plate glass, as is also the warm tube; these four plates should be absolutely alike. The warm tube is heated by a vapor bath at low temperatures, by an electric current passing through a spiral at high temperatures.

But there is a difficulty in that in the warm tube there exists a region of variable temperature between the warm zone and the cold atmosphere.

To eliminate the influence of this variable zone, there are inside the warm tube two tubes containing running cold water, whose distance apart can be changed; it is assumed that the variable region remains the same, and that distance between the two tubes gives the warm column actually utilized. It follows that

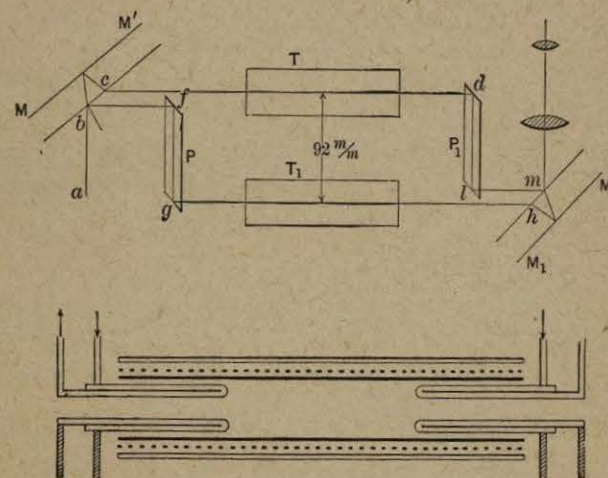


Fig. 16. D. Berthelot's Method.

the comparative lengths of the warm column and of the cold column (this latter remaining constant) are not the same; the formula to be used will be somewhat more complicated.

n being the index of refraction of a gas and d its density, we have

$$n - 1 = kd.$$

In the constant-pressure tube

$$\frac{d_1}{d_0} = \frac{p}{p_0}.$$

To obtain the invariability of the fringes, it is necessary that

$$(n_1 - n_0) L = (n' - n_0) l,$$

L being the length of the cold tube, and l the displacement of the warm tube.

$$k(d_1 - d_0)L = k(d' - d_0)l,$$

$$L\left(\frac{d_1}{d_0} - 1\right) = l\left(\frac{d'}{d_0} - 1\right),$$

$$L\left(\frac{p}{p_0} - 1\right) = l\left(\frac{T_0}{T} - 1\right),$$

an expression which gives a relation between the pressures and the temperatures.

This method, employed for the control of the boiling points, has given the following results:

	Pressure.	Temperature observed.	Temperature calculated.
Alcohol.....	741.5 mm.	77.69°	77.64°
Water.....	740.1	99.2	99.20
Water.....	761.04	100.01	100.01
Aniline.....	746.48	183.62	183.54
Aniline.....	760.91	184.5	184.28

Berthelot has standardized by the same method thermocouples which he used to determine the fusing points of silver and gold, and the boiling points of zinc and cadmium:

Silver, freezing	962° C.
Gold, freezing	1064
Zinc, boiling	920
Cadmium, boiling	778

The numbers found are nearly identical with those which result from the best determinations made by other methods.

We shall discuss further the determinations of fixed points in pyrometry in Chapter XI.

CHAPTER III.

CALORIMETRIC PYROMETRY.

Principle. — A mass m of a body, brought to a temperature T , is dropped into a calorimeter containing water at a temperature t_0 . Let t_1 be the final temperature of water and substance. M being the water equivalent of the substances in contact (water, calorimetric vessel, thermometer, etc.) which are raised from t_0 to t_1 , L_t^T the heat required to warm unit mass of the body from t_1 to T , we have

$$L_t^T \times m = M(t_1 - t_0).$$

Taking as origin of temperatures the zero of the centigrade thermometer, the heat required to warm unit mass of the body to the temperature T will be

$$L_t^T = L_{t_1}^T + L_0^t.$$

The quantity L_0^t is easy to calculate, because the specific heats at low temperatures are sufficiently well known:

$$L_0^t = ct_1.$$

The expression for the total heat becomes

$$L_0^T = \frac{M(t_1 - t_0)}{m} + ct_1.$$

t_1 and t_0 are the temperatures given by the direct readings of the thermometer.

The value of the second member is thus wholly known, and consequently that of the first member which is equal to it. If previous experiments have made known the value of the total heat L_0^T for different temperatures, one may from the knowledge of L_0^T determine the value of T . It will be sufficient to trace a curve on a large scale whose ordinates are temperatures, and