Fundamental Laws of Pyrometry

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THE word temperature has both a colloquial and a technical use. For everyday purposes of abusing the weather man, no very exact definition is necessary, but for the purpose of giving a simple summary of the physical laws that form the basis of practical pyrometry, something more precise is required. Beginning, therefore, with the common concept of "hotness" and "coldness," we must agree on a method of measuring differences in "hotness," on the unit to be used, and on the point from which measurements are to be taken. We shall then have a definite "scale of temperature," which can be used in all methods of pyrometry. But, as in many similar cases, it is much easier to define or describe something than it is to make practical application and use of the definition; so that much of our attention will be taken up with practical methods of realizing or applying the scale agreed upon.

It was early observed that changes in temperature produced large and easily measurable changes in gases, which may be most simply separated into changes in volume (expansion and contraction) under conditions of constant pressure, and changes in pressure under conditions of constant volume. These changes are much the same in magnitude for the common gases oxygen, nitrogen, and hydrogen and also for the rarer helium and argon. This relative uniformity in behavior led to the suggestion of "the gas thermometer" and "the gas scale" as the basis for all temperature measurements. However, as methods were refined, differences appeared between different gases and different ways of using gases, so that Lord Kelvin introduced his more fundamental notion of the "absolute thermodynamic scale" of temperature, which he defined as follows: Given two bodies, say two tanks of water, at different temperatures to determine these temperatures on the "absolute thermodynamic," or Kelvin, scale, operate a thermal engine between these two temperatures, letting it take in heat from the hot body and give out heat to the cold, which therefore corresponds to the boiler and the condenser of a steam engine. The engine we may imagine as a cylinder and piston inclosing a gas and operating with the well-known Carnot or isothermal-

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adiabatic cycle. We must imagine that the mechanical losses of energy due to friction and the thermal losses due to radiation convection and conduction have been determined and allowed for. We must also take care to run the engine slowly so that only an inappreciable difference or temperature exists between it and the hot and cold bodies when it is absorbing or giving out heat to them. Such an engine with the corrections applied as indicated, is called perfect because it is of maximum efficiency. If it is found that a quantity of heat H_1 is taken in at the high temperature and H_2 is given out at the low temperature we have

$$\frac{T_1}{T_2} = \frac{H_1}{H_2} \tag{1}$$

where T_1 and T_2 are the two temperatures in question on the K. scale. From this, $\frac{H_1 - H_2}{H_1} = \frac{T_1 - T_2}{T_1}$; and from this, the idea of an absolute zero is suggested as that temperature for which $H_2 = 0$ for then $T_2 = 0$. To complete the definition of the K. scale, it is only necessary to agree that the interval between the two most reliable fixed points, namely, the temperatures of melting ice and of boiling water, shall contain a certain number of degrees, 100 if we are working with the centigrade K. scale. This condition is expressed by $\frac{H_{100} - H_0}{H_0} = \frac{100}{T_0}$. (2)

and combining this with the general equation 1 we have

$$T_1 = \frac{H_1\, 100}{H_{100} - H_0} \tag{3}$$

which gives any temperature on the centigrade K. scale in terms of the quantities of heat taken in and rejected. How can this scale be realized and used in practice? Obviously not by means of any ideal engine as outlined above. There are, however, two distinct ways in which it may be done, both depending on theoretical deductions from the second law of thermodynamics, to which the K. scale is very intimately related.

First, by applying the second law expressions may be derived (Callendar-Berthelot-Buckingham) in which the pressure of a gas (volume constant) is given in terms of its temperature on the K. scale and of certain physical characteristics of the gas. By a different treatment of the problem, analogous expressions may be obtained giving the volume of gas (pressure constant) in terms of its K. temperature and physical properties. These expressions, in the form given by Buckingham, are:

A (volume constant $= v$)

$$\frac{p}{\theta} - \frac{p_0}{\theta} = -\int_{\theta_o}^{\theta} \frac{1}{\theta_2}\left[\frac{\delta}{\delta v}(pv) + \mu c_p \frac{\delta p}{\delta v}\right]_{\theta} d\theta$$

B (pressure constant $= p$)

$$\frac{v}{\theta} - \frac{v_0}{\theta_0} = \int_{\theta_o}^{\theta} \frac{\mu c_p d\theta}{\theta^2}$$

In these expressions

θ = temperature on K. scale;
θ_0 = initial temperature (say ice point) on K. scale;
c_p = specific heat under constant pressure;
$\mu \equiv \frac{\Delta t}{\Delta p}$ = under Joule-Kelvin conditions; that is, when expanded adiabatically through a porous plug;
p_0 = pressure at θ_0 and v;
v_0 = volume at θ_0 and p.

The physical properties involved, namely, the specific heat at constant pressure, the pressure-volume relations of the gas, the Joule-Kelvin coefficient or rate of change of temperature with pressure when expanded through a porous plug, should be known throughout the temperature interval that is to be determined for the volumes and pressures to be used, in order to evaluate these expressions. The initial volume or pressure, as the case may be, must also be known with especial accuracy. If these quantities are known for a given gas, the observation of the change in volume of this gas at constant pressure (v_0 to v) will enable us to compute the K. temperature at which the volume was observed to be v; and, similarly, if the pressure change is observed at constant volume, the temperature can be computed from the pressure change $p - p_0$. Unfortunately the experimental knowledge of c_p, μ, and the pv relation is very incomplete, being limited to a short temperature range, and great ingenuity and care are needed in handling and extrapolating the data to get the most reliable results.

The results of the thermodynamic computations just referred to are usually expressed in a somewhat different way by introducing various "gas scales" of temperature. For example, if we are operating with nitrogen, we may conveniently consider two nitrogen scales, one defined by

$$\left(\frac{T}{T_0}\right)_p = \left(\frac{v}{v_0}\right)_p$$

if the gas is maintained at constant pressure during the measurements, and the other by

$$\left(\frac{T}{T_0}\right)_v = \left(\frac{p}{p_0}\right)_v$$

if the volume is maintained constant. Every other gas would have its own two scales. Hence the previous fundamental equations may be described as giving the differences between any given gas scale and the K. scale, and these differences or corrections may be tabulated and applied to reduce gas-thermometer observations to the K. scale. These corrections have only been computed up to 1200° C. and are, in general, somewhat more than twice as large for the constant-pressure gas thermometer as for the constant-volume, but there are other compensating advantages in favor of the former.

Confining our attention to nitrogen as the most useful gas for high-temperature measurements, it may be briefly said that the correction to T_p is about 1.70° at 1000° C. and 2.15° at 1200° C., while it is only 0.96° for T_v at 1200° C. These errors are of significance when it comes to determining, by gas thermometry, the fundamental fixed points of the high-temperature scale, though too small to be considered in ordinary work. Above 1200° C. they are undoubtedly larger, but unfortunately data are not yet available for their computation.

There is one other fundamental matter that must be considered, and that is the value of the ice point on the Kelvin scale. This may be calculated from the same basic equations already given. The computations of Buckingham and Berthelot agree very well in giving $\theta_o = 273.13$; that is, for high-temperature work, the ice point may be taken as flat 273° on the Kelvin scale.

The second field in which it has been possible to connect practical methods of pyrometry with the Kelvin scale is the field of radiation. The fundamental facts of radiation are that it is an effect of one body on another that may take place across a vacuous space, and that it is closely related to the "hotness" of bodies and tends to equalize their temperature. Without attempting to distinguish between what we know and what we merely say, radiation may be described in the usual way as an electromagnetic disturbance sent off from bodies, which may be analyzed by spectroscopes of various types, and shown to contain waves of various lengths, of which those having lengths from 0.0003900 mm. to 0.00076 mm. directly affect the eye and are called "light" waves; waves longer than these are called "infra-red," those shorter "ultra-violet," and those still shorter x-rays. The entire range of waves is called a complete spectrum, and various radiating bodies emit, according to their nature and condition, various characteristic spectra; that is, different groupings of wave-lengths with different distributions of energy among them. The radiation from solids and liquids increases very rapidly with rising temperature, and their spectra are similar, and, in general, continuous; that is, there are no "gaps" if arranged according to wave-lengths. But the total energy radiated and its distribution among the wave-lengths is very different for different substances at the same temperature. At present, it is not possible, theoretically, to express the radiating power of a substance in terms of its other physical properties and temperature, but there is a special form of radiator which can be successfully dealt with both theoretically and experimentally, namely, the perfect or complete radiator, or black body. The original idea of this was due to Kirchhoff, and the experimental realization to Lummer and Pringsheim and many later workers. Given an inclosure with opaque walls at a uniform and constant temperature, the fundamental theorem is that the radiation inside the inclosure will be, both as to intensity and energy distribution in the spectrum, entirely independent of the material of the walls and dependent only on its temperature. Since, in general, bodies that are good radiators are poor inflectors and good absorbers, and vice versa, it is quite reasonable to conceive of the radiation, so to speak, accumulating in a closed space until an equilibrium condition is reached dependent only on the temperature. For immediately contiguous to one part of the wall the equilibrium condition might be maintained by strong absorption and correspondingly strong emission, while at another point the same condition might result from strong reflection and weak emission. Nevertheless, of the so-called proofs of this theorem that have been given by Kirchhoff, Pringsheim, and others, none is entirely satisfactory, and the most convincing evidence that it is possible to produce radiation independent of the qualities of special kinds of matter and dependent only on temperature, is furnished by experiment.

The first form of perfect radiator used for experimental purposes consisted of a hollow vessel with walls as uniformly heated as possible and provided with a small aperture through which radiation from the inside passed out to be examined spectroscopically and otherwise. If the area of the aperture is small, compared to the interior radiating walls, the condition of equilibrium, which must exist in order that the interior radiation should be complete, will be very little disturbed and the departure from equilibrium, and hence from completeness, may be made as small as desired by a proper choice of proportions. The experimental proof referred to consists in the fact that whereas radiation observations on free metal or other surfaces are very difficult to repeat, that is to say, the radiation from free surfaces is very much subject to changes in surface conditions, all observations with inclosures are much more uniform, and it is possible to arrange matters so that the emergent radiation is observably independent of interior surface conditions. Once we accept this as possible, eye observations of the interior furnish a most sensitive test as to whether the conditions of perfect radiation really exist in any given case. There are, of course, experimental difficulties in the way of producing sufficiently uniform temperature conditions, but these need not be discussed here.

Granted then that there is such a thing as a perfect radiator, we must consider Boltzmann's ingenious extension of the theory. First, however, it must be recalled that Bartolli had shown that in order to be consistent with the second law of thermodynamics, radiation must exert a pressure on any surface on which it impinges, the pressure being twice as great if the surface is perfectly reflecting as if it is perfectly absorbing—being, in fact, proportional to the amount of radiant energy per unit volume in front of the surface. Maxwell drew the same conclusion from his electromagnetic theory; and later Nicholls and Hull and Lebedew experimentally verified these theoretical deductions. On this basis, Boltzmann conceived of a "radiation engine," which might be a cylinder with reflecting walls and piston and a radiating base, in which radiation could be "expanded," so to speak, and allowed to do mechanical work through the pressure on the piston. By applying to this engine the second law, Boltzmann showed that the total radiation from a perfect radiator must vary in amount as the fourth power of the temperature of the radiator, measured on the Kelvin scale, that is

$$E = \sigma\theta^4$$

where E is total radiant energy, σ is a constant, and θ, as before, is Kelvin temperature.

This theoretical deduction is quite simple, is no more questionable than the direct thermo-mechanical deductions from the second law, such as are used in the theory of gas thermometry, and constitutes the second experimental hold on the Kelvin scale. It is known as the Stefan-Boltzmann law because Stefan had some years earlier deduced it from a discussion of bad observations on imperfect radiators, for which it does not hold—a case in which two negatives have apparently been equivalent to an affirmative, so to speak.

The next advance in radiation theory was by Wien, the radiation engine still being the basis; but the arguments are not quite so simple and free from objection as in Boltzmann's case. The result is Wien's displacement law, of which the usual statement

$$\theta\lambda_{\text{max.}} = \text{constant}$$

is a special case. Here θ is the Kelvin temperature at which a perfect radiator would have the maximum of its spectral energy curve at the wave-length λ_{max}. Wien proceeded further and, by still less satisfactory methods, deduced the equation of spectral energy distribution known as Wien's law

$$E_\lambda = c_1\lambda^{-5}e^{\frac{c_2}{\lambda\theta}}$$

wherein

E_λ = ordinate at wave-length λ of spectral energy distribution curve;
θ = corresponding Kelvin temperature;
c_1 and c_2 = constants.

Further work of Planck led to the well-known expression

$$E_\lambda = c_1\lambda^{-5}\frac{1}{e^{\frac{c_2}{\lambda\theta}} - 1}$$

which for small values of $\lambda\theta$, that is, short wave-lengths and not too high temperatures, becomes practically identical with Wien's law. While Planck's, and within the limits just mentioned, Wien's distribution formulas have been experimentally verified with a fair degree of accuracy and for temperatures below about 1500° C., unfortunately their theoretical deduction cannot be regarded as sound. They do not, therefore, furnish another independent connection between the Kelvin scale and observable quantities, but must be regarded as empirical equations whose accuracy has been demonstrated within limits. We must consider these three radiation formulas of Stefan-Boltzmann (total), Wien (displacement), and Planck (distribution) somewhat more in detail in their bearing on pyrometry. The first of these gives us a means, independent of corrected gas thermometry, of completely evaluating the Kelvin scale, beginning merely with the ice and steam points and the assumption of 100° between the two. For this purpose it is theoretically much simpler than gas thermometry, but whether it would work out to be of comparable accuracy, especially at low temperatures, cannot be said as no one has ever attempted to apply it in this comprehensible way. For high temperatures, more particularly for extreme high temperatures, the case is clearer. The limit of successful gas thermometry is at present the palladium point (1549° C.), and above this region experimental difficulties seem to be increasing at an appalling rate. On the other hand, the difficulties in applying the fourth-power law in a sense diminish with increasing temperatures because "stray" radiation in general becomes proportionately less compared to that which is to be measured. While beginnings have been made in the application of the Stefan-Boltzmann law to accurate pyrometry, the possibilities have not been in any sense exhausted. The law should be applied to determine the gold melting point (1062.6° C.) and especially the palladium melting point, as a check upon the determination by gas thermometry, and there is room for more work in determining other standard fixed points in the range beyond 1600° C., in which region the total radiation method seems to be about the only hopeful one. It should perhaps be pointed out that in using this method no absolute measurements of radiant energy are needed—one deals entirely with energy ratios, and enough work has been done to prove that very considerable accuracy is possible.

Wien's displacement law $\theta = \frac{\text{const.}}{\lambda_{\text{max.}}}$ has also been used in pyrometric work, but the disadvantages are several. In the first place the wave-length corresponding to maximum energy is difficult to determine, and as the inverse wave-length varies only as the first power of the temperature the shift is not sensitive to temperature changes, particularly at high temperatures. We may therefore dismiss this as of little value either for fundamental or practical measurements.

If we confine our attention to a single wave-length, or rather a narrow band of wave-lengths in the spectrum, the laws of Planck and Wien give the rate of variation of the energy in this band as a function of temperature, a very useful indicator of temperature change. Within the range wherein Wien's law is valid, it serves most conveniently to express this variation of partial radiation and may be written in this form

$$\log E_\lambda = \log \frac{c_1}{\lambda^5} - \frac{c_2}{\lambda\theta}$$

This equation which must be looked upon as empirical and which has been verified with a high degree of accuracy for temperatures up to 1600° C., and less accurately from there up to 3000° C., is the basis of all optical pyrometry. As such its importance warrants still more careful comparison between it and the Stefan-Boltzmann law up to the highest possible temperatures. For while the Stefan-Boltzmann equation gives our best, if not our only sound, connection with the Kelvin scale and while it is easy to work very accurately with this equation under laboratory conditions, the equation is subject to certain troublesome errors (notably that due to absorption by vapors or smoke and to windows and reflectors etc. that may intervene between the radiator and indicating instruments) which are difficult to eliminate in practice. Similar errors affect optical pyrometers, but perhaps not quite so seriously, and there is a certain safety as regards the detection of trouble in actually looking through the instrument into the space whose temperature is being determined. However, excellent instruments have been devised according to each principle, and the only object here is to point out that one may be regarded as fundamental in terms of which the other should be calibrated.

In all this discussion of radiation pyrometry it has been presupposed that the object whose temperature was to be measured was a perfect radiator, as the laws that have been used apply only to such a case. For fundamental measurements this is, of course, essential; and for practical measurements it is usually possible and always desirable, for a perfect radiator is the most definite and easily reproducible. A tube thrust into a furnace, a narrow deep hole bored into a large hot mass—a crack in such a mass—can usually be arranged so that they will approximate sufficiently to the "uniformly heated enclosure with small aperture" that is desired, especially if the surface actually observed through the aperture is itself a good radiator and a poor reflector. There are other ways of approximating a perfect radiator by using multiple reflection, but a discussion of these various methods is not germane to the present subject. It should be pointed out, however, that for purposes of practical pyrometry, ordinary non-perfect radiators may, and sometimes have, to be used; and if the radiation laws are applied directly in such cases, true temperatures will not be obtained, but instead lower values which are commonly referred to as "black body (or perfect radiator) temperatures," meaning thereby the temperatures at which a "perfect radiator" or "black body" would radiate as the real body is observed to do. If the real surface is sufficiently definite and reproducible, known corrections in some cases may be applied to reduce the observations to Kelvin temperatures, or it may be that black-body temperatures will suffice.

There are two methods of temperature measurement still to be touched upon—resistance and thermoelectric pyrometry—but in neither of these is it possible to deduce any theoretical connection between the observed quantities and the Kelvin scale. They are entirely empirical and all the instruments must be calibrated by comparison directly or indirectly with gas or radiation work. There are certain relations, such as Callendar's parabolic formula connecting the resistance of platinum with temperature, and various equations giving thermoelectromotive force as a function of temperature that are extremely useful and hold with great accuracy within certain temperature limits, but which cannot be called fundamental laws. They may, therefore, be left without further discussion, as most valuable methods both in the laboratory and in practice, but not contributing anything to our grasp of the fundamental temperature scale. Even as methods, their range is much more limited than the radiation processes.

This survey of the physical basis of pyrometry is of necessity superficial, and it may seem at first thought that the underlying idea of working to an "absolute scale" is unnecessary, any single arbitrary scale being, for all practical purposes, just as good. This is quite true, provided a single arbitrary scale could be agreed upon and accurately reproduced. But the general experience in such matters has been that the more fundamental and absolute the nature of any scale of measurement, the more accurately it can be maintained and reproduced. In other words, the absolute scale whose development has been described in this paper is of importance in pyrometry, not because of its "absoluteness" but because of its permanence and ease of reproduction.