platinum reservoir, for which *f* may be taken as 0∙000025 nearly, the correction amounts to -0∙0625° at 50° C., to 3∙83° at 445°C., and to 22∙5° at 1000° C.

The value of the fundamental coefficient *f*. can be determined with much greater accuracy than the coefficient over any other range of temperature. The most satisfactory method is to use the bulb itself as a mercury weight thermometer, and deduce the cubical expansion of the glass from the absolute expansion of mercury as determined by Regnault. Unfortunately the reductions of Regnault’s observations by different calculators differ considerably even for the fundamental interval. The values of the fundamental coefficient range from ∙00018153 Regnault, and ∙00018210 Broch, to ∙00018253 Wüllner. The extreme difference represents an un­certainty of about 4 per cent. (1 in 25) in the expansion of the glass. This uncertainty is about 100 times as great as the prob­able error of the weight thermometer observations. But the expansion is even less certain beyond the limits of the fundamental interval. Another method of determining the expansion of the bulb is to observe the linear expansion of a tube or rod of the same material, and deduce the cubical expansion on the assumption that the expansion is isotropic. It is probable that the uncertainty involved in this assumption is greater in the case of glass or porce­lain bulbs, on account of the difficulty of perfect annealing, than in the case of metallic bulbs.

Except for small ranges of temperature, the assumption of a constant coefficient of expansion is not sufficiently exact. It is therefore usual to assume that the coefficient is a linear function of the temperature, so that the whole expansion from 0° C. may be expressed in the form *d*V=*t*(*a*+*bt*)V0, in which case the funda­mental coefficient *f*=*a*+100*b*. Making this substitution in the formula already given, we obtain the whole correction

*dt=(f+bT)t(t-100)* (18)

It will be observed that the term involving *b* becomes of consider­able importance at high temperatures. Unfortunately, it cannot be determined with the same accuracy as *f*, because the conditions of observation at the fixed points arc much more perfect than at other temperatures. Provided that the range of the observations for the determination of the expansion is co-extensive with the range of the temperature measurements for which the correction is required, the uncertainty of the correction will not greatly exceed that of the expansion observed at any point of the range. It is not unusual, however, to deduce the values of *b* and *f* from observa­tions confined to the range 0° to 100° C., in which case an error of 1 per cent., in the observed expansion at 50° C., would mean an error of 60 per cent. at 445°, or of 360 per cent. at 1000° C. (Calendar, *Phil. Mag.* December 1899). Moreover, it by no means follows that the average value of *b* between 0° and 100° C. should be the same as at higher or lower temperatures. The method of extra­polation would therefore probably lead to erroneous results in many cases, even if the value could be determined with absolute pre­cision over the fundamental interval. It is probable that this expansion correction, which cannot be reduced or eliminated like many of the other corrections which have been mentioned, is the chief source of uncertainty in the realization of the absolute scale of temperature at the present time. The uncertainty is of the order of one part in five or ten thousand on the fundamental interval, but may reach 0·5° at 500° C., and 2° or 3° at 1000° C.

18. *Thermodynamical Correction.*—Of greater theoretical interest, but of less practical importance on account of its smallness, is the reduction of the scale of the gas thermometer to the thermo­dynamical scale. The deviations of a gas from the ideal equation *pv* = R0 may be tested by a variety of different methods, which should be employed in combination to determine the form of the characteristic equation. The principal methods by which the prob­lem has been attacked are the following :—

(l) By the comparison of gas thermometers filled with different gases or with the same gas at different pressures (employing both gravimetric and manometric methods) the differences in their indications are observed through as wide a range of temperature as possible. Regnault, employing this method, found that the differences in the scales of the permanent gases were so small as to be beyond the limits of accuracy of his observations. Applying greater refinements of measurement, Chappuis and others have succeeded in measuring small differences, which have an important bearing on the type of the characteristic equation. They show, for instance, that the equation of van der Waals, according to which all manometric gas thermometers should agree exactly in their indications, requires modification to enable it to represent the behaviour of gases even at moderate pressures.

. (2) By measuring the pressure and expansion coefficients of different gases between 0° and 100° C. the values of the funda­mental zero (the reciprocal of the coefficient of expansion or pres­sure) for each gas under different conditions may be observed and compared. The evidence goes to show that the values of the fundamental zero for all gases tend to the same limit, namely, the absolute zero, when the pressures are indefinitely reduced. The type of characteristic equation adopted must be capable of repre­senting the variations of these coefficients.

(3) By observing the variations of the product *pv* with pressure at constant temperature the deviations of different gases from Boyle’s law are determined. Experiment shows that the rate of change of the product *pv* with increase of pressure, namely *d(pv)∣dp,*is very nearly constant for moderate pressures such as those em­ployed in gas thermometry. This implies that the characteristic equation must be of the type

*v*=F(*0*)/*p*+*f*(*0*) (19)

in which F(*0*) and *f*(0) are functions of the temperature only to a first approximation at moderate pressures. The function F(0), representing the limiting value of *pv* at zero pressure, appears to be simply proportional to the absolute temperature for all gases. The function *f*(0), representing the defect of volume from the ideal volume, is the slope of the tangent at *p*=o to the isothermal of 0 on the *pv, p* diagram, and is sometimes called the “ angular coeffi­cient.” It appears to be of the form *b-c,* in which *b* is a small constant quantity, the “ co-volume,” of the same order of magni­tude as the volume of the liquid, and *c* depends on the cohesion or co-aggregation of the molecules, and diminishes for all gases continuously and indefinitely with rise of temperature. This method of investigation has been very widely adopted, especially at high pressures, but is open to the objection that the quantity *b-c* is a very small fraction of the ideal volume in the case of the permanent gases at moderate pressures, and its limiting value at *p=o* is therefore difficult to determine accurately.

(4) By observing the cooling effect *dθ∣dp,* or the ratio of the fall of temperature to the fall of pressure under conditions of con­stant total heat, when a gas flows steadily through a porous plug, it is possible to determine the variation of the total heat with pressure from the relation

S*dθ∣dp=θdv*/*dθ-v*  (20)

(See Thermodynamics, § 10, equation 15.) This method has the advantage of directly measuring the deviations from the ideal state, since *0dv∣d0=v* for an ideal gas, and the cooling effect vanishes. But the method is difficult to carry out, and has seldom been applied. Taken in conjunction with method (3), the observation of the cooling effect at different temperatures affords most valuable evidence with regard to the variation of the defect of volume *c — b* from the ideal state. The formula assumed to represent the variations of *c* with temperature must be such as to satisfy both the observations on the compressibility and those on the cooling effect. It is possible, for instance, to choose the constants in van der Waals’s formula to satisfy either (3) or (4) separately within the limits of experimental error, but they cannot be chosen so as to satisfy both. The simplest assumption to make with regard to *c* is that it varies inversely as some power *n* of the absolute tem­perature, or that *c = c0(00∣0)n*, where c0 is the value of *c* at the tempera­ture *0*0. In this case the expression *0dv∣dθ-v* takes the simple form (n+1)*c*-*b.* The values of *n, c* and *b* could be calculated from observations of the cooling effect *Sdθ/dp* alone over a sufficient range of temperature, but, owing to the margin of experimental error and the paucity of observations available, it is better to make use of the observations on the compressibility in addition to those on the cooling effect. It is preferable to calculate the values of *c* and *b* directly from equation (20), in place of attempting to integrate the equation according to Kelvin’s method *(Ency. Brit.* ed. ix. vol. xi. p. 573), because it is then easy to take account of the variation of the specific heat S, which is sometimes important.

*Calculation of the Correction.—*Having found the most probable values of the quantities *c, b* and *n* from the experimental data, the calculation of the correction may be very simply effected as follows: The temperature by gas thermometer is defined by the relation T = *pv*/R, where the constant R is determined from the observations at 0° and 100° C. The characteristic equation in terms of absolute temperature 0 may be put in the form *0*= *pv*/R'+q, where *q* is a small quantity of the same dimensions as temperature, given by the relation

q=(*c-b*)*p*/R (21)

The constant R' is determined, as before, by reference to the funda­mental interval, which gives the relation R'/R=1+(*q*1-*q*0)/100,where *q*1, *q*0 are the values of *q* at 100° and 0o C. respectively.

The correction to be added to the fundamental zero T0 of the gas thermometer in order to deduce the value of the absolute zero *0*0 (the absolute temperature corresponding to o° C.) is given by the equation,

*0*0-T0=*q*0-(*q*1-*q*0)*0*0/100 (22)

The correction *dt* to be added to the centigrade temperature *t* by gas thermometer reckoned from 0° C. in order to deduce the corre­sponding value of the absolute temperature also reckoned from o° C. is given by the relation, deduced from formula (14),

*dt*=(*q*-*q*0)-(*q*1-*q*0)*t*/100, (23)

where *q* is the value at *t*° C. of the deviation (*c-b)p∣R.* The formulae may be further simplified if the index *n* is a simple integer such as 1 or 2. The values of the corrections for any given gas at different initial pressures are directly proportional to the pressure.