

On Lord Kelvin's Absolute Method of Graduating a Thermometer

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VI. *On Lord Kelvin's Absolute Method of Graduating a Thermometer.* By J. ROSE-INNES, B.Sc.*

IN a paper "On the Thermal Effects of Fluids in Motion" Lord Kelvin has given the cooling effects exhibited by various gases in passing through a porous plug; and he found that the effects for any one gas kept at the same initial temperature were proportional to the difference of pressure on the two sides of the plug (Reprinted Papers, vol. i. pp. 333-455). He also found that the cooling effect for any one gas per unit difference of pressure varies as the inverse square of the absolute temperature; and this rule succeeds very well in the case of air. For carbonic acid, however, the results furnished by this rule are not so satisfactory, as may be seen by inspecting the table given by him comparing the actual with the theoretical cooling effect (*loc. cit.* p. 429). Moreover in the case of hydrogen it is found that there is a *heating* effect, which increases, if anything, when the temperature rises, so that here the law of the inverse square of the temperature is wholly inapplicable. It seemed to me that it might be possible to hit upon some simple algebraic expression which should reproduce the experimental results rather better than Lord Kelvin's rule does; and in fact it was found that a satisfactory agreement between observation and calculation might be obtained by putting

$$\text{cooling effect} = \frac{\alpha}{T} - \beta,$$

where α and β are constants characteristic of the gas, and T is the absolute temperature.

The following values of α and β were found from the experimental data:—

	α .	β .
Air	441.5	.697
Carbonic acid . . .	2615	4.98
Hydrogen	64.1	.331

A comparison of the actual results with those calculated by the new formula is given in the following table:—

* Read December 10, 1897.

Name of Gas.	Temp.	Actual cooling effect.	Calculated cooling effect (Kelvin's formula).	Calculated cooling effect (New formula).
Air	0°	0°92	°92	°920
	7·1	·88	·87	·879
	39·5	·75	·70	·716
	92·8	·51	·51	·510
Carbonic Acid.....	0	4·64	4·64	4·60
	7·4	4·87	4·40	4·35
	35·6	3·41	3·63	3·49
	54·0	2·95	3·23	3·02
	93·5	2·16	2·57	2·16
	97·5	2·14	2·52	2·08
Hydrogen .	4·5	—0·100	—·100
	91·0	—·155	—·155

It will be seen that the formula proposed in this paper, regarded simply as an empirical formula, is more efficient than Lord Kelvin's; there is nothing astonishing in this as it contains two disposable constants instead of only one. But it has the following further advantages:—

(i.) It includes the three cases of air, hydrogen, and carbonic acid under one form, and therefore enables us to treat them all in one common investigation.

(ii.) It renders more manageable the differential equation concerned in the thermodynamic scale of temperature, and leads to simpler algebraic results after integration.

This last proposition we must now proceed to prove. It is shown by Lord Kelvin that when a gas passes through a porous plug we must have

$$t \frac{dv}{dt} - v = \frac{JK}{\Pi} \theta,$$

where t and v denote the temperature and volume of the gas respectively, K its specific heat, θ the cooling effect per atmo of differential pressure, Π the value of one atmo, and J the value of Joule's mechanical equivalent (Reprinted Papers, vol. iii. p. 179). Hence

$$\frac{1}{t} \frac{dv}{dt} - \frac{v}{t^2} = \frac{JK}{\Pi} \frac{\theta}{t^2}$$

$$\frac{d}{dt} \left(\frac{v}{t} \right) = \frac{JK}{\Pi} \left\{ \frac{\alpha}{t^3} - \frac{\beta}{t^2} \right\}.$$

*Estimate of the Absolute Value of the Freezing-point
of Water.*

Integrate the last equation between the limits t_0 and t_1 , and we obtain

$$\begin{aligned} \frac{v_1}{t_1} - \frac{v_0}{t_0} &= \frac{JK}{\Pi} \left\{ \frac{\alpha}{2t_0^2} - \frac{\alpha}{2t_1^2} - \left(\frac{\beta}{t_0} - \frac{\beta}{t_1} \right) \right\} \\ &= \frac{JK}{\Pi} \left\{ \frac{1}{t_0} - \frac{1}{t_1} \right\} \left\{ \frac{\alpha}{2} \left(\frac{1}{t_0} + \frac{1}{t_1} \right) - \beta \right\} \\ &= \frac{JK}{\Pi} \left\{ \frac{1}{t_0} - \frac{1}{t_1} \right\} \frac{\theta_1 + \theta_0}{2}, \end{aligned}$$

where θ_1 and θ_0 are the values of θ at the temperatures t_1 and t_0 respectively.

Multiply the equation by $t_0 t_1$ and we get

$$\begin{aligned} v_1 t_0 - v_0 t_1 &= \frac{JK}{\Pi} (t_1 - t_0) \frac{\theta_1 + \theta_0}{2} \\ (v_1 - v_0) t_0 - v_0 (t_1 - t_0) &= \frac{JK}{\Pi} (t_1 - t_0) \frac{\theta_1 + \theta_0}{2}. \end{aligned}$$

Hence

$$\begin{aligned} t_0 &= \frac{t_1 - t_0}{v_1 - v_0} \left(v_0 + \frac{JK}{\Pi} \frac{\theta_1 + \theta_0}{2} \right) \\ &= (t_1 - t_0) \frac{v_0}{v_1 - v_0} \left(1 + \frac{JK}{\Pi v_0} \frac{\theta_1 + \theta_0}{2} \right). \end{aligned}$$

If t_1 and t_0 are taken as the boiling-point and freezing-point of water respectively, then this equation gives us the value of the freezing-point t_0 in terms of the interval $t_1 - t_0$; it is usual, as pointed out by Lord Kelvin, to take the interval $t_1 - t_0$ as containing 100 degrees (*loc. cit.* p. 175). It is evident that we should have obtained the same value for t_0 if θ had been constant throughout the range of temperature t_0 to t_1 , and equal to $\frac{\theta_1 + \theta_0}{2}$. This shows that the proper mean cooling-effect is simply the arithmetic mean of the cooling effects at the boiling-point and freezing-point. The following table gives us the value of the freezing-point derived from experiments on the three gases.

	Uncorrected estimate of temperature of freezing-point.	Correction.	Corrected estimate.
Hydrogen . . .	273·13	—·13	273·00
Air	272·44	·72	273·16
Carbonic acid . .	269·5	4·35	273·85

The first column of figures is taken from Lord Kelvin's paper (*loc. cit.* p. 177).

*Thermodynamic Correction for a Constant-pressure
Gas Thermometer.*

Suppose now we have a temperature t lying above both t_1 and t_0 , and fixed by some definite physical phenomenon. We require to know exactly how it lies with respect to t_0 and t_1 .

We start as before with the differential equation

$$\frac{d}{dt} \left(\frac{v}{t} \right) = \frac{JK}{\Pi} \left\{ \frac{\alpha}{t^3} - \frac{\beta}{t^2} \right\}.$$

We may put this

$$\frac{d}{dt} \left(\frac{v}{t} \right) = \frac{A}{t^3} - \frac{B}{t^2},$$

if $A = \frac{JK\alpha}{\Pi}$ and $B = \frac{JK\beta}{\Pi}$

Integrate between the limits t_0 and t ,

$$\begin{aligned} \frac{v}{t} - \frac{v_0}{t_0} &= \frac{1}{2} \left(\frac{A}{t_0^2} - \frac{A}{t^2} \right) - B \left(\frac{1}{t_0} - \frac{1}{t} \right) \\ &= \left(\frac{1}{t_0} - \frac{1}{t} \right) \left\{ \frac{A}{2} \left(\frac{1}{t_0} + \frac{1}{t} \right) - B \right\}. \end{aligned}$$

Hence

$$\frac{v}{t} - \frac{v_0}{t_0} = \frac{-t_0}{tt_0} \left\{ \frac{A}{2} \left(\frac{1}{t_0} + \frac{1}{t} \right) - B \right\}.$$

Multiply by $t_0(t-t_1)$ and we shall have

$$v \left(t_0 - \frac{t_0 t_1}{t} \right) - v_0(t-t_1) = \frac{(t-t_1)(t-t_0)}{t} \left\{ \frac{A}{2} \left(\frac{1}{t_0} + \frac{1}{t} \right) - B \right\}.$$

Similarly by interchanging t_0 and v_0 with t_1 and v_1 , we might obtain

$$v\left(t_1 - \frac{t_0 t_1}{t}\right) - v_1(t - t_0) = \frac{(t - t_1)(t - t_0)}{t} \left\{ \frac{A}{2} \left(\frac{1}{t_1} + \frac{1}{t} \right) - B \right\}.$$

Subtract the equation last but one from the last,

$$v(t_1 - t_0) - (v_1 - v_0)t + v_1 t_0 - v_0 t_1 = \frac{(t - t_1)(t - t_0)}{t} \frac{A}{2} \left(\frac{1}{t_1} - \frac{1}{t_0} \right).$$

We may write this

$$(v - v_0)(t_1 - t_0) - (v_1 - v_0)(t - t_0) = \frac{(t - t_1)(t - t_0)}{t} \frac{A}{2} \left(\frac{1}{t_1} - \frac{1}{t_0} \right).$$

Divide by $v_1 - v_0$ and transpose,

$$t - t_0 = \frac{v - v_0}{v_1 - v_0} (t_1 - t_0) + \frac{(t - t_1)(t - t_0)}{t} \frac{A}{2(v_1 - v_0)} \left\{ \frac{1}{t_0} - \frac{1}{t_1} \right\}.$$

Finally,

$$t = t_0 + \frac{v - v_0}{v_1 - v_0} (t_1 - t_0) + \frac{JK(\theta_0 - \theta_1)}{2\Pi(v_1 - v_0)} \frac{(t - t_1)(t - t_0)}{t}.$$

This last expression for t may be said to consist of three parts :—

(i.) There is the quantity t_0 , whose absolute value may be considered to have been determined once for all by means of its own equation. We may regard it as known numerically with sufficient accuracy.

(ii.) There is the term $\frac{v - v_0}{v_1 - v_0} (t_1 - t_0)$. This term gives us the degrees above freezing-point on the equi-expansion method of graduation. It is what is usually called the "temperature."

(iii.) The quantity $\frac{JK(\theta_0 - \theta_1)}{2\Pi(v_1 - v_0)} \frac{(t - t_1)(t - t_0)}{t}$ is due entirely

to the Joule-Thomson effect. It may be regarded as a correction necessary owing to the deviation of the substance from a perfect gas. It is this quantity which is calculated and tabulated so as to give us the means of arriving at the absolute scale. We notice that in order to calculate this term, we require to know the value of t , the very quantity we are seeking to find. Sufficiently accurate, however, for the purpose of calculating this small term, will be the value of t found by means of a first approximation.

*Thermodynamic Correction for Constant-volume
Gas-Thermometer.*

We will now compare the indications of a gas-thermometer kept at constant volume with the thermodynamic scale of temperature.

Let us start as before with the differential equation

$$\frac{d}{dt}\left(\frac{v}{t}\right) = \frac{A}{t^3} - \frac{B}{t^2}.$$

Integrate this between the limits t and ∞ and we have

$$P - \frac{v}{t} = \frac{1}{2} \frac{A}{t^2} - \frac{B}{t},$$

where P is the value of $\frac{v}{t}$, as v and t are made to grow indefinitely large with p constant. To determine the form of P we must appeal to experiment. We know that when a gas is made to expand to larger and larger volumes it obeys Boyle's law more and more closely; hence we infer that when v and t are made indefinitely large, the value of $\frac{v}{t}$ must vary inversely as the pressure. We may therefore write

$$P = \frac{C}{p}$$

where C is a constant characteristic of the gas.

Writing in this value we have as the complete solution

$$\frac{C}{p} - \frac{v}{t} = \frac{1}{2} \frac{A}{t^2} - \frac{B}{t}.$$

Multiply this by pt , and transpose,

$$pv = Ct - p\left(\frac{1}{2} \frac{A}{t} - B\right).$$

If we neglect the Joule-Thomson effect we have as a first approximation $pv = Ct$, or $t = \frac{pv}{C}$, which is the value for t in the case of a perfect gas; and this approximate value for t may be used in the term involving the Joule-Thomson effect on the right-hand side of the equation. We then get

$$pv = Ct - \frac{CA}{2v} + pB.$$

This equation represents our *second* approximation to the correct formula. We may also write it

$$p(v-B) = Ct - \frac{CA}{2v}.$$

Imagine now that we keep v constant, and use the equation to determine t when p is measured. Let the suffix 0 refer to the freezing-point, and the suffix 1 to the boiling-point as before. We then have

$$p_0(v-B) = Ct_0 - \frac{CA}{2v},$$

$$p_1(v-B) = Ct_1 - \frac{CA}{2v}.$$

By subtraction

$$(p_1 - p_0)(v-B) = C(t_1 - t_0),$$

$$(p - p_0)(v-B) = C(t - t_0),$$

$$\therefore \frac{p - p_0}{p_1 - p_0} = \frac{t - t_0}{t_1 - t_0};$$

or

$$t = t_0 + \frac{p - p_0}{p_1 - p_0} (t_1 - t_0).$$

To the degree of approximation to which we are working, therefore, there is no thermodynamic correction needed for a constant-volume gas thermometer. There may be a correction involving *squares* of small quantities, which would appear on a nearer approximation. Such a correction, however, would not be worth taking into account in the case of a thermometer constructed with air or hydrogen, as the unavoidable errors of experiment would certainly be much larger than the correction. It is satisfactory to know that for all practical purposes absolute temperature is to be obtained with very great accuracy from Regnault's thermometric system by simply adding the value of t_0 to his numbers for temperature on the centigrade scale.

This result differs from that obtained by Rowland*, who employed Lord Kelvin's law of the inverse square of the temperature, and inferred that there was a correction needed

* Proceedings Amer. Acad. Arts & Sciences. xv. (n. s. vii.) p. 114.

involving the first power of the cooling-effect. Both his investigation and my own involve the assumption that an empirical formula found to hold through a short range of temperature can be used for any temperature however high, and hence neither his result nor mine is conclusively established ; but it seems interesting to show that the employment of a new expression, at least as good as Lord Kelvin's, for the cooling-effect, leads to a smaller value for the correction.

DISCUSSION.

Dr. S. P. THOMPSON said the empirical expression,

$$\left(\frac{\alpha}{T} - \beta\right),$$

indicated that at some particular temperature the cooling effect vanished ; that was a point suggestive of useful results if investigated by experiment.

Mr. J. WALKER read a communication from Mr. BAYNES on the paper, and remarked on the desirability of adopting two constants. He thought that further experiments should be made to discover how specific heat at a constant temperature depends on temperature. The calculated values for hydrogen were too few to be taken as evidence of the validity of the rule.

Mr. ROSE-INNES, in reply, said that from what was known of hydrogen, it might be expected to behave at ordinary temperatures as air behaves at higher temperatures. His object was, if possible, to include in one formula the case of the three investigated gases. This was much better than having a separate formula for each gas. Whether or not hydrogen was confirmatory with air and carbonic acid might be considered as *sub judice* ; it required further experimental data to test the formula in that case.