

XXI. *Theory of the Constant-volume Gas-thermometer.*

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THE importance which the constant-volume gas-thermometer has assumed in practical physics justifies an attempt to improve the theory of the instrument.

Manipulation of the Fundamental Differential Equation.

In the customary theory of the constant-volume thermometer we start with the differential equation

$$t\left(\frac{dv}{dt}\right)_p - v = JK \frac{\partial t}{\partial p},$$

and after dividing by t^2 we integrate with respect to t . The integration is of necessity along an isopiestic owing to the occurrence of the term $\left(\frac{dv}{dt}\right)_p$. The result of integration involves an arbitrary function of p , and in order to evaluate this function we imagine the integration carried to infinite values of v and t along the isopiestic. This plan has been adopted by Lord Kelvin (Reprinted Papers, vol. i. pp. 429-430) and by subsequent investigators; it is also employed in the paper published by me "On Lord Kelvin's Absolute Method of Graduating a Thermometer" (Phil. Mag. xlv. pp. 232-233).

The weak point of this method is that we have to assume that $JK \frac{\partial t}{\partial p}$ is known at all temperatures, and that an empirical formula, which happens to fit the Joule-Thomson results fairly well throughout the small range of their experiments, necessarily holds at any temperature however high. An extrapolation to infinity of the above kind must inevitably introduce some uncertainty into the results obtained. But it is possible to abolish this extrapolation by properly transforming the differential equation before integration.

We start from the fundamental equation

$$t\left(\frac{dv}{dt}\right)_p - v = JK \frac{\partial t}{\partial p}.$$

In order to get rid of the isopiestic differential coefficient we may employ the relation

$$\left(\frac{dp}{dv}\right)_t \left(\frac{dv}{dt}\right)_p \left(\frac{dt}{dp}\right)_v = -1.$$

(See Baynes's Thermodynamics, p. 23.)

* Communicated by the Author.

We may write this

$$\left(\frac{dv}{dt}\right)_p = -\left(\frac{dp}{dt}\right)_v \left(\frac{dv}{dp}\right)_t.$$

Substituting this value in the differential equation we obtain

$$-t\left(\frac{dp}{dt}\right)_v \left(\frac{dv}{dp}\right)_t - v = JK \frac{\partial t}{\partial p}.$$

Multiply by $-\left(\frac{dp}{dv}\right)_t$

$$t\left(\frac{dp}{dt}\right)_v + v\left(\frac{dp}{dv}\right)_t = -JK \frac{\partial t}{\partial p} \left(\frac{dp}{dv}\right)_t.$$

Again, if we put Ψ for the product pv we have

$$v\left(\frac{dp}{dv}\right)_t = -p + \left(\frac{d\Psi}{dv}\right)_t.$$

Hence

$$t\left(\frac{dp}{dt}\right)_v - p + \left(\frac{d\Psi}{dv}\right)_t = -JK \frac{\partial t}{\partial p} \left(\frac{dp}{dv}\right)_t.$$

The quantity $\left(\frac{d\Psi}{dv}\right)_t$ may conveniently be removed to the other side of the equation; we thus obtain

$$t\left(\frac{dp}{dt}\right)_v - p = -JK \frac{\partial t}{\partial p} \left(\frac{dp}{dv}\right)_t - \left(\frac{d\Psi}{dv}\right)_t.$$

We also have

$$\left(\frac{d\Psi}{dv}\right)_t = \left(\frac{d\Psi}{dp}\right)_t \left(\frac{dp}{dv}\right)_t,$$

and employing this value the differential equation becomes

$$t\left(\frac{dp}{dt}\right)_v - p = -\left\{ JK \frac{\partial t}{\partial p} + \left(\frac{d\Psi}{dp}\right)_t \right\} \left(\frac{dp}{dv}\right)_t.$$

If by any method we are enabled to express the right-hand side of this equation in terms of v and t , the integral of the equation will give us the connexion between p and t at constant volume without an extrapolation to infinity. In order that t may be a linear function of p when v is kept constant, the necessary and sufficient condition is that the right-hand side of the equation should be a function of v only.

The quantities $JK \frac{\partial t}{\partial p}$ and $\left(\frac{d\Psi}{dp}\right)_t$ are both measurable for several substances; in the cases of hydrogen, nitrogen, and

air they are both found to be very small. Consequently their sum $JK \frac{\partial t}{\partial p} + \left(\frac{d\psi}{dp}\right)_t$ is also a small quantity; and if we use an approximate equation in finding the value of $\left(\frac{dp}{dv}\right)_t$ we shall only be introducing errors corresponding to squares of small quantities.

Now if $pv = Rt$
we have

$$\left(\frac{dp}{dv}\right)_t = -\frac{Rt}{v^2}.$$

Employing this approximate value for $\left(\frac{dp}{dv}\right)_t$ we obtain

$$t\left(\frac{dp}{dt}\right)_v - p = \left\{ JK \frac{\partial t}{\partial p} + \left(\frac{d\psi}{dp}\right)_t \right\} \frac{Rt}{v^2}.$$

It is further shown by experiment that for hydrogen, nitrogen, and air, the quantities

$$JK \frac{\partial t}{\partial p} \text{ and } \left(\frac{d\psi}{dp}\right)_t$$

are nearly independent of the pressure, and depend on the temperature only. Consequently to our present degree of approximation, the quantity

$$JK \frac{\partial t}{\partial p} + \left(\frac{d\psi}{dp}\right)_t$$

may be taken as a function of the temperature only; and in order that the constant-volume thermometer may give readings in accordance with the thermodynamic scale we must have the values of

$$JK \frac{\partial t}{\partial p} + \left(\frac{d\psi}{dp}\right)_t$$

varying inversely as the absolute temperature.

The Absolute Value of the Freezing-point of Water.

We may apply the formula obtained in the last section to the determination of the absolute value of the freezing-point of water. Estimates of the value of this important physical constant have already been given by Lord Kelvin (Reprinted Papers, vol. iii. p. 177), but his figures are based on the results of experiments with the constant-pressure gas-thermometer.

A careful determination of the increase of pressure of hydrogen at constant volume from the freezing-point to the boiling-point has recently been made by M. Chappuis (*Travaux et Mémoires du Bureau International*, tome vi. p. 108 ; see also Everett, C. G. S. System of Units, p. 115). The pressure at the freezing-point was 1 metre of mercury, and the increase of pressure was $\cdot 366254$ of a metre of mercury. If we could treat hydrogen as a perfect gas we should therefore obtain $\frac{100}{\cdot 366254}$ or $273^{\circ}034$ as the absolute

value of the freezing-point.

But it is of course necessary to inquire how far we need a correction owing to the deviation of hydrogen from the laws of a perfect gas ; for this purpose we take the equation

$$t \left(\frac{dp}{dt} \right)_v - p = -JK \frac{\partial t}{\partial p} \left(\frac{dp}{dv} \right) - \left(\frac{d\psi}{dv} \right)_t.$$

Divide by t^2 and we have

$$\frac{d}{dt} \left(\frac{p}{t} \right) = -JK \frac{\partial t}{\partial p} \left(\frac{dp}{dv} \right)_t \frac{1}{t^2} - \left(\frac{d\psi}{dv} \right)_t \frac{1}{t^2}.$$

Let the suffix 0 refer to the freezing-point, the suffix 1 to the boiling-point, and integrate the above equation with respect to t between the limits t_0 and t_1 . We obtain

$$\begin{aligned} \frac{p_1}{t_1} - \frac{p_0}{t_0} &= - \int_{t_0}^{t_1} JK \frac{\partial t}{\partial p} \left(\frac{dp}{dv} \right)_t \frac{dt}{t^2} - \int_{t_0}^{t_1} \left(\frac{d\psi}{dv} \right)_t \frac{dt}{t^2} \\ &= M \left(\frac{1}{t_1} - \frac{1}{t_0} \right) + N \left(\frac{1}{t_1} - \frac{1}{t_0} \right), \end{aligned}$$

where M is some mean value of $JK \frac{\partial t}{\partial p} \left(\frac{dp}{dv} \right)_t$ and N is some mean value of $\left(\frac{d\psi}{dv} \right)_t$. Hence

$$\frac{p_1 - M - N}{t_1} = \frac{p_0 - M - N}{t_0} = \frac{p_1 - p_0}{t_1 - t_0}$$

so that

$$\begin{aligned} t_0 &= \frac{p_0 - M - N}{p_1 - p_0} (t_1 - t_0) \\ &= \frac{p_0}{p_1 - p_0} (t_1 - t_0) - \frac{M + N}{p_1 - p_0} (t_1 - t_0). \end{aligned}$$

The expression $\frac{p_0}{p_1 - p_0} (t_1 - t_0)$ gives us the value of t_0 when

we treat the substance as a perfect gas; in the case of hydrogen at an initial pressure of 1 metre of mercury we have already seen that its numerical value is 273·034. The term $-\frac{M+N}{p_1-p_0}(t_1-t_0)$ gives us the thermodynamic correction necessary on account of the deviation of the behaviour of the substance from the laws of a perfect gas; it can be calculated when p_1 , p_0 , M , and N are known.

In order to discover the values of the mean quantities M and N accurately, we require to know in what way the two quantities

$$JK \frac{\partial t}{\partial p} \left(\frac{dp}{dv} \right)_t \text{ and } \left(\frac{d\psi}{dv} \right)_t$$

respectively vary with the temperature; such knowledge we do not at present possess. It is certain, however, that M must be less than the largest value of

$$JK \frac{\partial t}{\partial p} \left(\frac{dp}{dv} \right)_t$$

which occurs between t_0 and t_1 , and similarly N must be less than the largest value of $\left(\frac{d\psi}{dv} \right)_t$ which occurs between t_0 and

t_1 . We are thereby enabled to calculate a superior limit to each of the corrections corresponding to M and N respectively; and in the case of hydrogen we find that these corrections must be very small—so small that we may safely employ some rough method of finding the mean in order to reach the values of M and N . The errors introduced by taking an approximate mean instead of the true mean would not exceed the uncertainty involved in the value of

$\frac{p_0}{p_1-p_0}(t_1-t_0)$ owing to the ordinary errors of experiment.

For the purpose of calculating M we must employ the measurements, made by Joule and Kelvin, of the heating-effect which occurs when hydrogen is passed through a porous plug. The heating-effect amounted, at temperatures from 4° C. to 5° C., to 0°·100 C. per 100 inches of mercury; and at temperatures from 89° C. to 93° C. it amounted to 0°·155 C. per 100 inches of mercury (Reprinted Papers, vol. iii. p. 175). If the heating-effect had been constant and equal to the smaller of the two values quoted above, the value of M would have been ·000505 of a metre of mercury; if the heating-effect had been constant and equal to the larger of the two values, then M would have been ·001025 of a metre

of mercury. The value of M may be fairly taken as $\cdot 000765$, the arithmetic mean between $\cdot 000505$ and $\cdot 001025$.

For the purpose of calculating N we may employ the results of M. Amagat, who examined the relation of the pressure to the volume of various gases when the temperature is kept constant. In the case of hydrogen, the range of temperature of his experiments was from $17^{\circ}\cdot 7$ C. to $100^{\circ}\cdot 1$ C. He plotted the values of pv against p , and found that within the limits of temperature of his experiments the isothermals could be treated as a set of parallel straight lines. It is not possible to accept this conclusion as absolutely correct. For if the isothermals at all temperatures were taken as represented by a set of parallel straight lines, there would be no critical state, liquefaction would be impossible; and we should never have pv decreasing as p increases. We may therefore infer that M. Amagat's law is only an approximation, and that at higher temperatures pv really increases rather more rapidly with p than at lower temperatures. M. Amagat considers that the value of $\left(\frac{d\psi}{dp}\right)_t$ is $\cdot 00078$ when the unit of volume is the volume occupied by the gas under standard conditions. It is perhaps safest to attach this number to the isothermal of 50° C.; we then obtain for $\left(\frac{d\psi}{dv}\right)_t$ at 50° C. the value of $-\cdot 001215$ of a metre of mercury, which pressure may also be taken as equal to N .

The resulting value of $M + N$ is $-\cdot 000450$ of a metre of mercury; and the corresponding correction for t_0 is $0^{\circ}\cdot 123$. This yields as the final value of t_0 the figure $273^{\circ}\cdot 157$, which is very close to the estimate derived by Lord Kelvin from the constant-pressure air-thermometer (Reprinted Papers, vol. iii. p. 177).

The Characteristic Equation of a nearly Perfect Gas.

We have already seen that for substances like hydrogen and air the equation

$$t\left(\frac{dp}{dt}\right)_v - p = -JK \frac{\partial t}{\partial p} \left(\frac{dp}{dv}\right)_t - \left(\frac{d\psi}{dv}\right)_t$$

reduces to

$$t\left(\frac{dp}{dt}\right)_v - p = \left\{ JK \frac{\partial t}{\partial p} + \left(\frac{d\psi}{dp}\right)_t \right\} \frac{Rt}{v^2};$$

and we remarked that the condition necessary and sufficient to make t a linear function of p when v is kept constant is

that the quantity in curly brackets should vary inversely as the absolute temperature. An examination of the experimental results obtained with such gases shows us that $JK \frac{\partial t}{\partial p} + \left(\frac{d\psi}{dp}\right)_t$ is a positive quantity which decreases as the temperature increases; and it is quite consistent with the experimental evidence to assume that $JK \frac{\partial t}{\partial p} + \left(\frac{d\psi}{dp}\right)_t$ actually varies as the inverse temperature, making due allowance for the unavoidable errors of experiment. At the same time the measurements that have been made do not enable us to assert that the proposed law has been proved; it is conceivable that $JK \frac{\partial t}{\partial p} + \left(\frac{d\psi}{dp}\right)_t$ decreases rather more rapidly than the inverse temperature.

The simplicity of the proposed law, and its close approximation to the truth, render it interesting to examine what further deductions can be made therefrom. We start with the equation

$$t \left(\frac{dp}{dt}\right)_v - p = -JK \frac{\partial t}{\partial p} \left(\frac{dp}{dv}\right)_t - \left(\frac{d\psi}{dv}\right)_t,$$

and then suppose that the right-hand side of the equation is found by experiment to be equal to $\frac{\lambda}{v^2}$, where λ is a constant.

We thus have

$$t \left(\frac{dp}{dt}\right)_v - p = \frac{\lambda}{v^2}.$$

Integrating this we obtain

$$p = f(v)t - \frac{\lambda}{v^2},$$

where $f(v)$ is a function of the volume only. Multiply by v , and then differentiate with regard to v keeping t constant; we get

$$\left(\frac{d\psi}{dv}\right)_t = \{f(v) + vf'(v)\}t + \frac{\lambda}{v^2}.$$

Also since

$$-\left(\frac{d\psi}{dv}\right)_t - JK \frac{\partial t}{\partial p} \left(\frac{dp}{dv}\right)_t = \frac{\lambda}{v^2},$$

we may write

$$2 \left(\frac{d\psi}{dv}\right)_t + JK \frac{\partial t}{\partial v} \left(\frac{dp}{dv}\right)_t = \{f(v) + vf'(v)\}t.$$

Since

$$\begin{aligned} 2 \left(\frac{d\psi}{dv} \right) + JK \frac{\partial t}{\partial p} \left(\frac{dp}{dv} \right)_t &= \left\{ 2 \left(\frac{d\psi}{dp} \right)_t + JK \frac{\partial t}{\partial p} \right\} \left(\frac{dp}{dv} \right)_t \\ &= \left\{ 2 \left(\frac{d\psi}{dp} \right)_t + JK \frac{\partial t}{\partial p} \right\} \left\{ f'(v)t + \frac{2\lambda}{v^3} \right\}, \end{aligned}$$

we must also have

$$\left\{ 2 \left(\frac{d\psi}{dp} \right)_t + JK \frac{\partial t}{\partial p} \right\} \left\{ f'(v)t + \frac{2\lambda}{v^3} \right\} = \{ f(v) + v f'(v) \} t.$$

This equation is exact; but if $\left(\frac{d\psi}{dp} \right)_t$ and $JK \frac{\partial t}{\partial p}$ are small quantities, and if we are content to neglect squares of small quantities, we may put approximately

$$\left\{ 2 \left(\frac{d\psi}{dp} \right)_t + JK \frac{\partial t}{\partial p} \right\} f'(v)t = \{ f(v) + v f'(v) \} t;$$

so that

$$2 \left(\frac{d\psi}{dp} \right)_t + JK \frac{\partial t}{\partial p} = \frac{f(v)}{f'(v)} + v.$$

The expression $\frac{f(v)}{f'(v)} + v$ is a function of v only, and as we know independently $2 \left(\frac{d\psi}{dp} \right)_t + JK \frac{\partial t}{\partial p}$ is a function of t only we must have $\frac{f(v)}{f'(v)} + v$ a constant, say B . Then from the differential equation

$$\frac{f(v)}{f'(v)} + v = B,$$

we obtain by integration

$$f(v) = \frac{R}{v - B},$$

where R is a constant. The constant R has been introduced by an integration, and is therefore arbitrary as far as the differential equation is concerned; it is fixed, however, by the consideration that the interval of temperature between the freezing-point and the boiling-point has an arbitrarily chosen value. Since

$$p = f(v)t - \frac{\lambda}{v^3},$$

and

$$f(v) = \frac{R}{v-B},$$

we must have

$$p = \frac{Rt}{v-B} - \frac{\lambda}{v^2}.$$

The Difference between Joule's Method and Lord Kelvin's Method of Testing Mayer's Hypothesis.

The formula obtained in the first section may also be usefully employed to exhibit the precise connexion between Joule's method and Lord Kelvin's method of testing Mayer's hypothesis. The language of most text-books on this subject is far from satisfactory; it is often implied that Lord Kelvin's method is the same as Joule's except as regards delicacy; and the relation between the two methods is never given rigorously.

Mayer's hypothesis consisted in assuming that for common air and some other gases the amount of heat given out by the gas during an isothermal compression was exactly equal to the work done. Evidently, if this is so, there can be no change of energy during an isothermal compression; and we have the energy remaining constant whenever the temperature remains constant. This hypothesis was put to the test of experiment by Joule, and roughly verified. Joule's apparatus consisting of two large copper vessels is well known; and it is evident that his experiment tests Mayer's hypothesis directly. For if the temperature remains unaltered, as Joule found to be the case, the gas has received no heat and done no work, so that it has not gained any energy from surrounding objects; hence the constancy of temperature is accompanied by the constancy of energy.

The thermodynamics of Joule's experiment are easily given; we have in all cases

$$dE = kdt + \left\{ t \left(\frac{dp}{dt} \right)_v - p \right\} dv.$$

(See Baynes's 'Thermodynamics,' p. 88.) Joule's result shows that dE and dt are zero simultaneously, while dv does not vanish; hence we obtain

$$t \left(\frac{dp}{dt} \right)_v - p = 0.$$

The quantity $t\left(\frac{dp}{dt}\right)_v - p$ is therefore proved to be zero in so far as we can treat Joule's result as free from experimental error.

The great flaw in Joule's method is that it is not sufficiently delicate, and a sensible deviation from Mayer's hypothesis might occur without being detected. Lord Kelvin considerably improved Joule's apparatus as regards delicacy, but he also changed the theory of the experiment. The equation given in his writings as applying to his form of the experiment is

$$t\left(\frac{dv}{dt}\right)_p - v = JK \frac{\partial t}{\partial p};$$

so that when no change of temperature is observed we should have

$$t\left(\frac{dv}{dt}\right)_p - v = 0.$$

This condition is not necessarily the same as

$$t\left(\frac{dp}{dt}\right)_v - p = 0.$$

The precise manner in which the fall of temperature occurring in Lord Kelvin's form of the experiment may be made to test Mayer's hypothesis, is easily deduced from the formula obtained in the first section. Since

$$t\left(\frac{dp}{dt}\right)_v - p = -\left\{ JK \frac{\partial t}{\partial p} + \left(\frac{d\psi}{dp}\right)_t \right\} \left(\frac{dp}{dv}\right)_t,$$

we see that for Mayer's hypothesis to be true it is necessary and sufficient that

$$JK \frac{\partial t}{\partial p} + \left(\frac{d\psi}{dp}\right)_t = 0, \quad \text{or} \quad \partial t = -\frac{1}{JK} \left(\frac{d\psi}{dp}\right)_t \partial p.$$

Boyle's law is not rigorously fulfilled by any actual substance; hence we see that Mayer's hypothesis would be actually disproved by finding no change of temperature in the gas which had come through the porous plug.