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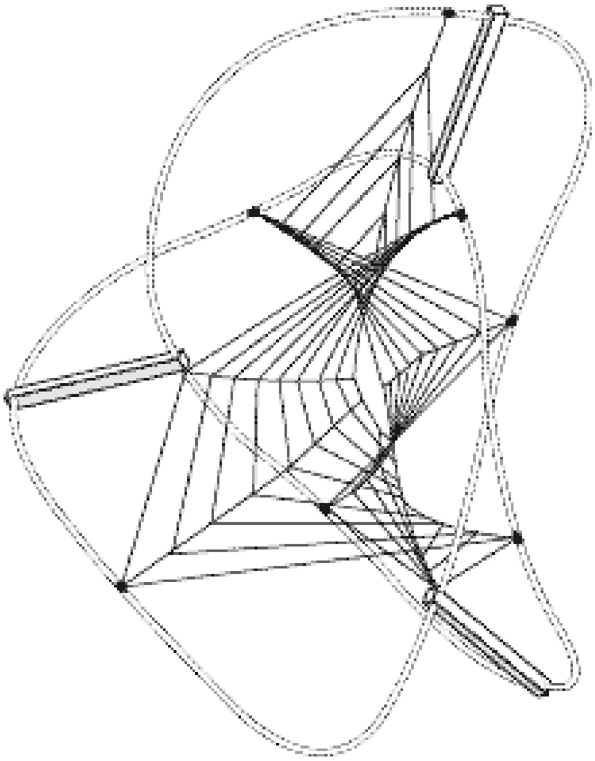

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Measuring the Absolute:

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Abstract

When William Thomson (Lord Kelvin) created the concept of "absolute" temperature, his main concern was to make the definition of temperature independent of the properties of particular thermometric substances, rather than to count temperature from an absolute zero. He tried out a succession of definitions based on the thermodynamics of ideal heat engines; most notably, in 1854 he gave the ratio of two temperatures as the ratio of quantities of heat taken in and given out at those temperatures in a Carnot cycle. But how could such definitions be used for experimental work, when it was not possible even to approximate an ideal Carnot engine in reality? More generally, how can one connect an entirely abstract concept to concrete situations in order to allow physical measurements? Thomson argued that an ideal gas thermometer would indicate his absolute temperature, and that the deviation of actual gas thermometers from the ideal could be estimated by means of the Joule-Thomson effect, namely the cooling (or heating) of a gas in expanding through a porous barrier. However, the measurement of the Joule-Thomson effect itself required measurements of temperature, so there was a clear circularity. The legitimacy of Thomson's procedure can be shown by understanding it as part of an iterative process of "successive approximations".

Key words: William Thomson (Lord Kelvin), absolute temperature, measurement, iteration

1. William Thomson's quest for the absolute

> *"This may justly be termed an absolute scale, since its characteristic is quite independent of the physical property of any specific substance."*
>
> *-- William Thomson (1848), p. 104.*

William Thomson, better known to posterity as Lord Kelvin, made pioneering efforts to create the concept known to us as "absolute temperature", counted in "degrees Kelvin" in his honor. Thomson's work laid the foundation of the thermodynamic concept of temperature established in the latter half of the 19th century, which still provides the theoretical underpinning for the most rigorous measurements of temperature. But it was no easy task to measure absolute temperature in concrete empirical situations. Thomson's definition of absolute temperature was intentionally and resolutely abstract, making no reference whatsoever to any properties of any particular material substances. How was such a concept susceptible at all to measurement by physical instruments? In this paper we conduct a close examination of how absolute temperature was rendered measurable. The results of our investigation should also provide some instructive insights for the general problem of linking abstract theoretical schemes to concrete physical situations.

In 1848, Thomson presented a brief paper on "an absolute thermometric scale" to the Cambridge Philosophical Society. The young Glaswegian professor of natural philosophy was still vividly impressed by the work of Victor Regnault that he had witnessed and assisted in Paris just a few years earlier. Thomson began this paper by recognizing that the problem of thermometry had received "as complete a practical solution . . . as can be desired" thanks to the "very elaborate and refined experimental researches" in recent years, particularly by Regnault. Still, he lamented, "the theory of thermometry is however as yet far from being in so satisfactory a state."[1] Regnault had consolidated his precision air thermometry by shrinking from theories of heat and temperature.[2] Much as

Thomson admired Regnault's work, his austere anti-theoretical manner of doing science did not appeal to Thomson.

Thomson did appreciate quite well the powerful way in which Regnault demonstrated that the air thermometer was a good instrument to use because it gave highly consistent readings even when its construction was made to vary widely. Such "comparability" was shown to be lacking in other common thermometers, for instance the mercury thermometer and the alcohol thermometer. Even so, Thomson complained:

> "Although we have thus a strict principle for constructing a definite system for the estimation of temperature, yet as reference is essentially made to a specific body as the standard thermometric substance, we cannot consider that we have arrived at an absolute scale, and we can only regard, in strictness, the scale actually adopted as an arbitrary series of numbered points of reference sufficiently close for the requirements of practical thermometry."[3]

So Thomson set about looking for a general theoretical principle on which to found thermometry. He first mentions the old idea that in a perfect thermometer equal increments of temperature should correspond to equal additions of heat. While not denying the theoretical cogency of this principle in itself, Thomson states that it cannot be used in practical thermometry because the specific heat of any given body will vary as a function of temperature; it is an "experimentally demonstrated fact that thermometry under this condition is impossible".[4] Since specific heat is generally a function of temperature, the addition of equal amounts of heat to a body actually results in different amounts of temperature increases at different points of the temperature scale. And this variation is impossible to investigate experimentally, unless we already have clear methods of measuring the increments of temperature and heat (and the latter independently of temperature measurements). Given this circular morass, it is understandable that Thomson declared: "We are left without any principle on which to found an absolute thermometric scale."[5]

It was clear to Thomson that the theoretical concept of temperature should be defined without recourse either to particular material substances, or to a circular reference to temperature itself. In other words, he needed to find a theoretical relation expressing temperature in terms of other general concepts. The conceptual resource Thomson needed for this purpose came from something that he had learned while working in Regnault's laboratory in Paris, namely Sadi Carnot's little-known theory of heat engines, which Thomson himself was to raise into prominence later. It is useful here to recall that "Regnault's great work" was the result of a government commission to determine the empirical data relevant to the understanding of steam engines, and the way he conceptualised the working of the steam engine was actually not so different from Carnot's theoretical framework.[6] Carnot's theory gave Thomson precisely what he was looking for:

> "The relation between motive power and heat, as established by Carnot, is such that quantities of heat, and intervals of temperature, are involved as the sole elements in the expression for the amount of mechanical effect to be obtained through the agency of heat; and since we have, independently, a definite system for the measurement of quantities of heat, we are thus furnished with a measure for intervals according to which absolute differences of temperature may be estimated."[7]

In short, Carnot's theory provides a theoretical relation between three variables pertaining to an idealized heat-engine: heat, temperature, and work. If we can measure heat and work directly, we can infer temperature by means of the theory.

Thomson's basic idea (to be modified later) was that the interval of one degree of temperature should be defined as the amount which would result in the production of unit amount of mechanical work in a "Carnot engine" operating with a unit amount of heat in that temperature interval. In his own words:

> "The characteristic property of the scale which I now propose is, that all degrees have the same value; that is, that a unit of heat descending from a body *A* at the temperature T° of this scale, to a body *B* at the temperature $(T-1)$°, would give out the same mechanical effect, whatever be the number T. This may justly be termed an absolute scale, since its

> characteristic is quite independent of the physical property of any specific substance."[8]

(Note that this work was done before he adopted energy conservation.) So Thomson created an impeccable theoretical definition of temperature. But in a way, that was the easy part; relating the theoretical concept back to the realm of observations was a different matter altogether. Linking up a theoretical concept with physical operations is generally a non-trivial problem, but it was made starkly difficult in Thomson's case, since he had deliberately fashioned the absolute temperature concept to make sure that any connections to any particular objects or materials were severed. How was Thomson going to turn around later and say, excuse me, but now I would like to have those connections back?

2. Measurement: How the concrete was smuggled into the abstract

In order to have a true appreciation of the epistemic problem that Thomson faced, we need to pause a moment to reflect on the nature of Carnot's theory. Although Carnot was interested in practical concerns of engine efficiency, he started with a completely general theory of heat-engines, which meant that the "working substance" in his theoretical engine was in the first instance conceived as an abstract body possessing only the properties of pressure, volume, temperature and heat content. How was Carnot able to deduce anything useful at all about the behaviour of a substance of such skeletal description? He made use of some general assumptions, such as the conservation of heat and some propositions found in the latest physics of gases, but they were still not sufficient to allow the deduction of anything definite about the efficiency of the heat-engine (the ratio of mechanical work produced to the amount of heat input). Quite plainly, in actual situations the efficiency will depend on the particular design of the engine and the nature of the particular working substance.

Carnot made theoretical headway by treating only a very restricted class of heat engines, though he still avoided invoking particular properties of the working substance. The following were the most important of Carnot's restrictions. (1) Carnot only treated engines that worked through a cyclical process, in which the working substance returned, at the end of a cycle, exactly to the macroscopic state in which it started. (2) The Carnot engine was not only cyclical, but cyclical in a very specific way, with definite strokes constituting the cycle. (3) Finally, the Carnot cycle was also perfectly reversible; not only did that imply the absence of friction and other forms of dissipation of heat and work, but also that heat was never transferred across any temperature differences.

With those restrictions in place, Carnot was able to prove some important results about his theoretical heat engines. But Thomson faced a great difficulty in the fact that the object of Carnot's theory was so utterly removed from any actually constructable heat engine. The conceptually straightforward scheme for measuring Thomson's absolute temperature would have been the following: take an object whose temperature we would like to measure; use it as a Carnot heat reservoir, run a Carnot engine between that and another reservoir whose temperature is previously known; and measure the amount of mechanical work that is produced, which gives the difference between the two temperatures. The difficulty of realizing that procedure can only be imagined, because there is no record of anyone ever who was crazy enough to attempt it. In order to meet the standard of precision in thermometry established by Regnault, the instrument used would have needed to be frighteningly close to the theoretical Carnot engine. That route to the operationalisation of absolute temperature would have been a non-starter.

So Thomson took a conceptual detour. Instead of attempting to measure temperature directly with a thermometer constructed out of an actual, fully-concrete Carnot engine, he constructed particularized theoretical systems, backed up by assurance of universality. The basic strategy was to consider versions of the Carnot engine that were concrete enough to allow the use of certain empirical data in the description of its workings. If a measure of absolute temperature could be established in any version of the Carnot engine, then it would have universal validity because Thomson's definition of absolute temperature was only based on those features that were shared by all Carnot engines. The key to making a reliable connection between the abstract definition of absolute temperature and actual empirical data was to use a model that was sufficiently concrete yet still idealized so that Carnot's propositions about engine efficiency would be satisfied. Thomson worked out two such models, following Carnot: a system made of water and steam, and a system with only air in it. Here we will only give the details of his water-steam system.[9] The important advantage of this system is that the pressure of "saturated" steam is only a function of temperature, which simplifies the reasoning a great deal as we shall see below. The theoretical model allowed Thomson to compute the heat-work relation from empirical data. As we shall see, the relevant empirical data were certain parameters measured as functions of temperature measured by an air thermometer. Putting such data into the definition of absolute temperature yielded a relation between absolute temperature and air-thermometer temperature, with which he could convert air-thermometer temperature into absolute temperature. Let us now see how this calculation was made.

The net outcome of a Carnot cycle is that a certain amount of work, W, is produced and a certain amount of heat, H, is passed through the system from the heat-reservoir at temperature S to the heat-reservoir at temperature T, where $S>T$. We need to evaluate W, which is visually represented by the area enclosed by the quadrilateral $AA_1A_2A_3$ in **Figure 1.**[10] In this pressure-volume diagram, the mechanical work done by an operation represented in a curve is given by the area under it (being the integral ?pdv). In the cycle, the net work is given by the area of the quadrilateral, which represents the amount of work done by the steam-water system in strokes (1) and (2), minus the amount of work done to the steam-water system in strokes (3) and (4).

***Figure 1**. Thomson's diagram representing the working of the ideal steam-water cycle. The numbers designating the four strokes have been added.*

Thomson actually estimated the area in question by performing the integration along the pressure axis, as follows:

$$W = \int_{p_1}^{p_2} \xi dp \qquad \text{…………….} \ (1)$$

where p_1 and p_2 are the pressures in strokes 1 and 3, which are constant because the temperatures are; ξ is the length of the line parallel to the volume-axis delimited by the curvilinear sides of the quadrilateral. Now, what does ξ represent physically? This is the crucial point:

> "We see that ξ is the difference of the volumes below the piston at corresponding instants of the second and fourth operations, or instants at which the saturated steam and the water in the cylinder have the same pressure *p*, and, consequently, the same temperature, which we may denote by *t*. Again, throughout the second operation the entire contents of the cylinder possess a greater amount of heat by *H* units than during the fourth; and, therefore, at any instant of the second operation there is as much more steam as contains *H* units of latent heat, than at the corresponding instants of the fourth operation."[11]

The operative assumption here is that there is a strict correlation between the temperature and pressure of saturated steam; by the time Thomson was writing, this was generally accepted as an empirical law. Now we must ask how much volume increase results from the production of the amount of steam embodying latent heat *H*. This volume increment is given as follows:

$$\xi = (1-\sigma)H/k, \qquad \ldots\ldots\ldots\ldots\ldots (2)$$

where k denotes the latent heat per unit volume of steam at a given temperature, and σ is the ratio of the density of steam to the density of water. The formula is to be read as follows: The input of heat *H* produces *H/k* liters of steam, from $\sigma H/k$ liters of water; the net increase of volume is given by subtracting the original water volume from the final steam volume.

Substituting that expression into the expression for the net work produced in the cycle, we have:

$$W = \int_{p_1}^{p_2} (1-\sigma)\frac{H}{k}\,dp \qquad \ldots\ldots\ldots\ldots\ldots (3)$$

Now, because all of the parameters in the above equation (except *H*) are empirical parameters measured as a function of air-thermometer temperature *t*, we can rewrite the integral in terms of *t* (taking *H* out as a constant), as follows:

$$W = H\int_{T}^{S} (1-\sigma)\frac{dp}{kdt}\,dt \qquad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

According to Thomson's definition, the difference between *S* and *T* will be the unit increment in absolute temperature if *W/H* is the unit amount; in that case the quantity (*S*-*T)* in air-thermometer degrees will give the conversion factor expressing how many air-thermometer degrees correspond to one degree of absolute temperature interval, at that point on the scale.

Therefore the measurement of absolute temperature by means of the steam-water cycle came down to the measurement of the pressure, density, and latent heat of saturated steam as functions of air-thermometer temperature. Detailed measurements of these quantities had been made, by none other than

Regnault. Using Regnault's data, Thomson constructed a table with "a comparison of the proposed scale with that of the air-thermometer, between the limits 0° and 230° of the latter".[12] **Table 1** gives some of Thomson's results, converted into a more convenient form. Note that the relationship between the air-temperature and the absolute temperature is not linear; the size of one absolute temperature degree becomes smaller and smaller in comparison to the size of one air-temperature degree as temperature goes up. (As we shall see later, this absolute scale had no zero-point but stretches to negative infinity.)

air-thermometer temperature	**absolute temperature**
0°C	0°C
5	5.660
10	11.243
15	16.751
20	22.184
25	27.545
30	32.834
35	38.053
40	43.201
45	48.280
50	53.291
55	58.234
60	63.112
65	67.925
70	72.676
75	77.367
80	82.000
85	86.579
90	91.104
95	95.577
100	100
150	141.875
200	180.442
231	203.125

***Table 1**. Thomson's comparison of air-thermometer temperature and his absolute temperature (first definition, without absolute zero), assuming that the two scales are made to agree at 0°C and 100°C.*

Let us now consider whether Thomson at this stage really succeeded in his self-imposed task of measuring absolute temperature. There are three major difficulties. The first one was clearly noted by Thomson himself: The formulae given above require the values of the latent heat of steam by volume (*k*), but Regnault had only measured the latent heat of steam by weight. Lacking the facility to make the required measurements himself, Thomson converted Regnault's data into what he needed by assuming that steam obeyed the laws of Boyle and Gay-Lussac. He knew that this was at best an approximation, but thought there was reason to believe that it was a sufficiently good approximation for his purposes.[13]

Secondly, in the derivation of the mechanical effect, the entire analysis is premised on the assumption that the pressure of saturated steam depends only on temperature. As noted above, that pressure-temperature relation was not something deducible a priori, but an empirically obtained generalization. The rigorous reliability of this empirical law was not beyond doubt. Besides, doesn't the use of the pressure-temperature relation amount to a reliance on an empirical property of a particular substance, just the thing Thomson wanted to avoid in his definition of temperature? In Thomson's defence, however, we must keep in mind that his use of the pressure-temperature relation was not in the definition of absolute temperature, but only in its operationalisation.

Finally, in the theoretical definition itself, absolute temperature is expressed in terms of heat and mechanical effect. We have quoted Thomson above as taking comfort in that "we have, independently, a definite system for the measurement of quantities of heat", but it is not clear what he had mind there. The standard laboratory method for measuring quantities of heat was through calorimetry based on the measurement of temperature changes induced in a standard substance (e.g. water), but of course that had to rely on a thermometer. Recall that Thomson's scheme for operationalising absolute temperature was to express *W/H* as a function of air-thermometer temperature. A complex circularity would have arisen if the measure of *H* itself depended on the use of the air thermometer (i.e. if it had to be kept inside the integral in **formula (4)**). In one place Thomson mentions using the melting of ice for the purpose of calorimetry,[14] but there were significant difficulties in any actual use of the ice calorimeter. Still, we could say that in principle heat could be measured by ice calorimetry (or any other method using latent heat), in which case the measure of heat would be reduced to the measure of weight and the latent heat of the particular change-of-state involved. But the last step would end up involving an empirical property of a particular substance, again contrary to Thomson's original intention!

3. Absolute temperature in the climate of energy conservation

How Thomson himself might have proposed to deal with the above-mentioned difficulties is an interesting question. However, it is also a hypothetical question. Almost as soon as Thomson advanced his initial concept of absolute temperature, he began to abandon the entire framework in which that concept was couched. This was in large part a consequence of his encounter with James Prescott Joule.[15] The general course of Joule and Thomson's collaboration is well known to historians of science.[16] When Thomson heard Joule present his idea about the interconvertibility of heat and mechanical work at the 1847 meeting of the British Association for the Advancement of Science in Oxford, he was interested but skeptical. After reading Thomson's 1848 paper on absolute temperature, Joule wrote urging him to reformulate his idea on the basis of the interconvertibility of heat and work, rather than holding on to Carnot's assumption that heat passed through the heat engine intact: "I dare say they [your ideas] will lose none of their interest or value even if Carnot's theory be ultimately found incorrect."[17] Thomson sent a lengthy reply, in which he was quite congenial to Joule: "I am quite [aware] of the importance of the objection you adduce to Carnot's theory … which I admit in its full force…." However, Thomson was not quite ready to renounce Carnot yet, and the contents of his letter, which we will discuss further later, make it clear that he was hard at work in trying to reach a better understanding of Carnot's theory.[18] The result was Thomson's paper of 1849 containing an exposition of Carnot's theory. While this was the paper in which Thomson gave the operationalisation of absolute temperature in terms of Carnot's theory, as discussed in the last section, it also expressed serious doubts about the caloric theory as employed in Carnot's memoir.[19]

By early 1851, Thomson had committed himself to a serious modification of Carnot's theory in the light of Joule's ideas about the interconversion of heat and work. The few years after Thomson's conversion to interconversion were both highly unsettled and highly productive. The entire basis on which he had defined absolute temperature in 1848 had to be changed, because the understanding of the Carnot engine had to be revised fundamentally if heat was no longer considered to be conserved, and the generation of mechanical effect was seen as the conversion of a fraction of the heat into work, rather than a by-product of the movement of heat.[20] It is fascinating to follow the twists and turns Thomson took in reshaping absolute temperature, but it may be most instructive to start by examining the final formulation (for this period), which was given in 1854 in one of Thomson's famous joint papers with Joule:

> "If any substance whatever, subjected to a perfectly reversible cycle of operations, takes in heat only in a locality kept at a uniform temperature, and emits heat only in another locality kept at a uniform temperature, the temperatures of these localities are proportional to the quantities of heat taken in or emitted at them in a complete cycle of operations."[21]

To put it simply,

$$T_1/T_2=Q_1/Q_2. \qquad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Essentially the same definition was also attached to a paper by Thomson on thermo-electricity published in the same year.[22]

Some explanation is required as to how Thomson crafted a definition of such pleasing simplicity, and what this new definition had to do with the original definition. Recall that the original definition of temperature rested on the amount of mechanical effect produced in a Carnot cycle, for a given amount of heat passing through the engine. A crucial factor in such consideration of engine efficiency was what Thomson called "Carnot's coefficient", which is the parameter μ in the following equation:

$$W = H\int_T^S \mu(t)dt$$

………………. (6)

W is the mechanical work produced in the cycle, *H* the amount of heat taken in and given out by the engine, and *t* the temperature. So μ, which is a function of temperature, gives an indication of how much mechanical effect is produced per unit amount of heat when a Carnot cycle is operated between temperatures *S* and *T*.[23] Then Thomson's original 1848 definition of temperature came down to defining *t* so that μ is a constant, which would make the work produced proportional to the temperature difference between the two reservoirs, as the above equation would reduce to:

$W=H\mu(S-T)$. ……………… (7)

When Thomson revised Carnot's theory, he preserved a very similar factor, which he still indicated by μ and called "Carnot's function".[24] This was defined similarly to the old Carnot coefficient, but with two differences. First of all, because heat was no longer a conserved quantity, *H* in the above equation became meaningless; therefore Thomson substituted it with the amount of heat absorbed from the high-temperature reservoir in the first stroke of a Carnot cycle. Secondly, this time μ was defined for an infinitesimal Carnot cycle, where τ is the infinitesimal difference in the temperatures of the two heat reservoirs. With those adjustments, Thomson defined μ through the following work-heat relation parallel to **equation (6)** above:

$W = (Mdv)\mu\tau$ ………………. (8),

where *Mdv* denotes the heat absorbed in the first stroke, which consists in an isothermal expansion by the volume increment *dv*.

The mechanical work, *W* above, produced in the whole cycle is also given by Thomson as follows:

$W = \frac{dp}{dt}\tau.dv$ ………………… (9)

Thomson simply says that this is "obviously the whole work done in the complete cycle", and does not provide a justification for the expression. The following is our intuitive understanding: The net work done in the complete infinitesimal cycle is, to the first order, the difference between the work done <u>by</u> the gas when it expands by absorbing heat, and the work done <u>to</u> the gas when it is compressed while releasing heat (the net work arising from the difference of mechanical effect between the two other strokes would be a second-order quantity, and can be ignored). The net work performed by the engine is positive because the expansive operation (1st stroke) takes place at a higher pressure than the compressive operation (3rd stroke); this is achieved by carrying out the expansive operation at a higher temperature than the compressive operation. The net work will be roughly proportional to the pressure difference between the two operations, because in both strokes the amount of volume change is essentially the same. The quantity $(dp/dt)\tau$ expresses this pressure difference, if the two operations differ by τ in temperature; multiplying it by the volume change in each stroke, *dv*, gives the net work as expressed in **formula (9)**.[25] (Here it is essential that there is a definite correlation between *p* and *t*, so this derivation is unproblematic only for a liquid-vapor system; for a simple-gas system and other systems for which *p* is not uniquely determined by *t*, Thomson would either have to make a different derivation, or appeal to the presumed universality of the Carnot cycle and say that the same expression for work holds for all kinds of working substances.) Inserting **equation (9)** into **equation (8)**, Thomson obtains the following expression for Carnot's function μ:

$$\mu = \frac{dp/dt}{M} \qquad \text{.................. (10)}$$

Having defined Carnot's function to suit the new thermodynamics with energy conservation, Thomson's next step was to liberalize the theoretical concept of temperature. The new Carnot's function did express something about engine efficiency, to which Thomson still wanted to tie the temperature concept. But Thomson now realized that nothing theoretical actually dictated the exact relation that Carnot's function should bear to temperature; his initial notion of defining temperature so that μ became a constant was much too restrictive, for no compelling reason. Therefore the Joule-Thomson paper of 1854 stated:

> "Carnot's function (derivable from the properties of any substance whatever, but the same for all bodies at the same temperature), <u>or any arbitrary function of Carnot's function</u>, may be defined as temperature".[26]

This theoretical liberalization allowed Thomson much more freedom in matching up the theoretical absolute temperature with existing practical temperature scales (or any other pre-existing meaning of temperature). In linking the abstract back to the concrete, one would look for a theoretically simple definition that was also maximally congruent with the already-established practical temperature measure. This was a substantially different configuration of constraints, compared to how Thomson dealt with the operationalisation of his original 1848 definition of absolute temperature.

But how was Thomson to go about finding a function of μ that meshed nicely with the air-thermometer temperature? As it turned out, the most valuable clue for this step came unsolicited from Joule. In 1854, Thomson made a very important point about absolute temperature in a very unlikely place, namely a long footnote attached to a paper on thermo-electric currents. There he noted an inconvenience with his first definition of absolute temperature, namely that the comparison with air-thermometer temperature showed "very wide discrepancies, even inconveniently wide between the fixed points of agreement." (See **Table 1** above.) Then he added:

> "A more convenient assumption has since been pointed to by Mr Joule's conjecture, that Carnot's function is equal to the mechanical equivalent of the thermal unit divided by the temperature by the air thermometer from its zero of expansion".[27]

What Thomson calls "the temperature by the air thermometer from its zero of expansion" harked back to Guillaume Amontons's idea that the absolute zero of temperature could be obtained by extrapolating the known pressure-temperature relation of gases out to the zero-point of pressure; we will refer to it as the <u>Amontons air-temperature</u>, or simply <u>Amontons temperature</u>.[28]

Joule's conjecture can be expressed as follows:

$$\mu = \frac{JE}{1+Et} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \text{(11)},$$

where *J* is the constant giving the mechanical equivalent of heat, and *E* is the coefficient of gaseous expansion.[29] Thomson took the value of *E* as "very nearly equal to 0.00366 (the centigrade scale of the air-thermometer being referred to)".[30] A more intuitive way of writing the formula would be:

μ=J/(273.2+t), or μ=J/T, ……………. (12),

where *T* is Amontons temperature. As Keith Hutchison demonstrates very clearly, Joule's conjecture and other related ideas that fall under the rubric of "Mayer's hypothesis" played a key role in the early development of thermodynamics.[31]

Before explaining how Joule's conjecture led to Thomson's new definition of absolute temperature (**equation (5)**), we will address another interesting question that is not clearly answered in the existing literature: How did Joule ever come up with such an idea? The answer turns out to be very instructive. In Joule's letter of 9 December 1848, where he states the conjecture to Thomson, it is evident that the idea arises from Joule's critique of the values of "*W/Q*" that Thomson had sent him in a previous letter.[32] What is this quantity *W/Q*? Tantalizingly, the letter in which Thomson discusses that quantity has been damaged and is hardly legible in the crucial portions. However, the parts that we are able to make out do suggest very strongly that what Thomson wrote to Joule there was reproduced almost verbatim in an appendix to his 1849 paper on Carnot's theory.[33] What Thomson discusses in that appendix (read 30 April 1849) is his attempt to understand the heat generated by the compression of air (adiabatic heating) in terms of Carnot's theory. The mysterious *W/Q* is the ratio of work spent in compressing the air, to the amount of heat generated by the compression.

Analysing this operation in terms of Carnot's theory (basically as the third stroke in a simple-gas Carnot engine), Thomson derived the following formula:

$$\frac{W}{Q}=\frac{\mu(1+Et)}{E} \qquad \text{………………. (13).}$$

Using the values of μ that he had calculated using Regnault's data, Thomson came to the conclusion that *W/Q* was a function of temperature, although at a given temperature it was a constant, in which case the work spent was proportional to the heat evolved. For Thomson this was merely another neat consequence of Carnot's theory, but to Joule it was a confirmation of his fundamental belief in the interconversion of heat and work. So the quantity *W/Q* embodied for Thomson the release of heat by mechanical pressure, and for Joule the transformation of work into heat. (The productive Joule-Thomson discourse on *W/Q* seems to be a perfect instantiation of Peter Galison's notion of "trading zones" in science.[34]) But Joule could not accept that *W/Q*, for him the mechanical equivalent of heat, was a function of temperature; it had to be a universal constant. Therefore Joule was convinced that there must be defects in Thomson's estimates of *W/Q* via the estimation of μ from available empirical data. Instead, Joule suggested that *W/Q* should be taken to be a constant a priori, and that μ should be inferred to have just the form that would make *W/Q* a constant. That is, μ should be proportional to $E/(1+Et)$. If we write $J=W/Q$ and simply rearrange **equation (13)**, we obtain **equation (11)**. This, we believe, was the origin of Joule's conjecture. (A rigorous energy-based analysis of adiabatic heating was a more complicated matter than Joule had realized, as we will see in detail in the next section.)

Now comes the final step. If Carnot's function has the form proposed by Joule, then it can be shown from thermodynamic theory that the ratio of the heat taken in and the heat given out in a Carnot cycle is proportional to the ratio of the absolute temperature of the hot reservoir and the temperature of the cold reservoir.[35] Thus we arrive at Thomson's revised definition of absolute temperature (**equation (5)**). The derivation of this result is not given by Thomson in a straightforward way, and it is more perspicacious to follow the exposition given by Andrew Gray's derivation in 1908, in his intellectual biography of

Thomson published shortly after his death.[36] Gray was Thomson's successor in the Glasgow chair of natural philosophy, and his account, though little known now, is probably the best available exposition of the technical aspects of Thomson's work.

From **equations (9) and (10)** above, we have the following expression for the work done in an infinitesimal Carnot cycle: $W=\mu M dv dt$. Putting that together with **equation (8)**, we get $W=\mu Q dt$, where Q denotes the amount of heat taken in by the engine in the first stroke. Now, if we adopt Joule's conjecture in the form of **equation (12)**, that reduces to $W=QdT/T$. If we translate this result into a cycle with a finite temperature interval (writing $T-T'$ instead of dT), we get $W=Q(T-T')/T$. But according to energy conservation, W is equal to the amount of heat destroyed in the operation of the Carnot engine; in other words, $W=Q-Q'$ if we write Q' for the amount of heat released by the engine into the cold reservoir in the third stroke. That gives $Q-Q'=Q(T-T')/T$, which reduces to $Q/Q'=T/T'$ on rearranging the terms. This is just **equation (5)** with a slightly different notation. Now there are some questionable steps in this derivation, especially the jump from the infinitesimal cycle to the finite cycle. But we will not enter into fine-tuned disputes about this derivation, since it rests in any case on the questionable assumption that Joule's conjecture is exactly true. The best test of Joule's conjecture was given in the series of researches which we now identify as the "Joule-Thomson experiment", which was also the crucial link in the measurement of Thomson's revised concept of absolute temperature.

4. The Joule-Thomson effect and the operationalisation of Thomson's second absolute temperature

Having clarified the nature of Thomson's revised concept of absolute temperature (which we will call his <u>second definition of absolute temperature</u>, or just his <u>second absolute temperature</u>), let us now see how he went about measuring it. Thomson, now in full collaboration with Joule, faced the same basic problem as before: A credible Carnot engine could not be constructed in reality. The operationalisation of Thomson's second absolute temperature was a long and gradual process, in which a variety of analytical and material methods were tried out by Joule and Thomson, and by later physicists. The initial method adopted by Joule and Thomson was based on the assumption that gas thermometers gave close enough approximations to Thomson's absolute temperature to provide a good starting point. An ideal gas would give the absolute temperature exactly. The Joule-Thomson experiment was taken to give a measure of how much the actual gases deviated from ideal behaviour, and hence a measure of how much the temperatures measured by actual gas thermometers deviated from absolute temperature. Then actual gas thermometers corrected by the results of the Joule-Thomson experiment would give the absolute temperature.

What was actually measured in the Joule-Thomson experiment (sometimes referred to as the "porous plug experiment") was the amount of cooling that gases experienced in passing through small orifices. The intuitive idea was the following: If it requires energy merely to expand a body of gas without changing its temperature (as is the case with stretching a spring), then in the absence of other sources of energy such an expansion would require the consumption of the heat contained in the gas itself, resulting in the cooling of the gas. The basic scheme of the experiment was laid out by Thomson in 1851, inspired by an 1845 paper of Joule's.[37] The procedure consisted in forcing a continuous stream of gas through two (spiral) pipes connected to each other through a very small orifice. The pipes are long enough for the incoming gas to be brought to the ambient temperature *t* before it enters the orifice, and for the exiting gas to be brought back to that same temperature by the time it reaches the far end of the pipe on the other side (whatever temperature change it may have suffered in the process of coming through the hole). A unit amount of gas (occupying volume V before the passage, and V' on the other side, V'>V because P'<P, where P and P' are the corresponding pressures) will emit (or absorb) a certain amount of heat (H) in thus being brought back to the original temperature. H gives a direct measure of the cooling effect.

As mentioned above, the measured cooling effect was used to derive an equation for the behaviour of actual gases as a function of absolute temperature, showing how they deviate from the ideal gas law. Joule and Thomson's "complete solution" was the following:[38]

$$v = \frac{Ct}{p} - \tfrac{1}{3} AJK \left(\frac{273.7}{t} \right)^2 \qquad \text{………. (14).}$$

This equation expresses *t*, "the temperature according to the absolute thermodynamic system of thermometry", in terms of other parameters, all of which are presumably measurable: *v* is the volume of a given body of gas; *p* is its pressure; *C* is a parameter "independent of both pressure and temperature"; *A* seems to be a constant that is characteristic of each type of gas; *J* is the mechanical equivalent of heat; and *K* is the specific heat per unit mass of the gas under constant pressure. So **equation (14)** in principle indicates a straightforward way of measuring *t*. The second term on the right-hand side gives the measure of deviation from the ideal; without it, **equation (14)** would simply reduce to the ideal gas law, which would mean that the conventional gas thermometer correctly indicates the "temperature according to the absolute thermodynamic system of thermometry".

The derivation of **equation (14)** was a complex theoretical and experimental matter on which Joule and Thomson spent a decade, but we can offer the following summary. Thomson started with an estimate of the heat absorbed (or emitted) by the gas in being brought back to the original temperature.[39] One part of this is "the heat produced by the fluid friction", and the other part (assumed to be negative) is the heat emitted from the gas "in virtue of its expansion".

In order to estimate the first part, begin by noting that the overall outcome of this process is to take a unit amount of the fluid from the initial state occupying volume *V* at pressure *P* and temperature *t*, to the final state occupying volume *V′* at pressure *P′* and the same temperature *t*. Thomson's derivation is quite murky after that point, but a corresponding passage in his 1854 paper with Joule is clearer.[40] As a result of the specified expansion, the gas would do the following amount of work:

$$w = \int_{V}^{V'} p\,dv \qquad \text{.............. (15).}$$

Part of this work, *P'V'*, would be spent in pushing out against the pressure *P'* on the exit end; on the other hand, an amount of work *PV* would be done on the gas by the external agent pushing on the entry end. So overall, the amount *P'V'-PV* would be spent by the gas in its interaction with its external environment. Subtracting that amount from *w* above gives the work done that is not spent in the above macroscopic dynamic effects, which must be turned into heat (internal energy).[41] That, divided by the mechanical equivalent of heat, gives the amount of heat produced by the fluid friction:

$$\frac{1}{J}\left\{\int_{V}^{V'} p\,dv + PV - P'V'\right\} \qquad \text{............. (16)}$$

The estimation of the second part (the heat emitted by the gas "in virtue of its expansion") is done by noting that the expansion of the gas with fixed temperature is equivalent to the first stroke of the Carnot cycle (isothermal expansion with heat input from hot reservoir). The heat absorbed in that process can be expressed as:

$$\int_{V}^{V'} M\,dv \qquad \text{................ (17),}$$

which can serve as the definition of the quantity *M*, as in **equation (8),** for the infinitesimal case. The next important step, for our current purposes, is to express this quantity in terms of μ --- if we could do that, then we would be able to express the observed Joule-Thomson effect as a function of μ. Substituting **equation (10)** into **equation (17)** gives the desired expression for the amount of heat absorbed by the expanding gas:

$$\frac{1}{\mu}\int_{V}^{V'} \frac{dp}{dt}\,dv \qquad \text{.................. (18)}$$

Finally, then, the total heat emitted in the Joule-Thomson process by a unit amount of gas is given by subtracting **equation (18)** from **equation (16)**:[42]

$$H = \frac{1}{J}\left\{\int_{V}^{V'} p\,dv + PV - P'V'\right\} - \frac{1}{\mu}\int_{V}^{V'} \frac{dp}{dt}\,dv \qquad \text{............ ... (19).}$$

This can be turned into a usable expression for μ (Carnot's function) by the following few simple steps: write $w = \int_V^{V'} p dv$ as above; write H = –Kδ, where δ is the cooling effect in temperature when the gas is allowed to cool, and *K* is the specific heat of the gas under constant pressure). Then simply re-arrange some terms, to get:[43]

$$\frac{1}{\mu} = \frac{\frac{1}{J}\{\mathrm{w} - (\mathrm{P'\,V'} - \mathrm{PV})\} + \mathrm{K}\delta}{\frac{\mathrm{dw}}{\mathrm{dt}}} \qquad \text{..............} \ (20)$$

(Here and elsewhere, we have changed Joule and Thomson's notation slightly.)

Equation (20) can be rearranged and simplified as follows, noting that *t=J/μ*, according to Thomson's new definition of absolute temperature.[44]

$$\mathrm{JK}\delta = \mathrm{t}\frac{\mathrm{dw}}{\mathrm{dt}} - \{\mathrm{w} - (\mathrm{P'\,V'} - \mathrm{PV})\} \qquad \ldots\ldots\ldots\ldots\ldots \ (21).$$

This, in turn, can be written as follows, putting in the definition of *w* from above, and exchanging the order of differentiation and integration:

$$\delta = \frac{1}{\mathrm{JK}}\left\{\int_{\mathrm{v}}^{\mathrm{v'}}\left(\mathrm{t}\frac{\mathrm{dp}}{\mathrm{dt}} - \mathrm{p}\right)\mathrm{dv} + (\mathrm{P'\,V'\text{-}PV})\right\} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \ (22),$$

which is the most convenient of the various possible relations which can yield *t* from other measurable quantities (in this case *J, K, p, v, δ*).[45] Picking up this relation again in the addendum to their paper of 1862, Joule and Thomson transform it further as follows. They use ϑ, the observed Joule-Thomson temperature rise, instead of δ (so, ϑ=–δ). They also re-write the formulae with *p* instead of *v* as the independent variable; this involves putting *w* as $\int_P^{P'} v dp$ into **equation (21)** above. And then they differentiate both sides of the equation with respect to *p*, to arrive at the following formula:[46]

$$\frac{d\vartheta}{dp} = -\frac{1}{JK}\left(t\frac{dv}{dt} - v\right) \qquad \ldots\ldots\ldots\ldots\ldots \ (23).$$

Given **equation (23)**, the next task was to reduce this equation so that it was only in terms of *p, v* and *t* (with no differentials), after which it could serve as "the equation of elasticity". That is where data from the Joule-Thomson experiments helped, because they provided an empirical formula for dϑ/dp.

The empirical formula given by the results of these experiments was an inverse-square function of *t*, with different coefficients *A* for different gases:

$$-d\vartheta/dp = A(273.7/t)^2 \qquad \ldots\ldots\ldots\ldots\ldots \text{(24).}$$

The value of *A* is 0.92 for air, and 4.64 for carbonic acid.[47] Substituting **(24)** into **(23)**, we get the following differential equation for *v* as a function of *t*:

$$t\frac{dv}{dt} - v = AJK\left(\frac{273.7}{t}\right)^2 \qquad \ldots\ldots\ \ldots\ldots \text{(25),}$$

to which Joule and Thomson give the following solution:

$$v = Bt - \tfrac{1}{3}AJK\left(\frac{273.7}{t}\right)^2 \qquad \ldots\ldots\ldots\ldots\ldots\ \text{(26),}$$

where *B* is "an arbitrary constant with reference to *t*, which, so far as this integration is concerned, may be an arbitrary function of *p*" . In determining the form of *B*, Joule and Thomson noted: "Now it is generally believed that at higher and higher temperatures the gases approximate more and more nearly to the rigorous fulfilment of Boyle's law."[48]. In that case, **(26)** should reduce to a simpler form indicating a proportionality between *v* and *1/p*; considering that the second term on the right-hand side will tend to 0 as *t* becomes large, this means that *B* should be "approximately *C/p*, *C* being independent of both pressure and temperature". Substituting that into **(26)** gives Joule and Thomson's "complete solution", namely **equation (14)** above.[49]

Now it seemed that Thomson and Joule had finally succeeded in reducing absolute temperature to measurable quantities, and they in fact proceeded to compute some numerical values for the deviation of the air thermometer from the absolute scale. The results (see **Table 2**) were quite reassuring for the air thermometer: although the air-absolute discrepancy increased steadily as the temperature increased, it was estimated to be only about 0.4°C at around 300°C for Regnault's standard air thermometer.[50] Joule and Thomson were quite justifiably pleased.

However, there remained a serious quandary, which Thomson clearly acknowledged many years later. The crucial empirical parameters entering into **equation (24)** above, namely *J*, *K*, and $d\vartheta/dp$, were all calculated from temperatures measured by ordinary thermometers. Thus the Joule-Thomson measurement of absolute temperature still had to rely on practical thermometers. The correction of the air thermometer to give absolute temperature was done by the measurement of the Joule-Thomson effect, but the latter measurement was given by the air thermometer itself (actually, by the mercury thermometer underwritten by the air thermometer). In that situation, how can we be assured that the correction was correct? Note that the situation here is fundamentally different from that of Thomson's scheme for operationalising his first definition of absolute temperature. In that case, the use of empirical data taken with the air thermometer did not pose a problem because Thomson was seeking an explicit correlation of absolute temperature and air-thermometer temperature. To see that the Joule-Thomson scheme is different, it is sufficient for now to note that the differential equation **(25)** cannot be solved if one *t* there denotes absolute temperature and the other *t* denotes air-thermometer temperature. But we will return to this issue in more detail in **section 6**.

Absolute temperature, with zero set at -273.7°C	Air-thermometer temperature, with zero set at the same point
0	0
20	20 + 0.0298
40	40 + 0.0403
60	60 + 0.0366
80	80 + 0.0223
100	100
120	120 - 0.0284
140	140 - 0.0615
160	160 - 0.0983
180	180 - 0.1382
200	200 - 0.1796
220	220 - 0.2232
240	240 - 0.2663
260	260 - 0.3141
280	280 - 0.3610
300	300 - 0.4085

***Table 2**. Joule and Thomson's (1854) comparison of absolute temperature with temperature indicated by a constant-volume air thermometer filled with a body of*

air at atmospheric pressure at the freezing point of water. The size of one absolute degree is set to be the same as one centigrade degree.

5. Thomson's re-formulation of the second definition of absolute temperature

As seen in the last section, Joule and Thomson by 1862 indicated quite clearly how Thomson's second absolute temperature could be operationalised, by taking the air thermometer or another gas thermometer and correcting its readings by means of the observed values of the Joule-Thomson effect. But we have not seen evidence that much use was made of this absolute temperature in any practical way in the following two decades. Perhaps spurred on by the dearth of application, Thomson returned to the subject of absolute temperature seriously when he was commissioned in 1878 to write the entry on "Heat" for the 9th edition of the Encyclopaedia Britannica. This contribution constituted a distinct advance over his joint work with Joule up to 1862, as will be explained below.

In the Britannica article, published in 1880, Thomson gave two new formulations of the absolute temperature concept, both meant to be equivalent to the second definition. Both are puzzling. We have not been able to make clear sense of the first formulation, but merely mention it here in the hope that someone with more insight will be able to propose a way of understanding it.[51] At any rate, the second formulation is the one that Thomson actually makes use of. It is only given verbally, as follows:[52]

> "Let the thermometric body be infinitesimally warmed by stirring a portion or the whole of itself if it be partially or wholly fluid, or by stirring a quantity of fluid in space around it if it be all solid; and during the process let the stress upon the body be kept unchanged. The body expanding or contracting or changing its shape with the heat, as the case may be, does work upon the surrounding material by which its stress is maintained. Find

> the ratio of the amount of work thus done to the amount of work spent in the stirring. For brevity we shall call this the work-ratio. Again, let the stress be infinitesimally increased, the thermometric body being now for the time enclosed in an impermeable envelope so that it may neither gain nor lose caloric. It will rise (or fall) in temperature in virtue of the augmentation of stress. The ratio of this infinitesimal elevation of temperature to the whole absolute temperature is equal to the work-ratio multiplied into the ratio of the infinitesimal augmentation of stress to the whole stress."

To the best of our knowledge, Thomson never published an explanation of how the above cumbersome formulation was equivalent to the simple definition of 1854. In the following we will give our own interpretation, in which we have been helped once again by Andrew Gray's exposition.[53]

The 1880 formulation can be understood as an intermediate product of a long chain of reasoning aimed at rendering Thomson's second definition of absolute temperature (1854) in more and more measurable terms without actually constructing a perfectly reversible Carnot engine. Let us start by making a definition of the efficiency of a heat engine, η, as the ratio of the overall work produced in one cycle of the engine's operation, to the amount of heat absorbed in the first stroke.[54] The efficiency can be written as follows:

$$\eta=\Delta W/Q \qquad \ldots\ldots\ldots\ldots\ldots \ (27).$$

Similarly as in the reasoning given in the last paragraph of **Section 3**, we can estimate ΔW as follows. Because of energy conservation, the work produced in the cycle would be equal to the amount of heat destroyed in the operation of the engine, which is just the difference between the amount of heat taken in by the working substance in the first stroke (Q) and the amount of heat given out by the working substance in the third stroke (Q'). Therefore the efficiency can be expressed as:

$$\eta = (Q-Q')/Q \qquad \ldots\ldots\ldots\ldots\ldots\ldots.. \ (28),$$

using the same units for work and heat. But, according to the 1854 definition of absolute temperature, such a ratio of heats would correspond directly to the ratio of absolute temperatures (T, T') at which the heat input and output take place:

$\eta = (T-T')/T$ ……………… (29).

Now, if we take this for a cycle in which T is just infinitesimally higher than T', we can write the above as:

$\eta = dT/T$ ……………….. (30).

Putting that together with the original definition of efficiency, **equation (27)**, we have a promising relationship:

$\Delta W/Q = dT/T$ …..…………… (31).

But the quantities ΔW and Q are still not measurable, since they refer to the perfect Carnot engine. So Thomson sought to express the $\Delta W/Q$ ratio in terms of the work and heat amounts involved in the first stroke of the cycle only.[55] If we can just deal with the first stroke, we do not have to deal with the full impossibility of creating a material version of the perfect Carnot cycle. The first stroke alone is quite a lot easier to realize in a material system: simply a working substance that does work by expanding with the absorption of heat. This still needs to be a reversible process, so by no means straightforward to realize, but the difficulty would be reduced. In order to simplify the theoretical derivation, Thomson stipulated that the first-stroke expansion should take place under constant pressure ("during the process let the stress upon the body be kept unchanged", in the passage quoted above). That is not a condition that can be met in an isothermal stroke of a Carnot cycle whose working substance is only a gas, but it would be conveniently met in a liquid-vapor system. Now conceive ΔW as the difference between the work done by the working substance in the first stroke and the work done to it in the third stroke, ignoring the second-order infinitesimal quantities of work involved in the second and fourth strokes. Then we can write: $\Delta W = W - W'$. That can be expressed in a simple way in terms of the pressures involved, since we are assuming the pressure to be constant in each of the two strokes. So,

$\Delta W = pdv - p'dv = dpdv$ …………… (32), where *dv* is the infinitesimal increment of volume in the first stroke, which is equal to the contraction of volume in the third stroke, to the first order. The above can be re-written as follows:

$\Delta W = (dp/p)(pdv) = (dp/p)W$ ……………. (33).

Inserting this into **equation (31)** above, we have:

$dT/T = \Delta W/Q = (W/Q)(dp/p)$ …. ……….. (34),

which is a formal expression of Thomson's verbal formulation cited initially, since W/Q is what he means by the work-ratio.

How about the case of the gas engine? The above derivation, premised on the assumption of constant pressure in the isothermal first stroke of the Carnot cycle, is not applicable when the working substance is a simple gas. In fact, as in an earlier derivation, it is quite puzzling how Thomson intended his new formulation of absolute temperature to be applied to the case of gas engines. A gas cannot stay at the same temperature if it is to increase its volume under constant pressure, but the 1854 definition of absolute temperature only applies to a cycle in which the working substance takes or loses heat at fixed temperatures. We can only conclude that Thomson's 1880 formulation constituted a non-trivial broadening of the absolute temperature concept, in effect a third definition.

Now let us see how Thomson made use of **relation (34)** in order to measure absolute temperature. How the operationalisation should go in the steam-water case is quite straightforward, at least in principle. In that case *Q*, reckoned per unit volume of the working substance, is simply the latent heat of steam evolved in mechanical units, which Thomson writes as $J\rho\kappa$, where ρ is the density of steam and κ is the latent heat of steam per unit mass, and *J* is the mechanical equivalent of heat. *W* is the work done by the created steam in pushing against pressure *p* for the relevant volume increment, which is $1-\sigma$, where σ is the density-ratio of steam to water, so $W=p(1-\sigma)$. Substituting these expressions for *Q* and *W* into **relation (34)** gives an easily soluble differential equation. Thomson was quite pleased with this result, and expressed his hope that the steam-pressure thermometer built on his scheme was "destined to be of great service both in the strictest scientific thermometry and as a practical thermometer for a great variety of useful applications."[56]

How was the Joule-Thomson effect treated in this new mode of analysis? What Thomson gives in his 1880 article is more elegant than the derivations in the original Joule-Thomson papers, but it is still somewhat elaborate, so we will give a simplified version, again taking our cue from Gray's exposition.[57] The Joule-Thomson experiment can be conceptualised as a process in which a body of gas at a higher pressure goes into a more expanded state at a lower pressure. We can write that the body of gas has pressure $p+\delta p$ and volume v before it enters the plug, and pressure p and volume $v+\delta v$ afterwards. The gas will change its temperature in the process. To conclude the experiment, the gas is brought back to its initial temperature; Thomson stipulates that this is done through a mechanical agitation that provides a certain amount of frictional heat by mechanical action, the amount of which is δw. Now consider the change (δe) made by this entire process in the internal energy (e) of the gas, which consists of two parts. First, the net mechanical work done on the gas in the process of pushing it through the plug is: $(p+\delta p)v - p(v+\delta v) = v\delta p - p\delta v$. Then there is the heat added by mechanical agitation. Summing the two, we have:

$$\delta e = v\delta p - p\delta v + \delta w \qquad \text{....... .... (35)}$$

Now imagine going from the same initial state of the gas to the final state, but in a different process. In particular, if we let the change take place isothermally, the gas would go through an expansion in which it does external work $p\delta v$ while absorbing a certain amount of heat, which we can simply write as δQ. But how can the work simply be $p\delta v$, when the pressure will be changing from $(p+\delta p)$ to p in the process? That would be because the contribution to the total work amount caused by the pressure change would be in the order of $\delta v\delta p$, which is second-order, and hence negligible if δv and δp are much smaller than v and p. Allowing that approximation, the change in internal energy for the isothermal case is the following:

$$\delta e = \delta Q - p\delta v \qquad \text{............. (36).}$$

Since the two processes have the same endpoints, they should have the same amount of overall change in internal energy. So we can equate **(35)** and **(36)**, which gives:

$$\delta Q = v\delta p + \delta w \qquad \text{.............. (37).}$$

We can now consider the isothermal expansion as the vehicle for the operationalisation of absolute temperature, referring back to **equation (34)** above. The work ratio is:

$$(p\delta v) / (v\delta p + \delta w) \qquad \text{.............. (38).}$$

If we consider the infinitesimal case, we can insert that expression into **equation (34)**, which gives the following:

$$\frac{dT}{T} = \left(\frac{pdv}{vdp + dw} \right) \frac{dp}{p} \qquad \text{............... (39).}$$

But it is not clear why the analysis of the infinitesimal case would be relevant, because the pressure and volume changes in the Joule-Thomson experiments are certainly not infinitesimal. Setting that point aside for now, if we carry on with the derivation for the infinitesimal case, the above equation can be rewritten as follows:

$$\frac{v}{T}\frac{dT}{dv} = \frac{vdp}{vdp + dw} = \frac{1}{1 + \dfrac{dw}{vdp}} = \frac{1}{1 + \dfrac{JK}{v}\dfrac{d\theta}{dp}} \qquad \text{................ (40).}$$

In the last step we have substituted *dw* with J*K(dθ)*, where *J* is the mechanical equivalent of heat, *K* is the specific heat of the gas under constant pressure, and *dθ* is the Joule-Thomson cooling effect obtained through an expansion accompanied by the reduction of pressure by *dp*. Therefore we have now an equation that expresses *T* in terms of *v* and *p*, and some empirically determined parameters. This equation is equivalent to **equation (23)** in **section 4**, and can be solved by putting in the empirical formula for $d\theta/dp$, inferred from the observed variation of cooling effect with pressure. More details about the solutions were given in that section.

Aside from increased theoretical sophistication (e.g. the explicit use of the internal energy function), Thomson's 1880 article was also epistemologically more aware than his previous works. He now noted clearly the epistemic quandary with which we closed **section 4** above, namely that the Joule-Thomson correction of the air thermometer was being calculated on the basis of measurements taken by the air thermometer itself. (Joule actually used mercury thermometers, which was justified by the fact that the mercury thermometer and the air thermometer agreed very well in the relevant temperature range.) In the 1880 paper, Thomson confessed:

> "We have no right to measure these [Joule-Thomson] heating and cooling effects on any scale of temperature, as we have not yet formed a thermometric scale…."

He indicated how the problem could be avoided, in principle: "Now, instead of reckoning on any thermometric scale the cooling effect or the heating effect of passage through the plug, we have to measure the quantity of work (δw) required to annul it". But he was aware, of course, that "the experiments as actually made by Joule and Thomson simply gave the cooling effects and heating effects shown by mercury thermometers".

Thomson's level of awareness was, however, not quite matched in the quality of the solution he proposed in the end:

> "The very thermometers that were used [in the Joule-Thomson experiment] had been used by Joule in his original experiments determining the dynamical equivalent of heat [J], and again in his later experiments by which for the first time the specific heat of air at constant pressure [K] was measured with sufficient accuracy for our present purpose. Hence by putting together different experiments which had actually been made with those thermometers of Joule's, the operation of

> measuring δw, at all events for the case of air, was virtually completed. Thus according to our present view the mercury thermometers are merely used as a step in aid of the measurement of δw, and their scales may be utterly arbitrary…."[58]

What Thomson claims here is that the temperature measurements are merely particular ways of getting at the value of the quantity δw, and the final result is independent of the particular method by which it is obtained. Thomson's claim is hollow, unless it happens to be the case that the resulting empirical formula for δw is not a function of mercury-temperature at all. But we have seen that δw is a function of mercury-temperature (t) in general.[59] The same point can be seen even more clearly if we take the view that certain errors are introduced into the values of J, K, and $d\theta/dp$, if those values are obtained on the basis of the assumption that the mercury thermometer readings indicate the absolute temperature. Under that view, Thomson's claim amounts to insisting a priori that all such errors cancel each other out in the final result. In this case, errors in J, K, and $d\theta/dp$ should cancel each other out in the expression $JK(d\theta/dp)$. That is just about possible, but by no means guaranteed.

6. Iteration in the measurement of absolute temperature

That seems to be where Thomson left the problem. In the corpus of Thomson's work after the time of the Britannica article, we have not found any further contributions to the measurement of absolute temperature. Thomson was apparently quite satisfied in 1880 with the theoretical understanding of absolute temperature that he had been able to secure in the framework of a fully developed theory of thermodynamics, and in practical terms he was happy with the old Joule-Thomson empirical results that gave sufficient indication that the deviations of gas-thermometer temperature from his second absolute temperature were quite small. But a much more satisfying epistemic understanding of the problem of operationalising absolute temperature was to emerge within a decade, apparently starting with the work of Hugh Longbourne

Callendar, English physicist and engineer who made important observations on the properties of steam and crucial contributions to platinum-resistance thermometry. In this section we will present the basic points of Callendar's work, mostly on the basis of the exposition given by Henri Louis Le Chatelier.[60]

The most important starting point of Callendar's analysis was to make it plainly explicit that air-thermometer temperature and absolute temperature had not been shown to be equal to each other. He also recognized that they could not be compared with each other in any direct way since there was no method of estimating absolute temperature without making use of measurements taken with the air thermometer (or some other practical thermometer). Therefore he consciously engaged in an iterative process, starting with air-thermometer temperature as given and sketching out loops of self-improvement to approach absolute temperature in stages.

In Le Chatelier's version of Callendar's method, we start by writing the law governing the thermal behaviour of actual gases as follows:

$$pv = RT(1-\phi) \qquad \ldots\ldots\ldots\ldots\ldots (41),$$

where R is a constant, T is absolute temperature, and ϕ is an as-yet unknown function of T (and p). The factor ϕ is what makes **(41)** different from the ideal gas law, and ϕ is presumed to be small in magnitude, although its exact form is unknown. The form of ϕ could be determined if a data series giving sets of values for p, v and T could be entered into **(41)**. But T is the absolute temperature and cannot be measured, so instead we enter t, the temperature values measured by the air thermometer (which is an instrument that assumes that ϕ is zero for air). If t is an approximation to T, then ϕ computed by this procedure will be an approximation to the true form of it. Using this approximate ϕ-function, corrections to t can be made so that it approximates T more closely. If the iteration works, repeating this procedure will bring t closer and closer to T, until it is close enough for whatever purposes we have.

The procedure using the Joule-Thomson measurements is somewhat more complicated. For that case the iterative procedure goes as follows. The theoretical framework is **equation (37)** from **section 5**, which is obtained by assuming that the change in internal energy of the gas in the Joule-Thomson experiment is the same as when the gas expands with pressure going from P_1 to P_2 but with no overall change in the temperature, which is *T* at the beginning and the end of the process. What **(37)** expresses is the amount of heat absorbed by the gas in the process, and it can be re-written in integral form, as follows:[61]

$$Q=\frac{1}{J}\int_{P_1}^{P_2} v\,dp+\frac{1}{J}\int_{P_1}^{P_2}\frac{dw}{dp}\,dp \qquad \ldots\ldots\ldots\ldots\ldots\ldots \text{(42).}$$

Similarly, if we have the same equation applying to a situation at a different temperature, *T'*, we have the following parallel relation:

$$Q'=\frac{1}{J}\int_{P_1'}^{P_2'} v\,dp+\frac{1}{J}\int_{P_1'}^{P_2'}\frac{dw}{dp}\,dp \qquad \ldots\ldots\ldots\ldots\ldots\ldots \text{(43).}$$

The theoretical set-up is completed by two further steps. First, substitute for *v* in (42) and (43) the expression $RT(1-\phi)/p$, which follows from the initial premise of Callendar's analysis. Then set $Q/T-Q'/T'=0$, which is simply Thomson's second definition of absolute temperature (from 1854). Then we have:

$$\log_e\frac{P_2P_1'}{P_1P_2'}-\int_{P_1}^{P_2}\left(\frac{\phi}{p}-\frac{J}{RT}\frac{dw}{dp}\right)dp+\int_{P_1'}^{P_2'}\left(\frac{\phi'}{p}-\frac{J}{RT'}\frac{dw'}{dp}\right)dp=0 \qquad \ldots\ldots\ldots\ldots\ldots\ldots \text{(44),}$$

where the primed quantities are those pertaining to processes taking place at temperature *T'*. Le Chatelier states that the first term in **(44)** is zero according to the law of adiabatic expansion, which is assumed to hold approximately. The only way, then, for **(44)** to hold generally is for the integrand to go to zero in each of the latter two terms. That gives an expression for the function ϕ, as follows:

$$\phi=\frac{dw}{dp}p\frac{J}{R}\frac{1}{T} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \text{(45).}$$

Now the theoretical part is over, and the experimental data can be entered into **equation (45)**. As before the Joule-Thomson data gives observations for the term *dw/dp*. Inserting the formula for the case of air, and the values of *J* and *R*, Le Chatelier gives the following empirical expression for ϕ:

$$\phi=0.001173\frac{p}{p_o}\left(\frac{T_o}{T}\right)^3 \qquad \ldots\ldots\ldots\ldots\ldots\ldots \text{(46),}$$

where p_o is the atmospheric pressure and T_o is the temperature of melting ice.

Le Chatelier was very clear that **equation (46)** did not give the final correction: "This is still an approximate result, for we have depended upon the experiments of Joule and Thomson and on the law of adiabatic expansion; however the approximation is more close. If it seems sufficient for air, it is certainly not so for carbonic acid. Neither is the formula rigorously exact for air."[62] More iterative loops would yield more fine-tuning. However, it seems that no one was worried enough to make the second-round corrections or beyond. Callendar calculated the first-round corrections on air up to 1000°C; the corrections did get larger with increasing temperature, but turned out to be only 0.62° at 1000°C for the constant-volume air thermometer, and 1.19° for the constant-pressure air thermometer. As 1000°C was about the very limit at which any gas thermometers could be made to function credibly,[63] the fact that the corrections would grow rapidly beyond that point was not so much of a practical concern. Le Chatelier was happy to declare: "The deviations of the air-thermometer at high temperatures are thus very slight if concordance is established at 0° and 100°; we shall not have to occupy ourselves further with the differences between the indications of the thermodynamic thermometer and those of the gas-thermometer." One only needed to avoided gases like carbon dioxide, for which the corrections were significantly larger.[64]

A similar assessment of the situation was given twenty years later by A. L. Day and R. B. Sosman, also with the greatest conceptual clarity on the matter that we have come across:

> "It is important at this point to recall that our initial measurements with the gas-thermometer tell us nothing about whether the gas in question obeys the law $pv=k\theta$ or not. Only measurements of the energy-relations of the gas can give us that information. But since such measurements involve the measurement of temperature, <u>it is evident that the realisation of the temperature scale is logically a process of successive approximations</u>. Practically, the first approximation is sufficient, so nearly do the gases commonly used in gas-thermometers conform to the 'ideal' behaviour expressed in the law $pv=k\theta$."[65]

We will close the discussion with a few epistemological points about the iterative process of "successive approximations". First of all we must recognize the wondrous groundlessness of it. No one whose work we have examined has demonstrated that there will certainly be a convergence to a well-defined limit in the successive approximations to absolute temperature, if they are carried out. In mathematics, conditions of iterative convergence can be discerned easily, because the true function we are trying to approximate is already known, or at least knowable. In the epistemic version of iteration the true function is not known. So the only thing we can do is to carry on with the iteration until we are pragmatically satisfied that a convergence seems destined to happen in further loops. And whether there will be such a satisfactory outcome cannot be predicted before actually carrying out the iteration. The case of absolute temperature is a happy story, because one iterative loop turned out to be enough for all practical purposes.[66]

The groundlessness of epistemic iteration means that one's exact starting point is not important, as long as it is within certain reasonable limits. **Equation (41)** happened to hit the nail nearly on the head, but the iterative correction process could have started from various other initial approximations and reached similar final results. This makes sense of why Thomson was able to make certain shortcuts and apparently unwarranted approximations in his various derivations without much of a tangible consequence, just as it was allowable for Callendar to use the Joule-Thomson data and the adiabatic gas law, knowing that both were not guaranteed to be exactly right. Therefore Thomson's defence of the use of the mercury thermometer in the Joule-Thomson experiment was not only invalid as noted in **Section 5**, but also unnecessary. The Joule-Thomson experiment was not the only way to obtain the desired results either. In fact, Joule and Thomson themselves noted in 1862, with evident pleasure, that Rankine had used Regnault's data to obtain a formula for the law of expansion of actual gases that was basically the same as their own result based on the Joule-Thomson experiment (our **equation (14)**).[67]

Similarly, identifying the operationalisation of absolute temperature as an iterative process also helps us recognize that the theoretical definition of temperature did not need to be very precise or restrictive, no more than the processes of reasoning used in its operationalisation. The use of the Carnot cycle was definitely unnecessary, and Thomson should have felt free to kick that ladder away. Even the liberalized definition of 1854 was overly restrictive, since it required the estimation of heat input and output in isothermal processes. A concept of temperature transcending the properties of particular gases could have been created by simply postulating an "ideal gas temperature", which is given by the expansion of an ideal gas. Seeing that actual gases expand nearly uniformly according to various gas-thermometer temperatures, one could have created a theoretical system in which an ideal gas expands uniformly with absolute temperature. The concepts of "ideal gas" and "absolute temperature" created in that way would have been rather empty and very imprecise in many ways, but they would have been sufficient to support iterative processes along the lines of Callendar's work, or Joule and Thomson's, or Rankine's.

Those last remarks lead to the question of truth. If the absolute temperature concept could be derived from an idealization of the behaviour of actual gases, doesn't that suggest a rather straightforward realist construal of the whole episode? Consider, for example, Stathis Psillos's take on the epistemic status of the ideal gas law: "The law of gases, $PV=RT$ …. is approximately true of real gases, since it is true of ideal gases and the behaviour of real gases approximates that of ideal gases under certain conditions." This brief example is given as an illustration of Psillos's intuitive theory of truth-likeness, in which a theoretical description is said to be truth-like about a real system if it is strictly true about a model that approximates the real system.[68] The trouble is that it is not so simple to know whether the behaviour of real gases approximates the behaviour of ideal gases. We can surely observe that real gases nearly obey the ideal gas law, but that is done by interpreting the "T" term in the law as temperature measured by an actual gas thermometer. The "T" term in the ideal gas law that is strictly obeyed by an ideal gas is Thomson's abstract absolute temperature. Therefore the observed approximation to the "ideal gas law" says nothing about how similar real gases are to ideal gases, unless we already know that gas-thermometer temperature is close enough to absolute temperature. It is this circularity that necessitates the process of successive approximations, or, epistemic iteration.

In terms of truth, then, what is it that we can really know? Can we ever say whether we have obtained the true values of absolute temperature? That question only makes sense if there is sufficient objective reality to the concept of absolute temperature so that there is an objectively determinate value of absolute temperature to each physical situation.[69] But whether or not there is such objective reality is only determined by the iterative procedure. And that determination is constitutive -- that is to say, Thomson's absolute temperature does not have objective reality aside from the convergence of its iterative operationalisation. When we have achieved convergence in some operationalisation of absolute temperature, and only then, can we meaningfully ask how much the temperatures indicated by various actual thermometers differ from absolute temperature. The kind of successive approximation we have witnessed is, when it works, surely an approach to a kind of truth. However, that truth is a destination that is only created by the approach itself.

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Notes

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[1] Thomson [1848] (1882), p.100; emphasis added.

[2] See Chang (2001) for further discussion of Regnault's minimalist metrology.

[3] Thomson [1848] (1882), pp. 101-102; emphases original; see also Joule and Thomson [1854] (1882), p. 393.

[4] Thomson [1848] (1882), p.100.

[5] Thomson [1848] (1882), p.101.

[6] See the introductory chapter in Regnault (1847).

[7] Thomson [1848] (1882), p.102; emphases original.

[8] Thomson [1848] (1882), p.104.

[9] For the treatment of the air engine, see Thomson [1849] (1882), pp. 127-133.

[10] This is adapted from the figure in Thomson [1849] (1882), p. 124.

[11] See Thomson [1849] (1882), pp. 125-126, for this passage and the following reasoning.

[12] This table, announced in Thomson [1848] (1882), p. 105, can be found in Thomson [1849] (1882), p. 139 and p. 141, in slightly different forms than originally announced.

[13] Thomson [1848] (1882), pp. 104-105. Thomson also had to use Boyle's and Gay-Lussac's laws to get anywhere in reasoning out the air-engine case; see pp. 129, 131.

[14] Thomson [1848] (1882), p. 106.

[15] For details about Joule's life and work, see Cardwell (1989), and Smith (1998).

[16] See e.g., Cardwell (1989), Ch. 5 and Ch. 8.

[17] Joule to Thomson, 6 October 1848, Kelvin Papers, Add. 7342, J61, University Library, Cambridge.

[18] Thomson to Joule, 27 October 1848, Kelvin Papers, Add. 7342, J62, University Library, Cambridge.

[19] Thomson [1849] (1882), pp. 116-117.

[20] Although Thomson clearly preserved as much as he could from the old analyses in the formal sense, the following claim made in 1881 seems to me like unhelpful bravado: "This paper [of 1848] was wholly founded on Carnot's uncorrected theory …. the consequently required corrections …. however do not in any way affect the absolute scale for thermometry which forms the subject of the present article." What Thomson did demonstrate was that there is a simple numerical conversion formula that holds between the two definitions of absolute temperature: $T_1=100(\log T_2-\log 273)/(\log 373-\log 273)$. See the retrospective note attached to Thomson [1848] (1882), p. 106.

[21] Joule and Thomson [1854] (1882), p. 394.

[22] Thomson [1854] (1882), p. 235: "Definition of temperature and general thermometric assumption. -- If two bodies be put in contact, and neither gives heat to the other, their temperatures are said to be the same; but if one gives heat to the other, its temperature is said to be higher. The temperatures of two bodies are proportional to the quantities of heat respectively taken in and given out in localities at one temperature and at the other, respectively, by a material system subjected to a complete cycle of perfectly reversible thermodynamic operations, and not allowed to part with or take in heat at any other temperature: or, the absolute values of two temperatures are to one another in the proportion of the heat taken in to the heat rejected in a perfect thermo-dynamic engine working with a source and refrigerator at the higher and lower of the temperatures respectively."

[23] Thomson [1849] (1882), pp. 133-134. Here we have written *W* (for mechanical work) where Thomson wrote *M*, in order to avoid confusion with another parameter that he also denoted as *M* in later papers. In various other places we have also changed Thomson's notation slightly, for clarity and consistency.

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[24] The following derivation of the form of Carnot's function is taken from Thomson [1851a] (1882), pp. 187-188 (§21).

[25] What we have here is a partial derivative ?p/?t. Thomson did not use a separate notation for partial derivatives.

[26] Joule and Thomson [1854] (1882), p. 393; emphasis added. It is stated there that all of this was already said in Thomson's 1848 paper, but that is incorrect.

[27] Thomson [1854] (1882), p. 233 (footnote). A similar statement was also given in Joule and Thomson [1854] (1882), pp. 393-394: "Carnot's function varies very nearly in the inverse ratio of what has been called 'temperature from the zero of the air-thermometer,' that is, Centigrade temperature by the air-thermometer increased by the reciprocal of the coefficient of expansion; and we may define temperature simply as the reciprocal of Carnot's function."

[28] Amontons temperature, whose main feature is counting up temperatures from the absolute zero point, is quite close to what people commonly mean by "absolute temperature" nowadays if they have not studied carefully what is meant by the notion in thermodynamic theory. When Thomson fashioned his new absolute temperature concept in close relation to Amontons temperature, the two different senses of "absolute" (not being related to particular materials, and having an absolute zero) became forever confounded.

[29] Thomson [1851a] (1882), p. 199. Here Thomson cited Joule's letter to him of 9 December 1848.

[30] For the value of E, see Thomson [1849] (1882), p. 131.

[31] Hutchison (1976).

[32] Joule to Thomson, 9 December 1848, Kelvin Papers, Add. 7342, J64, University Library, Cambridge; see also D. S. L. Cardwell's account of this letter, in Cardwell (1989), pp. 99-100.

[33] Thomson to Joule, 27 October 1848, Kelvin Papers, Add. 7342, J62, University Library, Cambridge.

[34] Galison (1997).

[35] Thomson [1854] (1882), p. 234 (footnote).

[36] Gray (1908), p. 126.

[37] This was Joule's paper "On the changes of temperature produced by the rarefaction and condensation of air", which in Thomson's view had "introduced an entirely new method of treating questions regarding the physical properties of fluids" by the considerations of the effect of "fluid friction" on mechanical effect. He noted that Joule had already employed two experimental methods for studying "the relation between the thermal effects, the external mechanical effects, and the internal mechanical effects (vis viva destroyed by fluid friction) due to compressions and expansions of air in various circumstances." Thomson especially liked Joule's second method and proposed to develop it further, because it afforded "in each experiment an independent test of the truth of Mayer's hypothesis at the temperature used". Thomson proposed a modified version of the second method, simpler than Joule's own and more easily applicable to a wide range of temperatures. See Thomson [1851b] (1882), pp. 210, 215-217.

[38] See Joule and Thomson [1862] (1882), pp. 427-431; reproduced here is the equation (a) from p. 430.

[39] Thomson [1851b] (1882), pp. 218-219.

[40] Joule and Thomson [1854] (1882), p. 379.

[41] We find Thomson's thinking here somewhat strange and unsatisfactory, and it is not clear to us that the brief exposition given in Thomson [1851c] (1882), pp. 230-232, is much of an improvement.

[42] Thomson [1851b] (1882), p. 219.

[43] This is the relation that Joule and Thomson [1853] (1882), p. 347, take as "equation (f), §74, or equation (17), §95, and (8), §88".

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[44] This is listed as equation (6) in Joule and Thomson [1854] (1882) p. 397, and explicated on pp. 393-396. It is the same as equation (12), which was an expression of Joule's conjecture.

[45] Joule and Thomson [1854] (1882), pp. 398-400; equation (22) in the text is Joule and Thomson's equation (15).

[46] Joule and Thomson [1862] (1882), p. 428. Joule and Thomson also stated that "a direct demonstration" of this equation could be "readily obtained" from "elementary thermodynamic principles", but did not actually give such a demonstration there.

[47] Joule and Thomson [1862] (1882), pp. 428-429. The data summarized in this formula are gathered and processed from various tables earlier in the paper, but are most conveniently summarized in two tables on p. 429. These tables also include theoretical values of the cooling effects, agreeing quite well with the actual values. It is not very clear how these are obtained. A quasi-empirical derivation of a similar result, building on Rankine's empirical formula for the pressure of carbonic acid, seems to be given in Joule and Thomson [1854] (1882), pp. 375-377; see also §1 of "Theoretical Deductions" in that paper, pp. 377-385.

[48] Joule and Thomson [1862] (1882), pp. 429-430.

[49] Unfortunately, Thomson left this derivation in a very precarious state, since in the reprint of this paper for his collected papers he added a note (dated Aug. 1879) that the assumption of the approach to "the rigorous fulfilment of Boyle's law at very high temperatures" is "certainly false".

[50] Joule and Thomson [1854] (1882), pp. 395-396.

[51] This is given in Thomson (1880), p. 43 (§35).

[52] Thomson (1880), pp. 43-44 (§37); emphasis original.

[53] See Gray (1908), Ch. 8.

[54] Note that the efficiency would not be measured as the ratio of work to the amount of heat converted into work; that would simply be the mechanical equivalent of heat, equal in all situations.

[55] This interpretation of what Thomson is doing works only if we take him to mean an input of heat while the temperature stays the same, when he says in the definition that the body is "infinitesimally warmed".

[56] Thomson (1880), p. 44 (§38).

[57] We follow here the outlines of the account given in Gray (1908), pp. 136-137. For Thomson's own derivations, see Thomson (1880), pp. 47-50 (§§47-58). The notation we use is basically Thomson's.

[58] Thomson (1880), p. 49 (§55).

[59] In the case of hydrogen, it was apparently not a function of temperature; see Thomson (1880), p. 49.

[60] Callendar (1887) gives the starting point of his analysis (p. 179) and much numerical detail, but for the structure of argument it is more instructive to consult Le Chatelier and Boudouard (1901), pp. 23-26. We follow the latter source in our exposition.

[61] This is equation (3) in Le Chatelier and Boudouard (1901, p. 24); the notation has been changed slightly to harmonize it with equations given earlier in this chapter.

[62] Le Chatelier and Boudouard (1901), p. 25.

[63] According to Day and Sosman (1922, p. 859), up to that time only four attempts had been made to reach 1000°C with gas thermometers.

[64] Le Chatelier and Boudouard (1901), p. 26.

[65] Day and Sosman (1922), p. 837; emphasis added.

[66] For further discussions of the character of what we call "epistemic iteration", see Chang (forthcoming).

[67] Joule and Thomson [1862] (1882), p. 430. They refer to Rankine's paper in the Philosophical Transactions, 1854, part II, p. 336. In an earlier instalment of their paper (Joule and Thomson

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[1854] (1882), pp. 375-377) Joule and Thomson had already reproduced a private communication from Rankine on the subject, with commentary.

[68] See Psillos (1999), p. 277 for the quoted statement, and pp. 275-279 for his explication of the notion of truth-likeness, which he relates to the approach found in Giere (1988), although Giere prefers to speak in terms of similarity instead of truth-likeness.

[69] It may seem odd to speak of the reality of temperature, which is a property and not an object. However, there are good arguments to the effect that it makes more sense to address the realism question to properties than to entities; see Humphreys (2002), section 15.