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JAMES JOULE, WILLIAM THOMSON AND THE CONCEPT
OF A PERFECT GAS

by

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In the **early 1850s** Joule and Thomson measured the cooling experienced by a flowing gas on passing an obstacle that caused a decrease in pressure. The mythical ‘perfect gas’, which conforms exactly to Boyle’s and Charles’s laws, would show no such cooling. They used their results to put the new theory of thermodynamics on a more secure foundation and to establish a practical route for converting the measurement of temperature on a gas scale to an absolute temperature based on the second law of thermodynamics. Their experiments were sound but their calculations were in error. Later in the century William Hampson and Carl von Linde independently devised a simple method of liquefying air based on Joule–Thomson cooling, but whereas Linde understood the theory, Hampson, and many chemists, confused the process with the cooling of a gas doing external work, which is an effect that would occur also with a perfect gas. James Dewar copied Hampson’s process, without acknowledgement, in his work on the liquefaction of air and hydrogen at the Royal Institution. He, too, did not at first understand the theoretical basis of the apparatus. In the twentieth century the effect was exploited to investigate intermolecular forces, but it is now rarely used.

**Keywords: perfect gas; Joule–Thomson effect; absolute temperature;
James Dewar; gas liquefaction; intermolecular forces**

BUILDING ON THE FOUNDATIONS OF THERMODYNAMICS

In 1851, at the opening of his great paper¹ on ‘The dynamical theory of heat’, William Thomson² (1824–1907; FRS 1851) ascribed what we now call the first law of thermodynamics to James Joule³ (1818–89; FRS 1850) and the second law to Sadi Carnot (1796–1832) and Rudolf Clausius (1822–88; ForMemRS 1868). The first law declares that heat and work are interchangeable at a fixed rate of exchange, and the second declares that although work is always easily exchanged for heat there are limitations on the conditions for the reverse transformation. However, the establishment of

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these foundations left many thermodynamic problems still to be solved, of which a leading one was the establishment of a thermodynamic scale of temperature.

It had been known for many years that scales of temperature could be founded on the expansion of fluids by heat, as, for example, in the familiar mercury-in-glass thermometer. A particularly important set of scales was that founded on the expansion of a gas held at a fixed pressure. Different gases give almost identical scales and it was widely, if informally, held that there was an ideal scale that could be ascribed to a mythical ‘perfect gas’. Thomson believed that there should be a scale that was independent of the properties of any particular substance, and he realized that Carnot’s theory provided a way of bringing this about because the efficiency of an engine running on his thermodynamic cycle is independent of the properties of the material—gas, liquid or solid—that is used in the engine. Thomson’s first effort in 1848 led to a scale that deviated substantially from the gas scales and so he was not satisfied with it. Six years later he proposed another scale, still founded on Carnot’s theory but close to the widely accepted gas scales.^{4,5} His arguments are not always easy to follow, but a ‘tidied up’ version was given by his successor in the chair at Glasgow, and first biographer, Andrew Gray^{5,6} (FRS 1896). On this second scale, the ratio of two absolute temperatures, T_2/T_1 , is the ratio of the heat taken in at the upper temperature of the Carnot cycle, Q_2 , to that rejected at the lower temperature, Q_1 . However, this elegant result does not in itself provide an experimental method for realizing the scale. It was here that the story became confounded with the properties of the perfect gas.

A perfect gas is one that satisfies Boyle’s law at all temperatures and Charles’s (or Gay-Lussac’s) law at all densities. That is, the product of pressure and volume is proportional to the product of the amount of gas and its temperature: $pV = R\Theta$, where R is the ‘gas constant’⁷ and Θ is the temperature of the gas. But on what scale is Θ to be measured? We now know that the only acceptable choice is Thomson’s second scale of absolute temperature, but this was not clear in 1854. It was agreed that all real gases approached ‘perfection’ as their density became lower, but the nature of the approach to this limit was not clearly understood. Moreover, making the connection between the gas temperature, Θ , and the thermodynamic temperature, T , requires some knowledge of the thermal properties of a gas, a point that is implicit in Thomson’s work but was emphasized later by Boltzmann,⁸ who argued again from the properties of the Carnot cycle. Thomson arrived at what came to be called the ‘thermodynamic equation of state’ in which the internal energy of the gas, U , is linked to the mechanical properties of pressure and volume:⁹

$$(\partial U/\partial V)_T = -p + T(\partial p/\partial T)_V. \quad (1)$$

An assumption that the energy is independent of the density of a gas, or $(\partial U/\partial V)_T = 0$, had been made, in different words, in the 1840s by J. R. Mayer and by H. Helmholtz (ForMemRS 1860); it follows from equation (1) if Boyle’s and Charles’s laws hold good. In 1845 Joule¹⁰ had tried to verify this assumption, which Thomson always called ‘Mayer’s hypothesis’, by expanding a cylinder of compressed gas into an empty cylinder but, as he later admitted, he failed because the heat capacity of his vessels was too large compared with that of the gas. We now know that for air at atmospheric pressure and temperature the difference between the two terms on the right of this equation is only about 3 parts per thousand of either of them.

The concept of a perfect gas raises what is perhaps a metaphysical problem. It was accepted that Carnot's results, and so Thomson's absolute temperature, are independent of the choice of the material substance used to exemplify the theory, and it was also accepted that no real gas is ever perfect. Was it therefore legitimate to base thermodynamic theory on the use of a perfect gas as the working substance in Carnot's cycle? The physicists of the day were divided, and the division seems to have been between those who accepted the new kinetic theory of gases and were then developing it, and those who had some reservations about it. The reason that the 'kineticists' were happy to use the properties of the perfect gas was that a kinetic theory of a model system of molecules without attractive forces between them, and whose size could be taken in the limit to be zero, conforms to the perfect-gas laws. So, they argued, the perfect gas is a legitimate, albeit model, substance to use in a thermodynamic argument. The kineticists included Joule, Clausius, W. J. Macquorn Rankine (FRS 1853), J. Clerk Maxwell (FRS 1861) and J. D. van der Waals; the critics included Thomson, Gray and Ernst Mach. All three inveighed against this mythical gas, Thomson writing:

intelligence in thermodynamic thermometry has been hitherto much retarded, and the student much perplexed, and a mere quicksand has been given as a foundation of thermometry, by building from the beginning on an ideal substance called a perfect gas, with none of its properties realized rigorously by any real substance, and with some of them unknown, and utterly unassignable, even by guess.¹¹

Gray expressed similar, if less vehement, views,¹² and Mach derided Clausius for basing his founding paper on thermodynamics on calculations based on a perfect gas rather on the properties of a real substance. When quoting Clausius on his reliance on the gas thermometer for a calculation of the absolute temperature, Mach added an exclamation mark after the word 'Berechnung!'¹³ Perhaps surprisingly, Pierre Duhem, although no kineticist, had no problem in using the perfect gas as a foundation of thermometry and made no mention of the Joule–Thomson effect in his four-volume treatise on thermodynamics.¹⁴

We now know of another example of a model system that can be used in thermodynamic explorations. In 1873 J. D. van der Waals¹⁵ introduced his equation of state for gases and liquids in which he modified the perfect-gas equation by substituting $(p + a/V^2)$ for the pressure, and $(V - b)$ for the volume, where the parameter a is a measure of the strength of the attractive forces between the molecules and b is a measure of their volumes; that is, he wrote

$$(p + a/V^2)(V - b) = RT. \quad (2)$$

For many years this equation served a purpose as a useful approximation to the true equation of state of a real gas; it was found always to yield sensible and internally consistent thermodynamic results when supplemented by 'Maxwell's construction' under conditions in which the system comprises both gas and liquid. Others soon tinkered with the equation, adding further parameters, up to seven in the twentieth century, which produced better results in some circumstances but often at the cost of generating thermodynamic nonsense in others. **The reason for the robustness of the original equation became clear only in 1963, when it was shown that it is the true equation of state of a one-dimensional model system of molecules of hard rods with weak but long-range**

attractive forces between them.¹⁶ The model is highly artificial, but its mere existence guarantees the robustness of the original equation.

We can therefore see today why the kineticists were justified in saying that a perfect gas is acceptable as the working substance of a Carnot engine. What may have aroused Thomson's apparently exaggerated fulminations may have been the behaviour of this gas when not at equilibrium. The application of the original form of the kinetic theory to a perfect gas leads, for example, to the prediction that such a gas has an infinite viscosity and infinite thermal conductivity. As the size of the molecules is decreased to zero, the distance over which they can carry momentum and energy before being deflected by a molecular collision becomes infinite, so increasing the viscosity and conductivity without limit. In practice, no real gas approaches this limit; the original form of the theory needs drastic modification when the density is so low that the ratio of the molecular diameter to the mean separation of the molecules approaches zero. This was a problem that Maxwell was tackling at the time of his death in 1879 but it is irrelevant to the thermodynamic issue.

THE APPROACH TO THE PERFECT-GAS LIMIT

Everyone agreed that the equation of state of all real gases approaches the perfect-gas limit as the pressure or density approaches zero, but there was surprisingly little discussion on how this limit is reached. Victor Regnault (ForMemRS 1852), the leading experimentalist of the day, lamented that the matter was too difficult to be solved in the laboratory and urged the mathematicians to give it their attention.¹⁷ In 1854 Joule and Thomson¹⁸ quoted an extraordinary expression proposed by Rankine in which the pressure of air is calculated from terms proportional to the density to the powers of $-3/5$ and $-1/2$. In the same paper, however, they also quote from a letter from Rankine to Thomson of 9 May 1854 in which he suggests more reasonably that the leading term in the departure from the perfect-gas laws is linear in the density, or $(1/V)$. This turned out to be so and Rankine had already made what is perhaps the earliest, if implicit, use of the equation

$$pV/RT = 1 + B/V + \dots = 1 + Bp/RT + \dots, \quad (3)$$

where B (now called the second virial coefficient) is proportional to the amount of gas and, for each gas or gas mixture, is a function only of the temperature. He took some measurements by Regnault¹⁹ of the mean increase in pressure (per °C) of a gas heated at constant volume over the range of temperature from 0 to 100°C, which may be represented as E_p . It is defined as $[(p_{100} - p_0)/100p_0]$ where p_{100} and p_0 are the pressures at the steam-point and the ice-point, respectively. He plotted $(1/E_p)$ against p_0 and took a linear extrapolation to zero pressure for air and carbon dioxide to obtain -274.6°C as his best estimate of the zero of the perfect-gas scale.²⁰ A comparison of his extrapolations with calculations based on modern measurements of the second virial coefficients is shown in figure 1. Regnault's results for air at the lowest pressures show why he was doubtful of determining how a real gas approaches the perfect-gas limit without some theoretical guidance. Regnault also measured the complementary coefficient of expansion, E_V , the rate of increase of volume of a gas heated at constant pressure, and if Rankine had used these results he would have obtained a better estimate of the absolute zero, now put at -273.16°C .

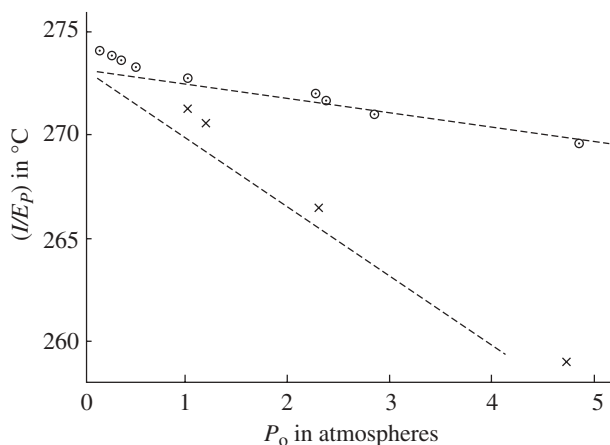


Figure 1. The expansion coefficient for the pressure in a constant-volume gas thermometer, as plotted by Rankine from Regnault's results for air (circles) and carbon dioxide (crosses). Rankine extrapolated these results to give $1/E_p$ at zero pressure as 274.6°C below the ice-point. The broken lines are calculations based on modern measurements of the second virial coefficients and a temperature difference of 273.15°C .

Meanwhile, Thomson and Joule had returned to the problem of determining a property of a real gas that would enable them to calculate the absolute temperature from a temperature measured on a gas scale. Joule's original attempt to measure $(\partial U/\partial V)_T$ had failed because of the great heat capacity of the metal vessels used to hold the gas under pressure. A similar problem had faced those trying to measure the specific heat capacity of a gas at constant volume, C_v , and they had solved it by determining instead the specific heat capacity at constant pressure in a flowing gas, C_p , an experiment in which the heat capacity of the confining tube is irrelevant. It may have been this analogy that suggested to Thomson that they should try to measure the change of temperature when a flowing gas is expanded from one pressure to another. When a gas passes an obstruction, such as a well-insulated porous plug, it does not expand at constant internal energy, U , because work is done in forcing the gas through the plug. The quantity that remains constant is the sum $(U + pV)$, now called the enthalpy and represented by the symbol H . A simple manipulation of the thermodynamic equation of state, equation (1), yields a parallel equation for $(\partial H/\partial p)_T$, and so for $(\partial T/\partial p)_H$, the expression for the change of temperature on adiabatically expanding a gas at constant enthalpy:

$$(\partial H/\partial p)_T = V - T(\partial V/\partial T)_p = -C_p(\partial T/\partial p)_H = B - T(dB/dT) + \dots \quad (4)$$

The experiment is a difficult one that calls for more facilities than most chemists and physicists could muster, but by dint of a government grant and the resources of the family brewery, Joule succeeded.²¹ He found that the change in temperature is proportional to the fall of pressure. What came to be called the adiabatic Joule–Thomson coefficient, $(\partial T/\partial p)_H$, is positive for air and carbon dioxide, but negative for hydrogen. For air they found that its magnitude is proportional to T^{-2} , at least for temperatures around ambient; that is,

$$\Delta T/\Delta p = 0.276(273.7/T)^2, \quad (5)$$

where Δp is the fall in pressure on passing through the plug, and where the numerical coefficient is in degrees Celsius per atmosphere. This expression for the cooling, and the constancy of C_p for air, ($7R/2$), implies that the quantity $B - T(dB/dT)$ also has the form $-\beta/T^2$, whence an integration gives $B = \alpha T - \beta/3T^2$, where α is the constant of integration. It was accepted that the departure of a gas from the perfect-gas laws increases as its temperature is reduced towards the point where it starts to condense to a liquid; the converse, which was thought to follow, is that a gas approaches perfection as the temperature increases without limit. Certainly Thomson, Joule and Maxwell all held this view at first.²² It became less tenable when van der Waals showed that the limiting behaviour at high temperature was probably $p(V - b) = RT$ (that is, $B = b$), which is not the behaviour of a perfect gas. Thomson had revised his original view by 1879 in a note attached to the reprint of his papers with Joule, but Maxwell seems never to have withdrawn the statement in his book, and Lord Rayleigh (FRS 1873) left it uncorrected in the editions published after Maxwell's death. However, it was unthinkable that the departure from the perfect-gas laws should increase without limit as the temperature rises and so the constant α must be put equal to zero. Hence the coefficient B is $(-\beta/3T^2)$. It is of note that although a real gas approaches the perfect-gas limit as the density goes to zero, in the sense that the pressure approaches the limit of RT/V , the Joule–Thomson coefficient approaches a finite but non-zero limit, $B - T(dB/dT)$.

Thomson was now in a position to determine how different the temperature observed in the laboratory on a gas thermometer is from the absolute or thermodynamic temperature that he sought to measure. The thermodynamic temperature on the Celsius scale, t , was chosen to coincide with that on the gas scale, θ , at the ice-point, $t = \theta = 0$, and at the steam-point, $t = \theta = 100$, although it is equally feasible, and, in fact preferable, to anchor the two scales together at one temperature only. Their calculation is not set out in their paper but the result is in error, although it has been quoted recently without comment.⁵ With the form of B set out above it can be shown that the difference between θ and t for a constant-volume thermometer has the form

$$V(\theta - t) = t(100 - t)[- \alpha + \beta/3T_0T_{100}T], \quad (6)$$

where V is the fixed volume of the gas at a low but variable pressure. The heat capacity C_p , shown in equation (4), the coefficient B , and thus the symbols α and β , refer to the same volume. They found, correctly, that the greatest difference in θ and t , between 0 and 100 °C, is at about 45 °C, and so it is convenient to consider only the result in their Table for 40 °C. Here they found the difference for a constant-volume air thermometer filled with air at a pressure of 1 atm at 0 °C to be +0.0403 °C, which is now easier to describe as 40.3 mK. The result from equation (6), with $\alpha = 0$, is, however, only 7 mK. There is a similar discrepancy in their calculation for a constant-pressure air thermometer, for which they found a difference of 47.7 mK, whereas their results should lead to 17 mK. Calculations based on modern measurements of B , so bypassing the Joule–Thomson coefficient itself, give about 13 ± 5 mK for the constant-volume thermometer and 22 ± 5 mK for the constant-pressure thermometer. Their errors of calculation were apparently first noticed by H. A. Rowland (ForMemRS 1889) of Johns Hopkins University in 1879. His paper was published in *Proceedings of the American Academy of Arts and Sciences*,²³ so Thomson would have seen it, because he had been a member of that body since 1873, but probably not in time for him to comment on it in his article ‘Heat’ for *Encyclopaedia Britannica*.¹¹

It was some years before anyone had the skill and resources to repeat Joule's experiments. Regnault made an attempt but soon decided that the results were not worth the trouble. He quotes only one number, which is close to that of Joule and Thomson.²⁴ Later in the century there were new measurements that broadly confirmed Joule and Thomson's experimental results but agreed with Rowland's revision of the difference between the gas and thermodynamic scales.²⁵ An important experimental proposal was that of Edgar Buckingham, of the US Department of Agriculture, who wrote that it would be better to heat the flowing gas at the point of expansion so as to keep its temperature constant.²⁶ Not only does this decrease the chance of heat leaks but it also leads directly to the thermodynamically more useful isothermal coefficient, $(\partial H/\partial p)_T$. His advice was often followed in the twentieth century.

International agreement on the adoption of the thermodynamic scale was slow to be achieved.²⁷ The first *Conférence Générale des Poids et Mesures* in 1889 adopted the constant-volume hydrogen thermometer as the standard scale—a good choice from a practical point of view because hydrogen exists as a gas at (what were then) all accessible temperatures and, moreover, it has an unusually small deviation from the perfect-gas laws. In 1911 the *Physikalisch-Technische Reichsanstalt* in Berlin proposed that the hydrogen scale be replaced by the thermodynamic scale, but this suggestion was not fully implemented until 1968 when it was decided that only one fixed point was needed to define that scale and it was agreed that the triple point of water be assigned the value of 273.16 K, thus confirming Joule and Thomson's belief of 114 years earlier that such a choice of one fixed point 'must be adopted ultimately'.¹⁸

LIQUEFACTION OF AIR

All early attempts to liquefy air by subjecting it to ever higher pressures had failed. The reason became clear in 1869 when Thomas Andrews (FRS 1849) showed that for each gas there is a critical temperature above which no amount of compression would induce liquefaction; the gas must first be cooled below this temperature, which is usually about twice the boiling point on the absolute scale of temperature. Air was first liquefied in 1877 by Raoul Pictet in Switzerland and by Louis Cailletet in France. Pictet, who was followed by Wroblewski and Olszewski in Krakow, used a 'cascade' of liquids, in which sulphur dioxide was used to condense carbon dioxide, this to condense ethene, and ethene boiling under reduced pressure to liquefy oxygen or air. It was a feasible but laborious route. Cailletet used precooled compressed air to do work in expelling part of the gas from a cylinder and so cooling further the gas left behind. Under sufficiently low starting temperatures and high starting pressures the remaining gas is partly liquefied. It was a wasteful batch process, but the primary cooling is an effect that occurs with both real and perfect gases and so is substantial and, indeed, universal. Neither Pictet's nor Cailletet's method makes use of the Joule–Thomson effect. In May 1895 the field underwent a revolution at the hands of two men, William Hampson in Britain and Carl von Linde in Germany. They combined cooling by Joule–Thomson expansion with a regenerative cycle in a heat exchanger in which the slightly cooled and expanded gas exchanged heat with the incoming gas on its way to expansion, so leading eventually to the decrease in the temperature to the point at which a small portion of the gas is liquefied in each cycle.

Linde and his work are the easier to describe. He had studied thermodynamics under Clausius at Zurich in the 1860s and understood exactly what he was doing, as is clear from his patent, in Germany and Britain.²⁸ In the provisional application he states that ‘the well known experiments of Thomson and Joule have shown, that as a matter of fact, at discharge a certain cooling takes place’, and in the complete application he quotes equation (5) above. His apparatus was on an industrial scale and had to run for several days before the first liquid air appeared, but it then produced it in quantity. His work became known in Britain on 4 October 1895, when the journal *The Engineer* carried a report of an address by M. Schröter to engineers in Aachen in which he again cites the Joule–Thomson effect as the essence of Linde’s process.²⁹

William Hampson’s work is more mysterious.³⁰ He was a classics graduate of Trinity College, Oxford, who trained as a barrister but never practised. It is not known how he became interested in gas liquefaction nor how he acquired a skill in physics and engineering. By 1895 he had qualified as a Licentiate of the Society of Apothecaries and later worked in London hospitals on their electrical and X-ray equipment. His patent application, which preceded Linde’s by a few weeks, shows no evidence that he understood the principle on which his apparatus worked. The provisional version runs only to one sentence in which he refers to the ‘usual cycle of compression, cooling and expansion’. He seems here to be describing the simple expansion that Cailletet had exploited and not to understand that in a continuous-flow system this leads to no net effect for a perfect gas. Linde spells out this point explicitly, and later noted Hampson’s misinterpretation when he wrote: ‘and he omitted to mention any words that would have described the use of the cooling found by Thomson and Joule in their experiment with flowing gas.’³¹ Hampson probably thought that combining a simple expansion with the principle of ‘regeneration’, which was itself not a novelty, was the patentable basis of his apparatus.

Six months earlier, in November 1894, he had approached Robert Lennox,³² the technical assistant to James Dewar³³ (FRS 1877) at the Royal Institution (RI), to suggest that he (Hampson) and the team at the RI might jointly develop his invention, of which he produced diagrams that he had prepared in April. Dewar was later to accuse him of going behind Dewar’s back in approaching Lennox directly, but Hampson explained that he had had an introduction to Lennox but did not know Dewar. Lennox said later that he had told Hampson that his method would not work and that the matter had then been dropped. But Hampson maintained that this was not so; he had paid a second visit later that year and, early in 1895, had written three times to Lennox but had had no reply.³⁴ It was only then that he had decided to take out a patent, which he later developed further in collaboration with K. S. Murray at Brins Oxygen Company in Westminster, the forerunner of BOC. There then seems to have been some controversy between the two camps, which came to a head when Dewar gave a lecture to the Chemical Society on 19 December 1895 in which he used an apparatus that was, to judge from the figure attached, very similar to Hampson’s.³⁵ Dewar had demonstrated ‘the making of liquid air by a simple method’ to the Managers of the RI two weeks earlier.³⁶ The apparatus had been made by Lennox, Reynolds and Fyfe and Co. at Rodebush Works, in Fulham, a company much used by Dewar for making his equipment. Lennox was primarily a chemist, but he described himself as a ‘chemical engineer’ in the 1901 census and claimed to have learnt the rudiments of the subject from the lectures of James Thomson (brother of William; FRS 1877), although he was a student at Anderson’s College, not at

Glasgow University.³² The equipment was not without its problems; Lennox lost an eye in an explosion of a pressure gauge on 13 June 1896.³⁶

In his Chemical Society lecture Dewar made no mention of Hampson or Linde. He coupled Joule and Thomson with Regnault in a comment that is in the context of the simple adiabatic expansion of the kind that he had used earlier. It is unlikely that either Lennox or Dewar understood the new principle behind the Hampson and Linde patents when they first used the process. When Dewar gave a tribute to Joule after his death in 1889 he said of the Joule–Thomson effect that ‘its chief object was to prove that in compressing a gas the amount of heat produced is equivalent to the amount of work done, and independent of the mere fact of the approach of the particles’³⁷—a comment that inverts their intention. The first he knew of the necessary involvement of the Joule–Thomson cooling in the new liquefiers may have come from the October article in *The Engineer*, a journal taken by the RI Library. For physical advice he relied on his brother-in-law, Hamilton Dickson, a mathematician at Peterhouse, Cambridge. Dickson wrote to him a week before his lecture to explain, not very clearly, how to calculate the Joule–Thomson cooling,³⁸ but this news cannot have influenced the design of Lennox’s apparatus. In his Chemical Society lecture Dewar wrote: ‘Apart, therefore, from important mechanical details, and the conduct of general working, nothing new has been added by any investigator to the principles involved in the construction and use of low-temperature apparatus since the year 1878.’³⁵ This sentence should not have been written by a man who had recently appreciated the fundamental novelty of Hampson’s and Linde’s liquefiers. In the discussion of the paper, Bertram Blount,³⁹ an ‘engineering chemist’, raised the matter of Schröter’s report and so of the necessity of Joule–Thomson cooling in Dewar’s apparatus. An editorial comment in *The Engineer* then added to the confusion by accusing Dewar of not acknowledging Linde’s priority in developing the process. Dewar may by then have known of Schröter’s report, but it was Hampson that he and Lennox had copied! The early forms of Hampson’s and Dewar’s liquefiers are compared in figure 2; Linde’s is quite different in layout.

Hampson gave a public demonstration of his own machine at the Brins Oxygen Company on 21 March 1896, but one of the audience said: ‘it is not certain that Dr Hampson . . . understood how the process works. It ought not to work. The more carefully a man has been taught thermodynamics, the more likely he is to regard the process as impossible.’⁴⁰ Some of the audience confused the Joule–Thomson effect with ‘Mayer’s hypothesis’, studied by Joule in 1845; some thought the Joule–Thomson effect too small to be effective. Others, including the writer of an American monograph,⁴¹ did not distinguish between the simple adiabatic cooling on doing work, common to both perfect and real gases, and the Joule–Thomson cooling found in most real gases. It is tempting to think that one writer, who called himself ‘M.A.’ and who asked for an explanation of the Linde process, was Hampson himself, because he seemed to be fond of quoting his Oxford degree when applying for patents.⁴² He received a confused answer.

One person missing from all this controversy is Thomson himself (by then Lord Kelvin). By 1896 he was as much an inventive engineer as a physicist and he must have known of the correspondence. Maybe he was distracted by his illness that year and by the competing news of the announcement of Röntgen’s X-rays at the end of 1895, on which he and his friend George Stokes exchanged 37 letters between February and June 1896.⁴³ Some years later, however, he wrote to congratulate Dewar on his Presidential Address to the British

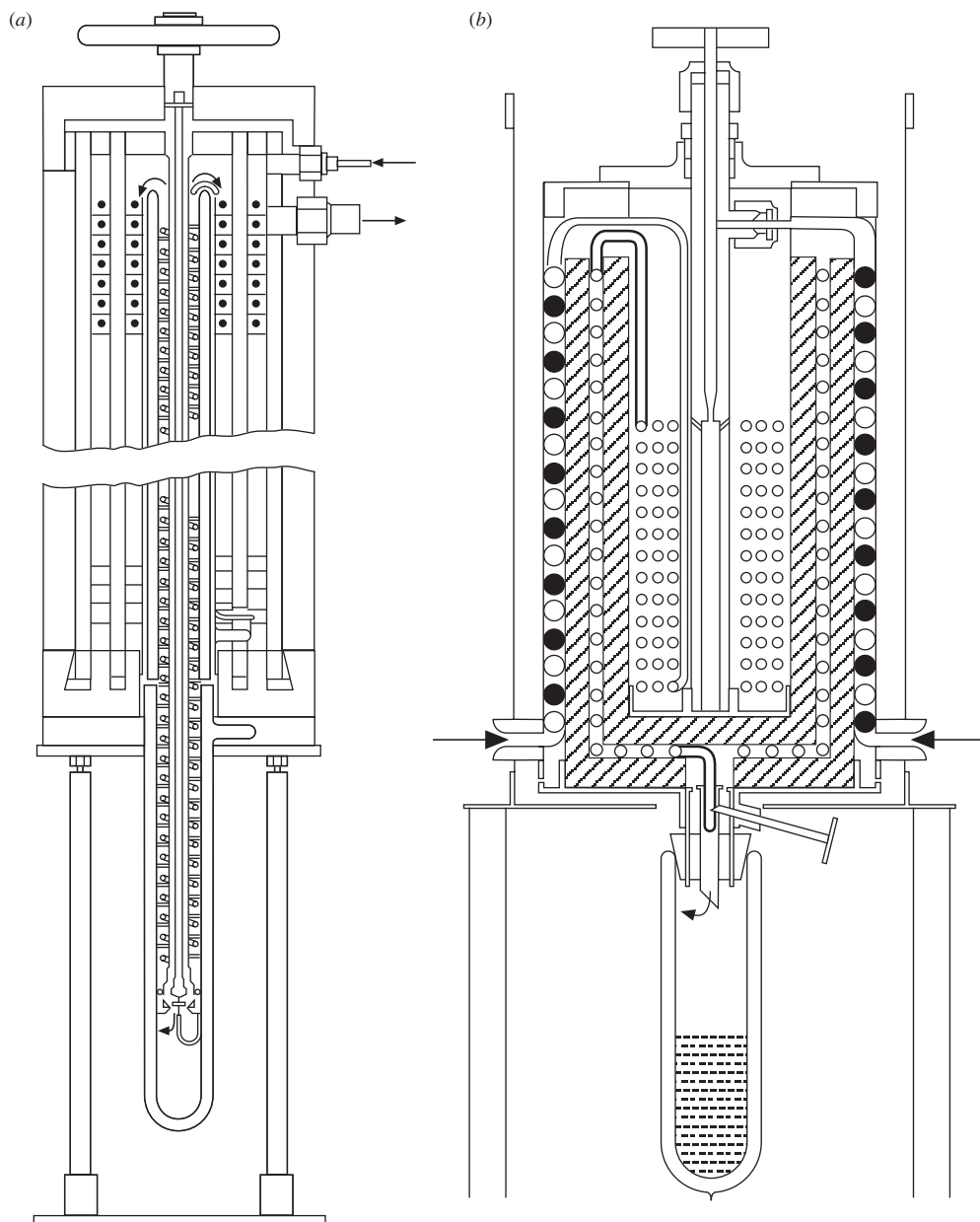


Figure 2. The apparatuses of (a) Hampson and (b) Dewar, as shown at their first public demonstrations on 21 March 1896 and 19 December 1895, respectively. The incoming gas was, in each case, passed through a heat exchanger in the core of the apparatus before being cooled at the expansion valve at its base. There the drops of liquid that eventually emerged were collected in a vacuum vessel. Hampson started with gas at room temperature but Dewar cooled the incoming gas with liquid carbon dioxide, which circulated through the coils shown in black. The well-insulated core of Hampson's apparatus was 28 inches (70 cm) high; Dewar gives no dimensions, but an undated liquefier at the RI is 25 cm high.

Association in 1902 but gently corrected Dewar's misunderstanding of Carnot's cycle and his confusion of Thomson's two definitions of absolute temperature.⁴⁴

Lord Rayleigh, another friend of Thomson's, and a colleague of Dewar's at the RI, did briefly intervene when he suggested in a short note⁴⁵ that using the Joule–Thomson effect is 'bad thermodynamics', by which he meant that more effort should be put into exploiting the simple expansion with the extraction of external work, so getting much greater cooling. He saw that there were difficulties of lubrication to be overcome, difficulties that Georges Claude managed to conquer a few years later.⁴⁶ Rayleigh had suggested evading this problem by using a turbine to extract the work, when the bearings could be well-removed from the cold region around the blades. Perhaps as a result of this letter, an engineer from Walton-on-Thames, Edgar Thrupp,⁴⁷ applied for a patent to do just this, but he seems never to have exploited it. Cailletet said, in the discussion in Paris of the second of Claude's papers,⁴⁶ that he and a M. Leblanc had tried to use a turbine and had showed that it worked, but again there seems to be no record of any exploitation. Cooling by a turbine was tried on an experimental basis by the Linde Company in Germany in the 1930s, but its first practical use seems to have been in the liquefaction of helium by P. L. Kapitza (FRS 1929) in Moscow in 1939.⁴⁸

THE TWENTIETH CENTURY

It is not necessary to follow here the use of the Hampson–Brins liquefier by William Ramsay (no friend of Dewar's) in his work on the inert gases at University College London,⁴⁹ nor Heike Kamerlingh Onnes's use of the Joule–Thomson effect in his liquefaction of helium,⁵⁰ nor the industrial arguments of the early twentieth century over the patents associated with Claude's exploitation of the cooling found in both perfect and real gases and the much smaller cooling in a Joule–Thomson expansion. In the twentieth century the academic interest moved to using the isothermal Joule–Thomson effect as a source of information about intermolecular forces. Maxwell was the first to point out that the second virial coefficient can be expressed as an integral over the forces between a pair of molecules, but unfortunately he arrived at this expression only in his referee's report on Thomas Andrews's Bakerian Lecture of 1876, and so it remained unknown to the world at large. It was a further 20 years before Boltzmann rediscovered the same result, which then rapidly passed into common use as a way of studying intermolecular forces.⁵¹ What can be done with the second virial coefficient, B , can also be done, but less conveniently, with the isothermal Joule–Thomson coefficient at low pressures, $B - T(dB/dT)$, and so measurements of this coefficient became part of the armoury for studying intermolecular forces, particularly at the University of Wisconsin, where the experiments of J. R. Roebuck were followed by theoretical calculations by J. O. Hirschfelder and his colleagues.⁵² Most laboratories had, however, accepted that the Joule–Thomson coefficient was more difficult to measure than the second virial coefficient, or, more generally, than the relation between pressure, volume and temperature, and that it was less simply related to the intermolecular forces. By the time of World War II few measurements were being made and it is not clear why M. G. Evans (FRS 1947), first at Leeds and then at Manchester University, decided to build an apparatus to measure the isothermal coefficient in the late 1940s. He was interested in intermolecular forces, but his choice of this technique may have arisen from his

acquaintanceship with Martin Ruhemann, an authority on gas liquefaction.⁵³ Ruhemann had worked at Kharkov with I. M. Gusak before the war, and the design of Evans's apparatus owed much to Gusak's work. By 1950 Ruhemann was with Petrocarbon Ltd, the development branch of the Manchester Oil Refinery, which supported the Joule–Thomson work financially. Evans was taken ill after I came to Manchester in October 1951, and he died soon afterwards of throat cancer. I was left to help run the apparatus and to supervise the students who were depending on it for the completion of their PhDs. But I and others soon saw that, for most purposes, this venerable technique had had its day and the Manchester programme came to an end.⁵⁴

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NOTES

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