

A History of Thermodynamics

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The Doctrine of Energy and Entropy

 Springer

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Preface

The most exciting and significant episode of scientific progress is the development of thermodynamics and electrodynamics in the 19th century and early 20th century. The nature of heat and temperature was recognized, the conservation of energy was discovered, and the realization that mass and energy are equivalent provided a new fuel, – and unlimited power.

Much of this occurred in unison with the rapid technological advance provided by the steam engine, the electric motor, internal combustion engines, refrigeration and the rectification processes of the chemical industry. The availability of cheap power and cheap fuel has had its impact on society: Populations grew, the standard of living increased, the environment became clean, traffic became easy, and life expectancy was raised. Knowledge fairly exploded. The western countries, where all this happened, gained in power and influence, and western culture – scientific culture – spread across the globe, and is still spreading.

At the same time, thermodynamics recognized the stochastic and probabilistic aspect of natural processes. It turned out that the doctrine of energy and entropy rules the world; the first ingredient – energy – is deterministic, as it were, and the second – entropy – favours randomness. Both tendencies compete, and they find the precarious balance needed for stability and change alike.

Philosophy, – traditional philosophy – could not keep up with the grand expansion of knowledge. It gave up and let itself be pushed into insignificance. The word came up about *two cultures*: One, which is mostly loose words and subjective thinking – in the conventional style –, and scientific culture, which uses mathematics and achieves tangible results.

Indeed, the concepts of the scientific culture are most precisely expressed mathematically, and that circumstance makes them accessible to only a minority: Those who do not shy away from mathematics. The fact has forced me into a two-tiered presentation. One tier is narrative and largely devoid of formulae, the other one is mathematical and mostly relegated to *Inserts*. And while I do not recommend to skip over the inserts, I do believe that that is possible – at least for a first reading. In that way a person may acquire a quick appreciation of the exciting concepts and the colourful personages to whom we owe our prosperity and – in all probability – our lives.

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1 Temperature

Temperature – also *temperament* in the early days – measures hot and cold and the word is, of course, Latin in origin: *temperare* - to mix. It was mostly used when liquids are mixed which cannot afterwards be separated, like wine and water. The passive voice is employed – the “-tur” of the present tense, third person singular – which indicates that some liquid *is being mixed* with another one.

For Hippokrates (460–370 B.C.), the eminent, half legendary Greek physician, proper mixing was important: An imbalance of the bodily fluids blood, phlegm, and black and yellow bile was supposed to lead to disease which made the body unusually hot or cold or dry or moist.

Klaudios Galenos (133–200 A.C.), vulgarly Galen, – another illustrious Greek physician, admirer of Hippokrates and polygraph on medical matters – took up the idea and elaborated on it. He assumed an influence of the climate on the mix of body fluids which would then determine the character, or temperament (sic), of a person. Thus body and soul of the inhabitants of the cold and wet north were wild and savage, while those of the people in the hot and dry south were meek and flaccid. And it was only in the well-mixed – *temperate* – zone that people lived with superior properties in regard to good judgement and intellect,¹ the Greeks naturally and, perhaps, the Romans.

Galen mixed equal amounts of ice and boiling water, which he considered the coldest and hottest bodies available. He called the mixture neutral,² and installed four degrees of cold below that neutral point, and four degrees of hot above it. That rough scale of nine degrees survived the dark age of science under the care of Arabian physicians, and it re-emerged in Europe during the time of the Renaissance.

Thus in the year 1578, when Johannis Hasler from Berne published his book “De logistica medica”, he presented an elaborate table of body temperatures of people in relation to the latitude under which they live, cf. Fig. 1.1. Dwellers of the tropics were warm to the fourth degree while the

¹ Galen: “Daß die Vermögen der Seele eine Folge der Mischungen des Körpers sind.” [That the faculties of the soul follow from the composition of the body] *Abhandlungen zur Geschichte der Medizin und Naturwissenschaften*. Heft 21. Kraus Reprint Liechtenstein (1977).

² It is not clear whether Galen mixed equal amounts by mass or volume; he does not say. In the first case his neutral temperature is 10°C in the latter it is 14°C; neither one is of any obvious relevance to medicine.

2 1 Temperature

eskimos were cold to the fourth degree. Persons between latitudes 40° and 50°, where Hasler lived, were neither hot nor cold; they were given the neutral temperature zero.

One must admit that the idea has a certain plausibility and, indeed, the nine degrees of temperature fit in neatly with the 90 degrees of latitude between the equator and the pole. However, it was all quite wrong: All healthy human beings have the same body temperature, irrespective of where they live. That fact became soon established after the invention of the thermometer.

PROBLEMA I. 2

Ordines ab extre- mo ad ex- tremum.	Ordines tempe- raturæ Numeri Numerati.	Tertiarum partium numeri & mediocri- tate, seu Numeri Numerati.	Tertiarum partium numerus ab extre- mo, seu Numeri Numerati.	Colleges gradus tertij ordi- num par- tium con- gruentes.	Gratus colleges, medij co- ordinatus respon- dentes.
9	4	12	20	90	90
		11	26	85½	85
		10	35	80	80
8	3	9	24	80	80
		8	23	76½	75
		7	22	73½	70
		6	21	70	70
		5	20	66½	65
		4	19	63½	60
6	1	3	18	60	60
		2	17	56½	55
		1	16	53½	50
5	0	0	15	50	50
		0	14	46½	45
		0	13	43½	40
4		1	12	40	40
		2	11	36½	35
		3	10	33½	30
		4	9	30	30
		5	8	26½	25
2	2	6	7	23½	20
		7	6	20	20
		8	5	16½	15
		9	4	13½	10
1	3	9	3	10	10
		10	2	6½	5
		11	1	3½	0

C.H.V.
F. S.C. II

Fig. 1.1. Hasler's table of body temperatures in relation to latitude

The instrument was developed in the early part of the 17th century. The development is painstakingly researched and well-described – as much as it can be done – by W.E. Knowles Middleton in his book on the history of the thermometer.³ Another excellent review may be found in a booklet by Ya.A. Smorodinsky.⁴ It is not clear who invented the instrument. Middleton complains that *questions of priority are loaded with embarrassment for the historian of science...*, and he indicates that the answers are often biased by nationalistic instincts.

³ W.E. Knowles Middleton: "The History of the Thermometer and its Use in Meteorology". The Johns Hopkins Press, Baltimore, Maryland (1966).

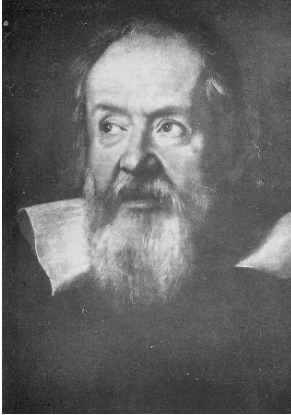
Hasler table of body temperatures, cf. Fig. 1.1, is the frontispiece of that book.

⁴ Ya.A. Smorodinsky: "Temperature". MIR Publishers, Moscow (1984).

So also in the case of the thermometer: According to Middleton there was some inconclusive bickering about priority across the Alps, between England and Italy. One thing is certain though: The eminent scientist Galileo Galilei (1564–1642) categorically claimed the priority for himself. And his pupil, the Venetian diplomat Gianfrancesco Sagredo accepted that claim after at first being unaware of it. Sagredo experimented with the thermometer and on May 9th, 1613 he wrote to the master ⁵:

The instrument for measuring heat, invented by your excellent self ...[has shown me] various marvellous things, as, for example, that in winter the air may be colder than ice or snow; ...

Another quaint observation on well-water is communicated by Sagredo to Galilei on February 7th, 1615, cf. Fig. 1.2⁶. It is clear what Sagredo means: If you bring water up in summer from a deep well and you stick your hand into it, it feels cool, while, if you do that in wintertime, the water feels warm.



GIOVANFRANCESCO SAGREDO a GALILEO
in Firenze
Venezia, 7 febbraio 1615
Molto Ill.re S.r Ecc.mo

... Con questi istrumenti ho chiaramente veduto,
esser molto più fredda l'aqua de' nostri pozzi il
verno che l'estate; e per me credo che l'istesso
avenga delle fontane vive et luochi soterranei,
anchorchè il senso nostro giudichi diversamente.

Et per fine li baccio la mano

In Venetia, a 7 Febraro 1615
Di V.S. Ecc.ma
Tutto suo Il Sag.

Fig. 1.2. Galileo Galilei. A cut from a letter of Sagredo to Galilei with the remarkable sentence: *I have clearly seen that well-water is colder in winter than in summer ..., although our senses tell differently*

Misconceptions due to the subjective feeling of hot and cold were slowly eliminated during the course of the 17th century. A serious obstacle was that no two thermometers were quite alike so that, even when there were

⁵ Middleton. loc.cit. p. 7.

⁶ “Le Opere di Galileo Galilei”, Vol. XII, Firenze, Tipografia di G. Barbera (1902) p.139. The letter, and other letters by Sagredo to Galilei are replete with flattering, even sycophantic remarks which the older man seems to have appreciated. Part of that may be attributed, perhaps, to the etiquette of the time. But, in fact, it may generally be observed – even in our time – that, the more eminent a scientist already is, the more he demands praise; and a diplomat knows that.

4 1 Temperature

scales on them, it was difficult to communicate objective information from one place to another.

Scales were just as likely to run upwards as downwards at that time. Middleton⁷ lists the scale on a surviving thermometer built by John Patrick in or around the year 1700; it runs downward with increasing heat from 90° to 0°, thus maintaining remnants of Galen's scale of 9 degrees, perhaps.

90° Extream Cold	55° Cold Air	15° Sultry
85° Great Frost	45° Temperate Air	5° Very Hott
75° Hard Frost	35° Warm Air	0° Extream Hott
65° Frost	25° Hott	

Fix-points were needed to make readings on different thermometers comparable. From the beginning, melting ice played a certain role – either in water or in a water-salt-solution – and boiling water, of course. But alternatives were also proposed:

the temperature of melting butter,
the temperature in the cellar of the Paris observatory,
the temperature in the armpit of a healthy man.

The surviving Celsius scale uses melting ice and boiling water, and one hundred equal steps in-between. However, since Anders Celsius (1701–1744) wished to avoid negative numbers, he set the boiling water to 0°C and melting ice to 100°C, – for a pressure of 1atm. Thus he too counted *downwards*. That order was reversed after Celsius's death, and it is in that inverted form that we now know the Celsius scale, or centigrade scale.

Gabriel Daniel Fahrenheit (1686–1736) somehow thought that three fix-points were better than two. He picked

a freezing mixture of water and sea-salt (0°F),
melting ice in water alone (32°F),
human body temperature (96°F).

Later he adjusted that scale slightly, so as to have boiling water at 212°F, exactly 180 degrees above melting ice. One cannot help thinking that 180° is a neat number, at least when the degrees are degrees of arc. However Middleton, who describes the development of the Fahrenheit scale in some detail, does not mention that analogy so that it is probably fortuitous. Anyway, after the readjustment, the body temperature came to 98.6°F. That is where the body temperature stands today in those countries, where the Fahrenheit scale is still in use, notably in the United States of America.

From the above it is easy to calculate the transition formula between the Celsius and the Fahrenheit scales: $C = 5/9(F - 32)$.

⁷Middleton: loc.cit. p. 61.

There were numerous other scales, advertised at different times, in different places, and by different people. It was not uncommon in the 18th and early 19th century to place the thermometric tube in front of a wide board with several different scales, – up to eighteen of them. Middleton⁸ exhibits a list of scales shown on a thermometer of 1841:

Old Florentine	Delisle	Amontons
New Florentine	Fahrenheit	Newton
Hales	Réaumur	Société Royale
Fowler	Bellani	De la Hire
Paris	Christin	Edinburg
H. M. Poleni	Michaelly	Cruquius

All of these scales were arbitrary and entirely subjective but, of course, perfectly usable, if only people could have agreed to use *one* of them, – which they could not.

A new *objective* aspect appeared in the field with the idea that there might be a lowest temperature, an *absolute minimum*. By the mid-nineteenth century, two hundred years of experimental research on ideal gases had jelled into the result that the pressure p and the volume V of gases were linear functions of the Celsius temperature (say), such that

$$pV = m \frac{k}{\mu} (273.15^\circ\text{C} + t)$$

m is the mass of the gas.⁹ Therefore, upon lowering the temperature to $t = -273.15^\circ\text{C}$ at constant p , the volume had to decrease and eventually vanish, and surely further cooling was then absurd. At first people were unimpressed and unconvinced of the minimal temperature. After all, even then they suspected that all gases turn into liquids and solids at low temperatures, and the argument did not apply to either.

However, in the 19th century it was slowly – painfully slowly – recognized that matter consisted of atoms and molecules, and that temperature was a measure for the mean kinetic energy of those particles. This notion afforded an understanding of the minimal temperature, because

⁸ Middleton: loc.cit. p. 66.

⁹ In much of the 19th century literature this equation is called the *law of Mariotte and Gay-Lussac*. Nowadays we call it the *thermal equation of state* for an ideal gas. The pioneers of the equation were Robert Boyle (1627–1691), Edmé Mariotte (1620–1684), Guillaume Amontons (1663–1705), Jacques Alexandre César Charles (1746–1823), and Joseph Louis Gay-Lussac (1778–1850). Their work is now a favourite subject of high-school physics courses. Therefore I skip over its motivation and derivation. I only emphasize that the value 273.15 is the *same* for all gases. That value was established by Gay-Lussac when he measured the relative volume expansion by heating a gas of 0°C by 1°C . [The value 273.15 is the modern one; in fact it is 273.15 ± 0.02 . Gay-Lussac and others at the time were up to 5% off.] [The factor k/μ is also modern. k is the Boltzmann constant and μ is the molecular mass. Both are quite anachronistic in the present context. However, I wish to avoid the ideal gas constant and the molar mass in this book.]

when temperature dropped, so did the kinetic energy of the particles – of gases, liquids, and solids – and finally, when all were at rest, there was no way to lower the temperature further.

Therefore William Thomson (1824–1907) (Lord Kelvin since 1892) suggested – in 1848 – to call the lowest temperature *absolute zero*, and to move upward from that point by the steps or degrees of Celsius. This new scale became known as the absolute scale or Kelvin scale, on which melting ice and boiling water at 1atm have the temperature values 273.15°K and 373.15°K respectively. K stands for Kelvin. It became common practice to denote temperature values on the Kelvin scale by T , so that we have

$$T = \left(273.15 + \frac{t}{^{\circ}\text{C}} \right) ^{\circ}\text{K}.$$

Kelvin’s absolute scale was quickly adopted and it is now used by scientists all over the world. However, the scale has subtly changed since its introduction. In 1954, by international agreement the temperatures of melting ice and boiling water were abolished as fix-points. They were replaced by a single fix-point:

$$T_{tr} = 273.16^{\circ}\text{K} \quad \text{for the triple point of water.}$$

The triple point of water occurs when ice, liquid water and water vapour can coexist; its pressure is $p_{tr} = 6.1\text{mbar}$, and its temperature is $t_{tr} = 0.01^{\circ}\text{C}$ on the Celsius scale. The modern *degree* is defined by choosing 1°K as $T_{tr}/273.16$. This unit step on the Kelvin scale was internationally agreed on in 1954 so as to coincide with the familiar 1°C . The 13th International Conference on Measures and Weights of 1967/68 even robbed temperature of its little decorative adornment “°” for degree. Ever since then we speak and write of temperature values prosaically as so many “K” instead of “degrees K”, or “°K”.¹⁰

The lowest temperatures reached in laboratories are a few μK – a few millionth of one Kelvin –, the highest may be 10MK – ten million Kelvin –, and we believe that the temperature in the centre of some stars are as high as 100 million K, cf. Chaps. 6 and 7.

For the early researchers there was no need to *define* temperature. They knew, or thought they knew, what temperature was when they stuck their thermometer into well-water, or into the armpit of a healthy man. They were unaware of the implicit assumption, – or considered it unimportant, or self-evident – that the temperature of the thermometric substance, gas or mercury, or alcohol, was equal to the temperature of the measured object.

¹⁰ Temperature measurements at extremely low temperatures are still a problem. The interested reader is referred to the publication “Die SI-Basiseinheiten. Definition, Entwicklung, Realisierung.” [The SI basic units. Definition, development and realization] Physikalisch Technische Bundesanstalt, Braunschweig & Berlin (1997) p. 31–35.

This in fact is the defining property of temperature: That the temperature field is continuous at the surface of the thermometer; hence temperature is measurable. Axiomatists call this the zeroth law of thermodynamics because, by the time when they recognized the need for a definition of temperature, the first and second laws were already firmly labelled.

2 Energy

The word energy is a technical term invented by Thomas Young (1773–1829) in 1807. Its origin is the Greek word *ἐνεργεια* which means *efficacy* or *effective force*. Young used it as a convenient abbreviation for the sum of kinetic energy and gravitational potential energy of a mass and the elastic energy of a spring to which the mass may be attached. That sum is conserved by Newton's laws and Hooke's law of elasticity, although the individual contributions might change.¹ The term *energy* was not fully accepted until the second half of the 19th century when it was extrapolated away from mechanics to include the internal energy of thermodynamics and the electro-magnetic energy. The *first law of thermodynamics* states that the *total* sum is conserved: the sum of mechanical, thermodynamic, electro-magnetic, and nuclear energies. We shall proceed to describe the difficult birth of that idea.

Eventually – in the early 20th century – energy was recognized as having mass, or being mass, in accord with Einstein's formula $E = mc^2$, where c is the speed of light.

Caloric Theory

In the early days of thermodynamics nobody spoke of energy; it was either heat or force. And nobody really knew what heat was. Francis Bacon (1561–1626) mentions heat in his book “Novum Organum” and – true to his conviction that the laws of science should be gleaned from a mass of specific observations – he tabulated sources of heat such as: flame, lightning, summer, will-o'-the-wisp, and aromatic herbs which produce the feeling of warmth when digested.²

A little later Pierre Gassendi (1592–1655), a convinced atomist, saw heat and cold as distinct species of matter. The atoms of cold he considered as tetrahedral, and when they penetrated a liquid that liquid would solidify, – somehow.

¹ The observation that mechanical energy is conserved is usually attributed to Gottfried Wilhelm Leibniz (1646–1716), who pronounced it as a law in 1693.

² Francis Bacon: “Novum Organum” (1620).

An important step away from such interesting notions was done by Joseph Black (1728–1799). Black melted ice by gently heating it and noticed that the temperature did not change. Thus he came to distinguish the *quantity* of heat and its *intensity*, of which the latter was measured by temperature. The former – absorbed by the ice in the process of melting – he called latent heat, a term that has survived to this day.

The next step – unfortunately a step in the wrong direction – came from Antoine Laurent Lavoisier (1743–1794), the pre-eminent chemist of the 18th century, sometimes called the father of modern chemistry. He insisted on accurate measurement and therefore people say that he did for chemistry what Galilei had done for physics one and a half century before. The true nature of heat, however, was beyond Lavoisier’s powers of imagination and so he listed heat – along with light – among the elements,³ and considered it a fluid which he called the *caloric*. Asimov⁴ writes that ... *it was partly because of his [Lavoisier’s] great influence that the caloric theory ... remained in existence in the minds of chemists for a half century*. The idea was that caloric would be liberated when chips were taken off a metal in a lathe (say) and thus the material became hot.

Benjamin Thompson (1753–1814), Graf von Rumford

Benjamin Thompson, later Graf von Rumford – ennobled by the Bavarian elector Karl Theodor – was first to seriously question the caloric theory. Thompson was born in Woburn, Massachusetts to poor parents, just like Benjamin Franklin (1706–1790), the other famous American scientist of the 18th century; their birthplaces are only two miles apart. Both, although congenial as scientists, subscribed to different political views. Indeed, Thompson supported the British in the war of independence; he spied for them and even led a loyalist regiment, – a *Tory regiment* for American patriots – the King’s American Dragoons.⁵

Perforce, after the colonials had won their independence, Thompson left America and, by his intelligence and his captivating demeanour, he became a man of the world, welcome in courts and scientific circles. He proved to be an inventor of everything that needed inventing: a modern kitchen – complete with sink, overhead cupboards and trash slot –, a drip coffee pot,

³ A.L. Lavoisier: “Elementary Treatise on Chemistry” (1789).

⁴ I. Asimov: “Biographical Encyclopedia of Science and Technology”.- Pan Reference Books, London (1975).

⁵ Kenneth Roberts: “Oliver Wiswell.” Fawcett Publications, Greenwich, Connecticut. (1940).

and the damper for chimneys.⁶ Also he was a gifted organizer of anything that needed to be organized:

- The distribution of a cheap, nourishing and filling soup – the Rumford soup⁷ – for the poor people of Munich,
- the transplanting of fully grown trees into the English garden of the elector of Bavaria,
- and a factory for military uniforms staffed by the beggars from the streets of Munich.

The grateful elector made him a count: Graf von Rumford, see Fig. 2.1. Rumford was a town in Massachusetts, where Thompson had lived; later it was renamed Concord – now in New Hampshire; it was a hotbed of the American revolution. Needless to say that the elector knew neither Rumford nor Concord. Actually, one cannot help feeling that the two of them, the elector and Thompson, may have had a good laugh together: The elector, who had no jurisdiction over Rumford county and Thompson, – the new Graf von Rumford – who could not show his face there without running the risk of being tarred and feathered and made to ride a fence.



Fig. 2.1. Lavoisier and Thompson (Graf Rumford), both married to the same woman, – at different times

Graf Rumford was put in charge of boring cannon barrels for the elector. He noticed that blunt drills liberated more *caloric* than sharp-edged ones, although no chips appeared. By letting the blunt drill grind away for some length of time he could liberate more caloric than was known to be needed to melt the whole barrel. Thus he came to the only possible conclusion that the caloric theory was bunk and that

⁶ According to Varick Vanardy: “Gen. Benjamin Thompson, Count Rumford: Tinker, Tailor, Soldier, Spy.” <http://www.rumford.com>.

⁷ A variant of that soup was handed out in German prisons until well into the 20th century. It was then known as “Rumfutsch”. According to Ernst von Salomon: “Der Fragebogen” [The Questionnaire] Rowohlt Verlag Hamburg (1951).

...it was inconceivable to think anything else than that heat was just the same as what was supplied to the metal as continually as heat was appearing in it namely: *motion*.⁸

Considering the jargon of the time that was a direct hit. Even fifty years later Mayer could not express the 1st law more clearly than by saying: *motion is converted to heat*, – and Mayer did still shy away from saying: *Heat is motion*.

Rumford even made an attempt to give an idea of what was later called the *mechanical equivalent of heat*. His drill was operated by the work of two horses – *of which one would have been enough* – turning a capstan-bar, and Rumford notes that the heating of the barrel by the drill

equals that of nine big wax candles.

Actually, he became more concrete than that when he said that *the total weight of ice-water that could be heated to 180°F in 2 hours and 30 minutes amounted to 26.58 pounds*.⁹ Joule fifty years later¹⁰ used that measurement to calculate Rumford's equivalent of heat to 1034 foot-pounds.¹¹ For the calculation Joule adopted Watt's measurement of one horsepower, namely 33000 foot-pounds per minute.

It is probably too much to suppose that Rumford thought about conservation of energy, but he did say this:

One would obtain more heat [than from the drill], if one burned the fodder of the horses. Thus he gave the impression, perhaps, that he may have suspected those amounts of heat to be the same.

Rumford *through his arrogance and the general unpleasantness of his character* – so the American author Asimov¹² – *eventually outwore his welcome in Bavaria*. He went to England where he was admitted into the Royal Society. He founded the Royal Institution, an institute which may be regarded as the prototypical postgraduate school. Rumford engaged Thomas Young and Humphry Davy as lecturers, who both became eminent scientists in their own time. Jointly with Davy, Rumford continued his

⁸ Rumford: "An inquiry concerning the source of the heat which is excited by friction". Philosophical Transactions. Vol. XVIII, p. 286.

⁹ Rumford: loc.cit. p. 283.

¹⁰ J.P. Joule: "On the mechanical equivalent of heat". Philosophical Transaction. (1850) p. 61ff.

¹¹ This means that a weight of 1 pound dropped from a height of 1034 feet would be able to heat 1 pound of water by 1°F. [Joule's best value in 1850 is 772 foot-pounds, see below.]

¹² I. Asimov: "Biographies...." loc.cit.

Americans do not like their countryman Graf Rumford because of his involvement in the war of independence on the side of the loyalists. They scorn him and revile him, and largely ignore him. This is punishment for a person who fought on the wrong side – the side that lost. *We* must realize though that the American revolutionary war was as much a civil war as it was a war against the British rule; and civil wars have a way of arousing strong feelings and long-lasting hatred.

experiments on heat: He carefully weighted water before and after freezing and found the weight unchanged, although it had given off heat in the process. Therefore he concluded that the caloric, if it existed, was *imponderable*. This observation should have disqualified the caloric, but it did not, not for another 40 year.

After England, Rumford went to Paris where, posthumously, he crossed the path of Lavoisier, because he married the chemist's widow. Asimov writes

The marriage was unhappy. After four years they separated and Rumford was so ungallant as to hint that she was so hard to get along with that Lavoisier was lucky to have been guillotined¹³. However, it is quite obvious that Rumford was no daisy himself.

Rumford's insight into the nature of heat was largely ignored and the caloric theory of heat prevailed until the 1840s. At that time, however, in the short span of less than a decade three men independently – as far as one can tell¹⁴ – came up with the first law of thermodynamics in one way or other. Basically this was the recognition that the gravitational potential energy of a mass at some height, or the kinetic energy of a moving mass, may be converted into heat by letting it hit the ground. The three men who realized that fact in the 1840s were Mayer, Joule and Helmholtz. All three of them are usually credited with the discovery. And although all three devote part of their works to the discussion of the weightless caloric – actually to its refutation – it is clear that that theory had run its course. Says Mayer in his usual florid style: *Let's declare it, the great truth. There are no immaterial materials.*

Robert Julius Mayer (1814–1878)

Mayer was first and he went further than either of his competitors, because he felt that energy *generally* was conserved. He included tidal waves in his considerations and conceived of falling meteors as a possible source of solar heat- and light-radiation. Nor did he stop at chemical energy, not even chemical energy connected with life functions.

Mayer was born and lived most of his life in Heilbronn, a town in the then kingdom of Württemberg. Württemberg was one of the several dozen independent states within the loose German federation, whose rulers

¹³ Lavoisier was executed on May 8, 1794 because of his involvement in tax collection under the *ancien régime*. On the eve of his execution he wrote a letter to his wife. The chemist was being philosophical: “*It is to be expected*” the letter reads “*that the events in which I am involved will spare me the inconvenience of old age.*”

¹⁴ This is what is usually said. It is not entirely true, though. To be sure, it is likely that Joule and Helmholtz were unaware of Mayer's ideas, but Helmholtz was fully aware of Joule's measurements, he cites them, see below.

suppressed all activity to promote German unity. Unity, however, was vociferously clamoured for by the idealistic students in their fraternities; therefore fraternities were declared illegal. But in Tübingen, where Mayer studied medicine, he and some friends were indiscreet enough to found a new fraternity. He was arrested for that – and for *attending a ball indecently dressed* – and relegated from the university for one year.

Mayer made good use of the enforced inactivity by continuing his medical education in Munich and Paris and then took hire as a ship's physician – a *Scheeps Heelmeester* – on a Dutch merchantman for a round-trip to Java. This left him a lot of free time since, in his words, *on the high seas people tend to be healthy*. He learned about two important phenomena which he lists in his diaries:

- The navigator told him that during a storm the ocean water becomes warmer,¹⁵ and
- while bleeding patients he observed that in the tropics venous blood is similar in colour to arterial blood.

The first observation could be interpreted as motion of the water waves being converted to heat and the second seemed to imply that the des-oxidization of blood is slower when less heat must be produced to maintain the body temperature.

The flash of insight, a kind of ecstatic vision, came to Mayer when his ship rode at anchor off Surabaya taking on board a consignment of sugar. Henceforth he was a changed man, a fanatic in the effort of spreading his gospel. And he hurried back home in order to let the world know about his discovery.¹⁶

The gospel, however, left something to be desired. At least nobody wanted to hear it. Right after his return from Java Mayer rushed out a paper: “Über die quantitative und qualitative Bestimmung der Kräfte.”¹⁷ Actually there was nothing quantitative in the paper and, moreover, it was totally and completely obscure. There was hapless talk in hapless mathematical and geometrical language which could not possibly mean anything to anybody. The only saving grace is the sentence: *Motion is converted to heat*, which Rumford had said 40 years before. The paper ends characteristically in one of the hyperbolic statements which are so typical for Mayer's style: *In stars the unsolvable task of explaining the continuous creation of force, i.e. the*

¹⁵ This observation is also mentioned by J.P. Joule: “On the mechanical equivalent of heat”. Philosophical Transaction (1850) p. 61 ff.

¹⁶ Later, in 1848, Mayer was involved in a political squabble and he was ridiculed publicly as having travelled as far as East India without setting his foot on land. This, however, seems to be untrue, if Mayer's diary is to be believed. He did leave the ship for a short excursion; cf. H. Schmolz, H. Weckbach: “Robert Mayer, sein Leben und Werk in Dokumenten”. Veröffentlichungen des Archivs der Stadt Heilbronn. Bd. 12. Verlag H. Konrad (1964) p. 86.

¹⁷ “On the quantitative and qualitative determination of forces”.

differentiation of 0 to MC – MC, is solved by nature; the fruit of this is the most marvellous phenomenon of the material world, the eternal source of light. And in unshared enthusiasm Mayer finishes the paper with the hopeful words

Fortsetzung folgt = to be continued.

Well, Poggendorff, to whose “Annalen der Physik and Chemie” Mayer had sent the paper on June 16th 1841, was unimpressed. Certainly and understandably he did not want to encourage the author. Despite several urgent reminders by Mayer – the first one on July 3rd 1841 (!) – Poggendorff never acknowledged receipt, nor did he publish the paper.¹⁸ He must have thought of Mayer as of some queer physician in Heilbronn with an unrequited love of physics.

Mayer had started a practice in Heilbronn, and in May 1841 he was appointed *town surgeon* which gained him a regular salary of 150 florin. Later he changed to *Stadtarzt*, at the same salary, and in that capacity he had to treat the poor, – free of charge – and also the lower employees of the town, like the prison ward or the night watchman.¹⁹

Mayer’s problem in physics was that he did not know mechanics. He took private instruction from his friend Carl Baur who was a professor of mathematics at the Technical High-School Stuttgart, but Mayer never graduated to the knowledge that the gravitational potential energy mgH of a mass m at height H is converted to the kinetic energy $\frac{m}{2}v^2$ when the mass falls and acquires the velocity v ; specifically the factor $\frac{1}{2}$ remained a mystery for him. To be sure, he never used the word energy in the above sense: gravitational potential energy was *falling force* for him and kinetic energy was *life force*.²⁰

All he knew was, that motion, or the *life force* of motion could be converted into heat and he even came up with a reasonable number: the *mechanical equivalent of heat*, cf. Insert 2.1.

$$1^\circ \text{ heat} = 1 \text{ gram at } \left\{ \begin{array}{c} 365 \text{ m} \\ 1130 \text{ Parisian feet} \end{array} \right\} \text{ height .}$$

¹⁸ The manuscript did survive and, when Mayer’s work was eventually recognized, the paper was published in journals and books on the history of science, e.g. P. Buck (ed): “Robert Mayer – Dokumente zur Begriffsbildung des Mechanischen Äquivalents der Wärme”. [Robert Mayer – documents on the emergence of concepts concerning the mechanical equivalent of heat] Reprinta historica didactica. Verlag B. Franzbecker, Bad Salzdetfurth (1980) Bd. 1, p. 20–26.

¹⁹ H. Schmolz, H. Weckbach: “Robert Mayer ...” loc.cit p. 66, p. 78.

²⁰ The *life force* must not be confused with the *vis viva* of the vitalists. In German the kinetic energy was called *lebendige Kraft* at that time, while the *vis viva* was called *Lebenskraft*. In English the distinction is not so clear and sometimes not strictly maintained, although usually the context clarifies the meaning.

Mayer's calculation of the mechanical equivalent of heat

Mayer knew – or thought he knew – that the specific heats of air are $0.267 \frac{\text{cal}}{\text{gK}}$ and $\frac{0.267}{1.421} \frac{\text{cal}}{\text{gK}}$ at constant pressure and volume respectively. To heat 1 cm^3 air at a density of $1.3 \cdot 10^{-3} \text{ g/cm}^3$ by 1°C it should therefore take

$$\begin{aligned} &0.347 \cdot 10^{-3} \text{ cal at fixed pressure, and} \\ &0.244 \cdot 10^{-3} \text{ cal at fixed volume.} \end{aligned}$$

At constant pressure the volume expands. The difference in heat is $1.03 \cdot 10^{-4} \text{ cal}$ and that difference can lift a 76 cm tube of mercury of mass 1033g which exerts a pressure of 1 atm. At 1°C the lift amounts to $\frac{1}{274}$ cm according to Mariotte's law, which nowadays we call the thermal equation of state of ideal gases, like air. Thus now it is a simple problem of the *rule of three*:

$$\begin{aligned} 1033 \text{ g at } 1/274\text{cm} &\text{ corresponds to } 1.03 \cdot 10^{-4} \text{ cal} \\ 1 \text{ g at } H = ? &\text{ corresponds to } 1 \text{ cal.} \end{aligned}$$

It follows that $H = 365 \text{ m}$ and so Mayer wrote:

$$1^\circ \text{ heat} = 1 \text{ g at } 365 \text{ m height}$$

Note that Mayer did not measure anything. He took his specific heat from some French experimentalists whom he quotes as Delaroche and Bérard. And the ratio of specific heats he took from Dulong. Both numbers are slightly off and therefore Mayer's mechanical equivalent of heat was low.

Insert 2.1

In words: The fall of a weight from a height of ca. 365 m corresponds to the heating of the same weight of water from 0°C to 1°C . Later, with reference to Joule's better measurements, he changed to 425 m or 1308 Parisian feet. The old value – but not its calculation – is included in Mayer's second paper, see Fig. 2.2, which otherwise is not much clearer than the first one. Anyway that paper established Mayer's priority when Justus von Liebig (1803–1873) published it in his "Annalen der Chemie und Pharmacie". To be sure, Mayer did not give Liebig much of a choice; his accompanying letter would have flattered any hard-nosed editor into acceptance, cf. Fig. 2.3. Those readers who have a command of German may learn from the letter how editors should be approached.

There is a peculiar type of reasoning in the paper. Mayer, rather than just postulate the conversion of motion to heat and make it plausible, attempts to *prove* his discovery from some perceived *theorem of logical cause* or from an assumed axiom *causa aequat effectum*. On another occasion, the conservation of energy – *force* for Mayer – is summarized in the slogan

Ex nihilo nil fit. Nil fit ad nihilum.

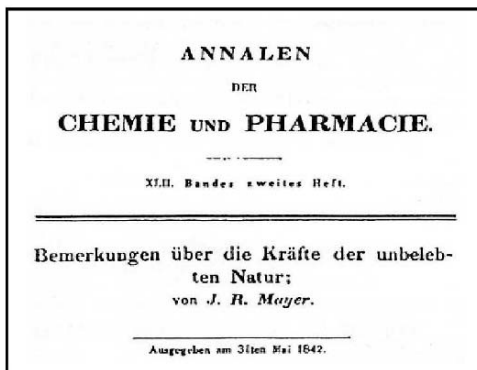


Fig. 2.2. Robert Julius Mayer. Cut from the title page of his first published paper

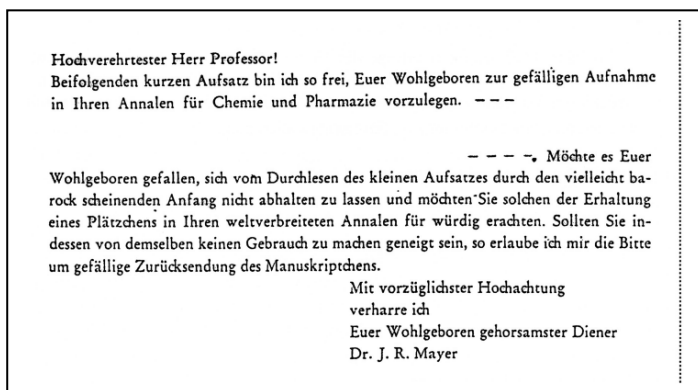


Fig. 2.3. Cut from Mayer's letter accompanying the paper submitted to Liebig

We have to make allowance, however, for Mayer's almost complete isolation. Occasionally he sought scientific advice from physics professors, but then he was fobbed off with the demand to support his theory by experiments and, in one case, he was sent home with the information that the area of science was already so big that an extension was undesirable.²¹

So he was thrown back to his family and a few friends for scientific monologues. They understood nothing and naturally they thought that their husband and friend was more than a little crazy. The pressure on Mayer mounted when his priority claim was ignored by Joule, and Helmholtz, and by a lesser man – a Dr. Otto Seyffer – who ridiculed Mayer's ideas in an article in the daily press.²² Two of his children died and Mayer came close

²¹ Reported by Mayer in a letter to his friend W. Griesinger on June 14th 1844. Mayer's correspondence with some of his friends is included in the collection of his works. Reprinta historica didactica. loc cit. Bd. 1, p. 121.

²² "Augsburger Allgemeine Zeitung" from May 21st, 1849.

to being executed as a spy by some republican radicals who – in the course of the revolution of 1848/49 – briefly won the upper hand in parts of Württemberg. In 1850 all this led to an attempted suicide when Mayer jumped from the third floor of his house into the yard 9 meters below. He survived but was permanently slightly crippled.

Mayer's relatives sought the professional help of an alienist who was a friend of the family. However, the man was also young, and new in his practice, and he needed the money. Therefore he had no intention to let Mayer go anytime soon. He put him behind bars and for good measure kept him in a straightjacket. Eventually, after 13 months of this, Mayer succeeded to escape and he reached home by foot in his nightgown. After that he was indeed a trifle neurotic, patients stayed away from him and the street urchins would taunt him: *There he goes, the dotty Mayer*.

However, my former critical remarks on Mayer's papers must not give the impression that Mayer was anything less than a very original scientist. And despite the evidence of the papers mentioned above, he *could* write well, if he did not force himself to be excessively brief, – and if he did not attempt to use mathematics. The style of his brochure “Die organische Bewegung in ihrem Zusammenhang mit dem Stoffwechsel”²³, published in 1845 by a small Heilbronn printing shop, is still idiosyncratic, but it is clear. Among the subjects which Mayer takes up in that extensive memoir, I mention a few in order to show the scope of his purpose:

- Mayer overcomes Carnot and Clapeyron and paves the way for Clausius when he speaks of the heat engine and says ... *the heat absorbed by the vapour is always bigger than the heat released during condensation. Their difference is the useful work.*
- He explains in detail how he calculated the mechanical equivalent of heat, cf. Insert 2.1. That argument was too brief in his 1842 paper to be understood and appreciated. The calculation is a solid piece of thermodynamics – now very elementary – and it had nothing to do with horses stirring paper pulp in cauldrons, as folklore has it. To be sure, those horses are mentioned in the article, and some rough measurements of the temperature of the pulp, but these were far from good enough to calculate the mechanical equivalent of heat. Incidentally, in this context Mayer mentions Rumford; therefore he knew about Rumford's experience with boring cannon.
- He also reports that a cannon barrel which shoots a ball becomes less hot than if the powder alone is ignited in the barrel. Mayer says that the fact is *common knowledge*. Well, maybe it was at the time. Anyway, the observation makes sense: Part of the chemical energy of the powder is

²³ [Organic motion and metabolism] Verlag der C. Drechslerschen Buchhandlung, Heilbronn (1845).

converted into the kinetic energy of the ball, if there is a ball. Otherwise all goes into heat.

- Mayer extrapolates that observation to the metabolism in animals, and men. The heat liberated by the chemical process of digestion, or of internal combustion of food, can partly be converted into work, he says, whereupon the body becomes colder. In order to support this idea he cites an observation that was published in the “Journal de Chimie médicale, VIII Année, Février”, where the author – a man by the name of Douville – measured the temperature of

a negro lazy and inactive in the cabin			37°
ditto	ditto	in the sun	40.20°
ditto	active	in the sun	39.75°.

- Pursuing the idea further, Mayer says that a man sawing wood freezes in the arm which moves the saw. Also a blacksmith who heats a piece of iron to red-heat with three strokes will be cold in the arm that wields the hammer. He says that he has observed that the busy parts of the body sweat less during continual hard work than the inactive ones. For this latter observation he cites biblical proof. Namely when God says to Adam: *In the sweat of your brow you shall eat bread*. Mayer seems to think that Adam will henceforth work with his hands and feet, which will therefore sweat less than the head which is involved but little, or not at all.
- In the same memoir Mayer comes out strongly against the *vis viva*, the hypothetical force postulated by physiologists of the time – even Liebig – to explain organic processes, or rather to set them aside as unexplainable.
- The heat of the earth – put in evidence by warm springs and volcanoes – is explained by Mayer as the equivalent of the kinetic energy with which the constituent masses crashed together at the time when the earth was formed. In a rough-and-ready calculation he estimates the original temperature to have been 27600°C, enough for the earth to have been liquid, or actually gaseous.

We could continue the list of Mayer’s thoughts on mechanics, astronomy, biology, and physiology by dozens of more item. Maybe they are not all correct, but they are all original. Like the theory of the heat of the earth, or when he thinks that the solar energy stems from the meteors which fall into the sun. Sometimes he capitulates, like when he wonders why planets have orbits with rather small ex-centricities. He suspects that this might be explainable by his ideas on the conversion of motion into heat but cannot do it. Calculations of tidal forces were far beyond his mathematical ability.

Most of the brochure of 1845 is written in a matter-of-fact style, but at the very end Mayer’s propensity for hyperbole breaks through again. Thus

the work ends with the sentence: ...*may the phenomena of life be compared to a wonderful music full of melodious sounds and touching dissonances; only in the concert of all instruments lies harmony and only in harmony lies life.*

For all that, however, Mayer never knew what the nature of heat was. In his brochure “Bemerkungen über das mechanische Äquivalent der Wärme”²⁴ in 1851 he says that ... *the connection between heat and motion is one of quantity rather than quality* and he tends to assume that ... *motion must stop in order to become heat.* Here he was wrong and he could have known it. Indeed, the fledgling mechanical theory of heat existed already and in a short time – in the hands of Maxwell – it should rise to its first peak. By that theory, the kinetic energy of motion of a body was just re-distributed among its atoms when it seemed to disappear; and heat was how that re-distributed motion was felt. Helmholtz, about whom Mayer complains for not having given his work proper credit, explains the relation between heat and atomic motion very well.

Mayer in some way was burned out by that time, he missed the further development of what he had helped to start, although he lived until 1878, one year before Maxwell died. Ironically he did receive some recognition after he had stopped working seriously. John Tyndall (1820–1893), a well-regarded physicist and prolific science author,²⁵ supported Mayer in his priority quarrel with Joule, and Mayer received the Copley medal from the Royal Society of London. In 1858 Liebig called Mayer *the father of the greatest discovery of the century* and in 1859 Mayer received an honorary doctorate from his old *alma mater* in Tübingen.

The chamber of commerce of Heilbronn elected Mayer to honorary membership, and the king of Württemberg ...*whose pleasure it is to reward great achievements*²⁶ made Mayer a knight of the order of the Württemberg crown. Mayer could now call himself “von Mayer”.

Yet, Mayer is largely forgotten, but *not* in his hometown Heilbronn. The people in the town archive look after his memory with loving care.²⁷ His bronze statue is displayed in a prominent spot of the town, and the monument carries the somewhat pompous quatrain

²⁴ [Remarks on the mechanical equivalent of heat] Verlag von Johann Ulrich Landherr, Heilbronn (1851) Bd. 1, p. 169.

²⁵ Tyndall is best known for his work on light scattering. It was he who explained the blue colour of the sky, but he also wrote a book on thermodynamics entitled “Heat as a mode of motion” which appeared in 1863.

²⁶ So Mayer in an autobiographical note. Reprinta historica didactica. loc.cit. Bd. 1, p. 8.

²⁷ When I visited the archive, I had to park my car precariously. A policeman promptly showed up, but, as soon as he heard that I was interested in Mayer he promised to watch over my car: “Take as long as you like, sir.”

Wo Bewegung entsteht, Wärme vergeht
 Wo Bewegung verschwindet, Wärme sich findet
 Es bleiben erhalten des Weltalls Gewalten
 Die Form nur verweht, das Wesen besteht.

James Prescott Joule (1818–1889)

Joule was the son of a rich brewer who was tolerant enough of the scientific interests of his son to furnish him with a home-laboratory. Joule is best known for the discovery of the *Joule heating* of a current that runs through a wire. That heat is proportional to the square of the current. In the course of those studies Joule conceived the idea that there might be a relation between the heating of the current and the mechanical power needed to turn the generator.

And indeed he established that relation and came up with a *mechanical value of heat* which he expresses in the words²⁸

The amount of heat which is capable of raising [the temperature of] one pound of water by 1 degree on the Fahrenheit scale, is equal and may be converted into a mechanical force which can lift 838 pounds to a vertical height of 1 foot.²⁹

Joule's memoir is full of tables with carefully recorded observations. He describes his experiments painstakingly, discusses possible sources of experimental error, and attempts to compensate for estimated losses. In that sense his paper has set standards, although to this day thermal and, in particular, caloric measurements are notoriously difficult, time-consuming and inaccurate to boot.

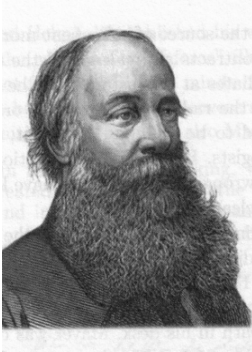
And indeed, in later experiments – reported in a similarly exemplary fashion in the article “On the temperature changes by expansion and compression of air”³⁰ – Joule obtains the values 820, 814, 795, and 760 instead of the 838 pounds cited in his article of 1843. And there were other values from other experiments so that in 1845 Joule proposed a mean value of 817 pounds³¹ as the most likely one. In the letter to the editors of the *Philosophical Transactions* he says:

²⁸ J.P. Joule: “On the heating effects of magneto-electricity and on the mechanical value of heat.” *Philosophical Magazine*, Series III, Vol. 23 (1843) p. 263ff, 347ff, 435ff.

²⁹ The paper was read to the Section of Mathematical and Physical Sciences of the British Association, Convention in Cork on August 21st, 1843.

³⁰ J.P. Joule: *Philosophical Magazine*, Series III, Vol. 26 (1845), p. 369 ff.

³¹ J.P. Joule: “On the existence of an equivalence relation between heat and the ordinary forms of mechanical power”. Letter to the editors of the *Philosophical Magazine and Journal*. *Philosophical Magazine*. Series III, Vol. 27 (1845), p. 205 ff.



Joule criticizes Carnot's and Clapeyron's analysis of the steam engine, see Chap. 3

He says: *Since I hold the view that only the creator has the power to destruct, I agree with ... Faraday, that any theory that leads to the destruction of force is necessarily false.*³²

Fig. 2.4. James Prescott Joule. A pious version of the first law

Each one of your readers who is lucky enough to live in the romantic areas of Wales or Scotland could indubitably confirm my experiments, if he measured the temperature of a waterfall on top and at the bottom. If my results are correct, the fall must create 1° heat for a fall of 817 feet height; and the temperature of the Niagara will therefore be raised $1/5$ of a degree by the fall of 160 feet.

Asimov³³ writes that Joule in fact made that experiment at the waterfall himself during his honeymoon when he and his wife visited a scenic waterfall.

In 1850, after many more experiments, Joule came up with 772 which is a really good value, see below.³⁴

We have already seen that Joule knew Rumford's work and, in fact, that he tried to calculate the mechanical equivalent of heat from Rumford's observation. This came out too high – 1034 foot-pounds – but it was close enough to Joule's spectrum of values that he could say that Rumford's *result confirms our conclusions satisfactorily.*³⁵

In the same postscript Joule says that he observed that water pressed through narrow tubes heats up, and that gave him yet another value, – 770 foot-pounds. And he expresses his believe in the conservation of energy by saying: *I am convinced that the mighty forces of nature are indestructible by virtue of the Creator's: F I A T!*

To this day the conservation of energy is an assumption – well-documented, to be sure, but still an assumption. But like Mayer, Joule feels that he needs to *prove* the law. And since he cannot do that, he comes up with strange formulations: *We may a priori assume that a complete destruction of force is supposedly impossible, since it is obviously absurd,*

³² J.P. Joule: "Temperature changes by expansion and compression of air." *Philosophical Magazine Series III*, 26 (1845) p. 369 ff.

³³ I. Asimov: "Biographies...." loc.cit.

³⁴ J.P. Joule (1850) loc.cit.

³⁵ *Post Scriptum* to Joule's memoir of 1843. loc.cit.

that the properties, with which God has endowed matter, could be destructed.

The attentive reader will have noticed that after Mayer had adjusted his heat-equivalent to Joule's better measurements – as mentioned before – he had

$$1^\circ \text{ heat} = 1 \text{ gram at } \left\{ \begin{array}{l} 425 \text{ m} \\ 1308 \text{ Parisian feet} \end{array} \right\} \text{ height .}$$

Let us see how Mayer came up with those numbers: If 1308 feet is multiplied by 5/9 to convert from °F to °C we obtain 727 feet, – considerably lower than any of Joule's numbers. But then we must realize that an English foot is 30.5 cm while the Parisian one was 32.5 cm. Thus Joule's value, as quoted by Mayer, was indeed 772 English foot-pounds as stated before.

Of course, foot-pounds are out nowadays. The older ones among the readers may remember their university days, when they learned the mechanical equivalent of heat in the form:

$$1 \text{ calorie} = 4.18 \text{ Joule.}$$

Yes, indeed, *Joule* is the modern unit of energy! It is equal to 1 kgm²/s². Joule gets the honour, because he was most accurate for the time and he backed up his figure with a large variety of careful measurements.³⁶ Actually, the calorie went also out as a unit when the SI units were introduced,³⁷ and nowadays all energies are measured in Joule, be they mechanical, thermal, chemical, electric, magnetic, or nuclear. This was a great relief indeed for everybody concerned.

A good case can be made that the first law of thermodynamics, the law of conservation of energy, was the greatest discovery of the 19th century. And how was it received? We have already described how Mayer had to grovel in order to have his paper accepted for publication, and Joule fared no better. Asimov writes³⁸

His [Joule's] original statement of his discovery was rejected by several learned journals as well as by the Royal Society and he was forced to present it as a public lecture in Manchester and then get his speech published in full by a reluctant Manchester newspaper editor for whom Joule's brother worked as a music critic.

³⁶ Of course, 418 m is not Mayer's and Joule's 425 m. The difference lies in the gravitational acceleration 9.81 m/s², because Mayer's grams and Joule's pounds were weights, not masses. We have to correct for that.

³⁷ Système International d'Unites. It was introduced by international agreement in 1960.

³⁸ I. Asimov: "Biographies" loc.cit.

The lecture was given on April, 28th 1847 in the St. Ann's Church Reading-Room in Manchester. It was published by the Manchester Courier on May 5th and May 12th.