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The Mayer-Joule Principle: The Foundation of the First Law of Thermodynamics

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To most students today the mechanical equivalent of heat, called the Mayer-Joule principle, is simply a way to convert from calories to joules and vice versa. However, in linking work and heat—once thought to be disjointed concepts—it goes far beyond unit conversion. Heat had eluded understanding for two centuries after Galileo Galilei constructed an early thermometer. Independently, Julius Robert Mayer and James Prescott Joule found the connection between heat and work, the Mayer-Joule principle.

Some argued that the source of heat was motion, others that it was a massless, subtle conserved fluid called caloric. Several *different* calorics, with different properties, were proposed, including those used by Joseph Black and Nicolas Sadi Carnot.^{1,2} Before 1840 heat and work quantities were believed to be as different as apples and oranges, with different physical dimensions and units.

The Mayer-Joule principle led to the first law of thermodynamics, an expression of total energy conservation that links heat and mechanical work with the *internal energy* function. While heat and work quantities are process dependent, changes in internal energy are process independent. The importance of the Mayer-Joule principle far transcends the role of a mere conversion factor. Indeed the path-breaking work of Mayer and Joule fusing heat and work is as fundamental to physics as the ideas of James Clerk Maxwell and Albert Einstein fusing electricity and magnetism.

Only by appreciating the knowledge base and mindsets of these early scientists can we see the power and beauty of the Mayer-Joule principle. We trace the 250-year evolution needed to realize that heat and work have the same physical dimension, energy, with an exchange rate, J . In contrast, if one *begins* with the notion that heat and work are dimensionally equivalent, it is impossible to appreciate the subtleties of heat. Our goal is to review relevant historical developments relating to temperature and thermometry, the tortuous history of heat, the Mayer-Joule principle and its fundamental importance, and existing language difficulties generated by the circuitous history.

Temperature and thermometry

Although Isaac Newton had laid the foundations of classical mechanics in his *Principia* (1687), thermal physics had no comparable unifying set of principles, and there was no way to relate thermal phenomena to dynamic mechanical concepts.

For centuries *hot* and *cold* had been used to describe the thermal states³ of bodies, but there was no quantitative measure of the degree of heat. Comparing the thermal states of two bodies was almost impossible. The word *temperature* first appeared in the 16th century, but not in its modern sense, and meant the fact or state of being mixed or tempered. Its first use to describe the degree of heat was in the mid-17th century⁴ and coincided with progress in thermometry. To develop thermometers it was necessary to find a property of a material that depended on its thermal state. As early as the Hellenistic age, the expansion of a heated gas was used for toys and mechanical devices. Galileo was the first to apply this principle to construct a type of thermometer^{2,5} that was sensitive to changes in both the thermal state and atmospheric pressure (it was actually a *barothermoscope*). Having no fiducial points, it did not provide quantitative information.

By the beginning of the 18th century, the ability to make glass capillaries made possible the use of liquids instead of gases as practical materials for thermometers. With the introduction of fiducial points, e.g., the boiling and freezing points of water, one could construct a thermometer scale. It was recognized that the expansion of liquids is not linear and differs for different materials. Thus each thermometer was unique but could be compared with others. Placing a thermometer in contact with a second body allowed the assignment of a number, the temperature, to describe the thermal state. Notably the dimension of temperature, like those of length, mass, time, and charge, is a fundamental dimension; i.e., the temperature unit cannot be derived from other units.⁶

Using a thermometer to assign a number to describe the thermal state required an axiom. The zeroth law of thermodynamics was formalized in the 1930s by Ralph Fowler,⁷ and was named by Arnold Sommerfeld.⁸ Interestingly, Ernst Mach had foreseen its essence:⁵ “If two bodies A and B are, as the common phraseology goes, both as warm as, or both provoke the same sensations of heat as, a third body C, then A is, in the same sense, just as warm as body B. This is a logical necessity, and we are incapable of thinking it otherwise.” Mach was not referring to subjective sensation but rather to *quantitative* measurement of temperature. Iron and wood at the same temperature are in the same thermal state even though our sensations signal that the iron feels cooler to the touch because of its higher thermal conductivity. The zeroth law implies that if two bodies A and B are put in thermal contact, they equalize their temperatures i.e., they are in thermal equilibrium.

Heat

As early as the 1620s, Bacon and Galileo (separately) hypothesized that heat was a consequence of the microscopic motion of the invisible particles that made up the hot body.⁹ However it was impossible to describe and relate this motion to any Newtonian dynamic quantity. In the mid-18th century a second theory appeared, namely that heat is a substance. Even after thermometers existed, the interpretation of temperature was unclear. Were temperature and quantity of heat identical or distinct physical concepts? Black¹⁰ was the first to make a distinction between the two, viewing temperature as the *degree of heat* of a body, an intensity. He recognized mercury as a good thermometric material and measured heat in terms of heating times using a constant heating source. Bodies in thermal equilibrium would have the same temperature independent of size. Equally important, Black viewed heat as a measurable quantity, an impossibility with the heat as-motion-theory. He knew that the time required to boil water depended on its mass; the greater the mass, the longer the heating time, and the more heat supplied.

Recognizing the need for quantitative heat measurements, Black developed calorimeters. He perfected the method of mixtures in which two masses of liquid at two different temperatures were mixed and a final intermediate temperature was reached. He repeated this procedure with different liquids, masses, and temperatures. These experiments led to the concept of specific heat capacity, the quantity of heat (proportional to heating time) per unit mass required to raise the temperature of a body by one degree. Black's experimental skills and analytic ability led him to discover¹¹ latent heats of fusion and liquefaction.¹² Black interpreted his experiments as proof that heat was a conserved substance; i.e. when mixing two liquids the amount of heat lost by one equaled that gained by the other. In 1820, Nicolas Clement defined the calorie as the heat needed to raise water from 13.5°C to 14.5°C.¹³

Conservation was very much in the air at the end of the 18th century, strongly supported by Antoine Lavoisier, who named the substance *calorique* or *caloric*. As a substance, caloric was subtle, massless, invisible, and had no known relation to classical mechanics. Count Rumford (Benjamin Thompson)¹⁴ revived the theory of heat as motion, showing that the work done in cannon boring produced limitless amounts of heat. This destroyed the idea that heat was a conserved substance. He also proved that caloric was by necessity massless. Oddly enough Rumford had little influence on the development of thermal physics because he did not envisage a new conservation law to replace that of caloric.^{15,16}

In some ways caloric achieved its greatest success when Carnot¹⁷ applied it to analyze the efficiency of steam engines. Despite Rumford's work, Carnot based his analysis on the conservation of caloric in the operation of his heat engine cycle. Although caloric was transferred from a high temperature reservoir to one at low temperature and then back to the high, zero caloric was lost in the cycle, yet work was done. Carnot reasoned from the analogy of a waterfall, for which

work is done but no water is destroyed. For the waterfall, the work depended on the difference in height, while Carnot's engine depended on a difference in temperature.¹⁸ Notably, his caloric had units of work per degree of temperature (reminiscent of entropy), quite different from Black's caloric, whose thermal unit was akin to today's calorie. Although Carnot's work suggested a relation between heat and mechanical work, no such connection was made until the independent efforts by Mayer and Joule.

Mayer-Joule principle and its meaning

As of 1840, the year of Mayer's first discoveries, heat as motion was an inadequate concept because it did not relate to Newtonian dynamic quantities. Caloric as a substance was inadequate because Rumford showed it was not conserved. Although Rumford could produce heat from mechanical work and Carnot could produce work from heat (albeit not with 100% efficiency), no one had appreciated that heat and work were different aspects of the same physical entity.

What then did Mayer propose? As a physician in Java, he observed that venous blood drawn in the tropics was far brighter than that drawn in Germany. Familiar with Lavoisier's studies on combustion, he argued that the combustion of food provided the power for muscular work and also maintained the amount of heat in a body. In the tropics less heat was lost to the surroundings than in colder Europe. The difference in color arose from fewer oxidation products in the blood. Although not a physicist by training, Mayer used existing data to arrive at a quantitative value for the exchange rate J that made heat and work comparable.

Using modern notation and terminology, László Tisza¹⁵ describes Mayer's argument. Suppose the energy needed to heat a mass m of dilute gas through temperature difference dT is dQ_p for constant-pressure heating and dQ_v for constant-volume heating. These heating energies are in "heat units," namely calories. Mayer knew that $dQ_p - dQ_v > 0$, and he attributed the difference to the work done by the gas expanding during constant-pressure heating. This work, in joules, is PdV , where P is pressure and dV is the volume change.

The heating energy difference is $dQ_p - dQ_v = Jm(c_p - c_v)dT$, where J converts calories to joules. The specific heats c_p and c_v at constant pressure and volume respectively have units $\text{cal}^\circ\text{C}^{-1}\text{g}^{-1}$. Using Mayer's assumption that the heating energy difference equals the constant-pressure work, we obtain

$$Jm(c_p - c_v)dT = PdV. \quad (1)$$

If the mass m of gas corresponds to n moles, then at constant pressure, $PdV = nRdT$, where R is the gas constant. A bit of algebra leads to the result

$$J = \frac{nR}{m(c_p - c_v)}. \quad (2)$$

Using available, but flawed, specific heat data, Mayer's result was equivalent to $J = 3.58$ joules/cal.¹⁹

Joule independently established a value for J in numerous calorimetry experiments. The one most often cited used a shaft with paddles rotating in a liquid. Joule measured the amount of work done by the shaft and the consequent rise in temperature of the liquid. He also did experiments using galvanic and induction currents as sources of electric work. Lord Kelvin (William Thomson) was an enthusiastic supporter of Joule's experiments. For a detailed account of the experiments of Mayer and Joule, see Mach.⁵ Joule's best value, published in 1850, was 4.16 joules/cal, quite close to the modern value 4.18 joules/cal.²⁰ The question of priority gave rise to considerable acrimony between Mayer and Joule, an acrimony with nationalistic overtones.²¹

It remained for Rudolf Clausius²² to introduce the concept of internal energy U and write the first law of thermodynamics in its modern form,

$$dU = dQ - dW. \quad (3)$$

Here dU represents an *exact* differential of the internal energy state function, meaning that changes in U are independent of path. In contrast, the symbol d indicates a path-dependent change and dQ and dW depend explicitly on the thermodynamic path. Although Q and W are *not* functions of a system's thermodynamic state, the difference $dQ - dW$ is an exact differential. Notably, an infinite number of combinations of heat and work, along different paths, can lead to the same change in U .

For an ideal gas, $dU = mc_v dT$, and for constant-pressure heating, $dQ = mc_p dT$ and $dW = nRdT$, so that Eqs. (3) and (1) are equivalent. This shows that Mayer's assertion that the difference between constant-pressure and constant-volume heating energies equals the work done by the gas at constant-pressure is correct for an ideal gas.²³ Once it was understood that heat and work are both energy transfers expressible with the same units, the factor J was no longer needed; i.e., heat and work could both have the *same* energy unit. Equation (3) states that a change in the internal *energy* of a system equals the amount of *energy* absorbed from heating less the amount of work *energy* done by the system. It is a conservation law that reconciles heat and work processes and establishes the existence of internal energy.

Persistent language difficulties

Because the concept of heat had its roots in the now defunct caloric theory, remnants of those roots remain,²⁴ and people who teach and study physics should be aware of this. Succinctly, there are five main points in this regard.

1. Strictly speaking, heat and work are *processes* that transfer energy. Thus thermodynamically, heat and work are best viewed as adjectives. Robert Romer argues that "heat is not a noun,"²⁵ while John Jewett²⁶ observes that in fact heat *can* be a noun, but is the name of a process rather than the name of *what* is transferred. The main point is that using

heat as a noun to designate "the heat in a body" is incorrect, and one way to avoid error is to use heat either as an adjective (e.g., "heat process") or verb (e.g., "heat water").

2. It is no more appropriate to speak of heat in a body than work in a body. Both statements are not sensible. As pointed out by Mark Zemansky,²⁴ "Heat and work are methods of energy transfer, and when all flow is over, the words heat and work have no longer any usefulness or meaning . . . and once the transfers are over, we can speak only of the internal energy of the system. It is impossible to subdivide the internal energy into two parts, one due to a heat transfer and the other to work."
3. In a dissipative process, e.g., a block sliding across a horizontal table and then stopping, people often describe the mechanical energy decrease as "going to heat." This is unsatisfactory because heat cannot be stored. Although a heat process might occur as the block and table temperatures rise, it is transitory. After the process culminates, the original kinetic energy has become *internal energy* stored by the block, table, and their environment.
4. The term heat transfer is misleading at best. As Leff²⁷ wrote, "Transfer of an entity implies movement of that entity from one storage region to another. . . . We conclude that because heat cannot be stored, the term heat transfer is an oxymoron." Despite this, terms such as *heat transfer* and *transfer of heat* are commonplace and will likely (and unfortunately) persist in the scientific literature.
5. Given the foregoing, it is well to heed the words of Walter T. Grandy,²⁸ "*In the 21st century it is still common to speak of heat as if it were a 'substance' that flows and can be thought of as a fluid; scientifically we still use the phrase 'heat capacity' that connotes an amount of something, although we know better. We take note of these foibles only to emphasize that human perception remains a bit 'fuzzy' in discussing the concept of heat, difficult to pin down at times. Technically, however we have no trouble agreeing that heat is not a substance, but a process of energy exchange between macroscopic systems and their environments.*"

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References

- a. Deceased March 2010. Ronald Newburgh wrote the original submission of this manuscript. After his death, the section on persistent language difficulties was added and miscellaneous editing was done by Harvey S. Leff. The spirit and substance of the original manuscript have been preserved.
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 2. D. Roller, *The Early Development of the Concepts of Temperature and Heat* (Harvard University Press, Cambridge MA, 1950), pp. 12–47, 61–81.

3. *Thermal state*, as used here, differs from a *thermodynamic state*, which typically requires two or more variables—e.g., temperature and pressure—for a complete specification.
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6. In thermodynamics and statistical physics, temperature subtly enters equations via Boltzmann's constant $k = 1.38 \times 10^{-23}$ J/K. A relevant discussion can be found in H. S. Leff, "What if entropy were dimensionless?" *Am. J. Phys.* **67**, 1114–1122 (1999).
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19. In 1841, Mayer wrote that the fall of a weight $m \cdot g$ from a height of 365 m corresponds to the heating of an equal mass of water by 1°C. Although he did not give a value for J explicitly, his result implies $(9.8 \text{ m/s}^2)(365 \text{ m})(m \cdot \text{kg}) = (J)(m \cdot \text{kg})(1 \text{ kcal/kg/}^\circ\text{C})(1^\circ\text{C})$, or $J = 3.58 \text{ J/cal}$. This value was low primarily because Mayer used early and flawed specific heat values for air. He did not publish the derivation outlined in the text until 1845, in a paper entitled, "The motions of organisms and their relation to metabolism – An essay in natural science." Mayer's failure to provide supporting details in 1841 exacerbated a controversy about whether he or Joule was first to arrive at the "mechanical equivalent of heat." In 1851 Mayer published a corrected result using improved specific heat data, which implied $J = 4.165 \text{ J/cal}$, close to Joule's value, 4.18 J/cal. English translations of the 1841 and 1845 papers are in R. B. Lindsay, *Julius Robert Mayer – Prophet of Energy* (Pergamon Press, Oxford, 1973), pp. 73–74, 84.
20. The value of J depends upon the specific definition of calorie, among several that are common. For example, the thermochemical calorie is defined as 4.184 J exactly, while the International Table calorie = 4.1868 J. See A. Thompson, B. N. Taylor, *NIST Special Publication 811: Guide for the Use of the International System of Units (SI)* (2008), available online at <http://physics.nist.gov/cuu/pdf/sp811.pdf>.
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