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

Ronald Newburgh,a Harvard Extension School, Cambridge, MA
Harvey S. Leff,b Reed College, Portland, OR

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 states 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 century 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 thermometer2,5 that was sensitive to changes in both the thermal state and atmospheric pressure (it was actually a barothermroscope). 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. 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? Black 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 discover latent heats of fusion and liquefaction. 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 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 boiling time, and the more heat supplied.

Using available, but flawed, specific heat data, Mayer's result was

\[ dT, \quad \frac{dT}{m} = \frac{\text{work}}{\text{mass}}. \]

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 qualitative value for the exchange rate J that made heat and work comparable.

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

\[ Jm(c_p - c_v)dT = PdV. \]  

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

\[ J = \frac{nR}{m(c_p - c_v)}. \]  

Using available, but flawed, specific heat data, Mayer's result was equivalent to \( J = 3.58 \text{ joules/cal} \).
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. Joule’s best value, published in 1850, was 4.16 joules/cal, quite close to the modern value of internal energy.

It remained for Rudolf Clausius to introduce the concept of internal energy in its modern form,

$$dU = dQ - dW.$$  (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, $dU = mc_p dT$, 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. Once it was understood that heat and work are both energy transfers expressible with $Q$ and $W$, along different paths, can lead to the same change in $U$.

The question of priority gave rise to considerable acrimony between Mayer and Joule, an acrimony with nationalistic overtones. It remained for Rudolf Clausius to introduce the concept of internal energy. In its modern form, the first law of thermodynamics

$$\sum dU = \sum dQ - \sum dW.$$  (4)

Here the $\sum$ denotes a sum over the process.

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References

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.


12. On a personal note, one of us (Newburgh) did this experiment in high school in 1942. It remained as one of his most satisfying scientific experiences.


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 $(9.8\text{ m/s}^2)(365\text{ m})(m^2\text{ kg}) = (J)(m\text{ kg})(1\text{ kcal/kg°C})(1°C)$, 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.


23. This holds for an ideal gas whose internal energy is a function of temperature but not volume. For gases with intermolecular interactions, the internal energy is generally volume dependent. Then the difference between the constant-pressure and constant-volume heating energies is *not* simply the work done for the constant pressure process. Specifically $\Delta m(c_p - c_v)\text{dT} = [(\Delta U)/\text{dT}].\text{p} - (\Delta U/\text{dT})_v + (\Delta P/\text{dT})_v\text{dT}$. Mayer’s assertion holds only if the difference between the derivatives of internal energy is zero, which is not so for non-ideal gases in general.


Harvey Leff is 2010-2011 Visiting Scholar at Reed College and Emeritus Professor, California State Polytechnic University, Pomona.