Perspectives on the History of Chemistry



Gary D. Patterson

From Heat to Thermal Science

A History of Thermodynamics

Springer

Perspectives on the History of Chemistry

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Preface

Heat flows from a hot body to a cold body! But what is heat? And how does it flow? The history of these questions is fascinating and is certainly not finished.

Serious thinking about heat is associated in the sixteenth century with the Italian Academia del Cimento. Actual thermometers were constructed and employed in both chemistry and medicine. The concept of temperature, T, is one of the central issues in the history of heat. This issue will be discussed from antiquity to the present.

During the seventeenth century, great thinkers like René Descartes and Francis Bacon wrote extensively about heat. They explored the many opinions expressed about heat and considered many common meteorological phenomena. Robert Boyle and Robert Hooke carried out many experiments exploring the transfer of heat from hot bodies (at temperatures above ambient) and even considered whether there was such a thing as "cold."

The eighteenth century started with the monumental study of heat flow by Isaac Newton. He established Newton's Law of Cooling that is the basis for all later work. He also demonstrated many "fixed points" for the calibration of temperature. Modern recreation of Newton's work revealed just how accurate it was!

Herman Boerhaave referred to himself as a "Philosopher of Fire." He discussed a large number of experimental phenomena that remain true today. His eighteenth century interpretations have not survived, but they were coherent at the time. One of his most important contributions was the notion that "fire" is a process that leads to chemical change.

Joseph Black set the standard for chemical education in the late eighteenth century. His lectures were compiled and edited by his fellow Edinburgh Professor, John Robison. Black carried out many measurements of the change in temperature due to the flow of heat. He established the "heat capacity" as an important material property. Black also noted that, during a phase change, the temperature remains the same, even though heat is flowing. He called this phenomenon "latent heat."

The French team of Lavoisier and Laplace published *Mémoire sur La Chaleur* in 1780. While it erroneously assumes that "heat is conserved," the book is still worth reading today for its other insights. The world of chemistry in which Lavoisier

lived was associated with a primal material and a set of principles that could be added to produce known substances. One of these principles was *calorique*, a massless fluid that could be added to all matter.

Joseph Fourier brought the full power of French mathematics to the description of heat flow in his *Théorie Analytique de la Chaleur* (1822). This book presents the full three-dimensional mathematics for the flow of heat in objects of arbitrary shape and environment. It is still in print and forms the basis for all future work.

The science of heat flow is an essential part of Chemical and Mechanical Engineering. Sadi Carnot published his *Réflexions sur la Puissance Motrice du Feu et sur les Machines Propre a Développer cette Puissance* in 1824. This is an essential book in the history of heat. Carnot explained how the flow of heat can produce work. Both heat and work are forms of energy that are associated with dynamic processes. Carnot's discussion of cyclic processes remains the ground for all future thinking about such processes.

James Joule carried out many experiments that demonstrated that energy is conserved. He made sure that all other workers in the field of thermal physics and chemistry knew of his work and was joined by all of them in creating Thermodynamics. He determined the "mechanical equivalent of heat" that emphasized that all changes in energy can be understood when compared with the same units. In honor of his accomplishments, the current unit of energy is the Joule.

Another major contributor to the experimental understanding of heat was Victor Regnault. He made precise measurements of the heat capacities of gases and solids. All the other thermal scientists of the mid-nineteenth century consulted with Regnault and used his data in their development of Thermodynamics.

Another major contributor to the development of the Chemical Engineering of Heat was William Rankine. He combined both the mathematical rigor of a Scottish engineer, and the thoroughgoing appreciation for the realities of industrial processes. He collaborated with Joule, Thomson, and Regnault to complete the development of the key Laws of Thermodynamics.

William Thomson (later Lord Kelvin) was a great experimentalist, a precise mathematician, and a natural philosopher. One of his goals was to construct correct statements of thermal reality that could be called Laws of nature. He developed the concept of absolute temperature and calculated the minimum possible value: 0 K. He understood that heat flow was a dynamic process and that all dynamic processes are subject to loss of energy.

Rudolph Clausius published the essential theory of classical Thermodynamics in 1867: *The Mechanical Theory of Heat*. He took all the known experimental results, all the known Laws, and reduced them to a consistent mathematical form that is still taught today. He coined the term "entropy" that describes the chemical reality of actual material systems, in addition to the energy.

He understood both heat and work as dynamic processes. He understood the concept of an irreversible process. He derived the relationships between all the measurable thermodynamic properties of a chemical system.

The world in which we live is filled with mixtures of different substances and chemical reactions. Josiah Willard Gibbs formulated the complete theory of chemical processes. The key concept that was articulated was the "chemical potential." Gradients in chemical potential produce chemical processes.

The world of continuum physics is both coherent and useful. But matter is characterized by a range of critical dimensions. René-Just Haüy demonstrated that single crystals of many substances are characterized by a unique "unit cell." But at some much smaller length scale, this symmetry must fail. James Clerk Maxwell was both one of the greatest classical physicists, as demonstrated by his theory of electro-magnetism, as well as one of the founders of "statistical physics." He adopted the perspective that gases are composed of "molecules" that are in constant motion and that interact with one another. He derived a mathematical expression for the distribution of particle velocities that remains as an important part of modern physics and chemistry. He then used this model to calculate the observed "transport coefficients" for gases: viscosity and thermal conductivity. Molecules have a characteristic "collision diameter." Each molecule undergoes a trajectory that can be modeled as a random walk. These concepts remain as a standard part of condensed matter physics.

Ludwig Boltzmann was also a master of classical physics and the perfector of statistical thermodynamics and kinetic theory. He appreciated both the phenomenological, macroscopic theory of heat (Thermodynamics) and the "Special Theory of Heat," microscopic particle dynamics. He also appreciated the role of "waves" in understanding heat. Perhaps the best explanation of the meaning of entropy is found in the work of Boltzmann. In addition to his contributions to equilibrium thermodynamics, Boltzmann constructed a sound basis for the understanding of kinetics. The Boltzmann equation for transport is even more important than his more famous relationship between the entropy and the classical "partition function."

The Royal Institution in London was the site of some of the greatest scientific work in the nineteenth century. John Tyndall was known for his experiments on "Radiant Heat." He established the full spectrum of sunlight; most of the intensity is in the infrared region! He then invented specific infrared sources to use in his experiments. He also constructed "thermopiles" to detect the light. In order to increase his sensitivity, he created "differential detectors." He recorded the spectra of many known gases. The intensities varied widely. Polar molecules absorbed the most. Another phenomenon discovered by Tyndall was "calorescence" the absorption of infrared radiation can be converted to the full black-body spectrum. Energy is conserved, but it can be redistributed into other energetic channels. Tyndall befriended many of the scientists in the world in the late nineteenth century. He completely understood the work of Lord Rayleigh on the scattering of light by molecules. He also published a massive volume: *Heat: A Mode of Motion* (1900). The illustrations were remarkable, both then and now!

The last of the great 19th century thermal physicists was Walther Nernst. He received the Nobel Prize in 1920 for his analysis of the thermodynamics at low temperatures. He showed that the internal energy, U, and the Helmholtz energy, $A = U - TS$, approached one another at $T = 0$. He also showed that the entropy, S, approaches 0 as well. This is now called the Third Law of Thermodynamics. Nernst also explored the consequences of the entropy at high temperatures, where TS becomes the dominant contribution to the Helmholtz energy.

The key transitional figure in the history of heat is Max Planck. He mastered all of classical physics. He knew that new experimental results could not be explained within the classical model. He was the greatest philosopher of science in his era. He was "open to reality" and followed his own path towards the future. He received the Nobel Prize in 1918 "in recognition of the services he rendered to the advancement of Physics by his discovery of energy quanta."

Albert Einstein is celebrated for many aspects of science. He was a master of thermal physics. He understood that, at finite temperature, the local state of the system fluctuates. This is the key to defeating Zeno's Paradox. He calculated the intensity of light scattering due to fluctuations in the local dielectric tensor. He invented the concept of a local "random force" due to the fluctuations and calculated the transport of particles in a viscous medium. Einstein also followed up the work of Max Planck on black-body radiation with a theory of the heat capacity of solids. Local vibrational states were quantized and the observed heat capacity of diamond as a function of temperature was calculated well, but not perfectly.

Leon Brillouin was a master of "all things heat." Three types of heat include sound (phonons), light (infrared photons) and moving electrons. He combined a deep understanding of classical physics and a brilliantly intuitive grasp of the consequences of quantum mechanics for the understanding of the "energy that moves." After Brillouin, there were many details to be considered, and many experimental demonstrations to be made, but the essence of the story of heat was known.

Max Born received the Nobel Prize in 1954 for "fundamental research in quantum mechanics, especially in the statistical interpretation of the wave function." He finished the work on the solid state started by Brillouin and published the book: *Dynamic Theory of Crystal Lattices* (1954) written with Kun Huang (1919–2005). He also addressed the question of the mechanism of thermal conductivity in solids. In nonmetallic solids, the dominant carrier of heat is phonons. Born explained why electrons contribute a small amount to the heat capacity of metals but are the dominant carrier of heat.

Thermal Science is alive and well in the twenty-first century. Many new materials have led to new concepts and new channels for the transport of energy. Even "holes" can transport energy in semi-conductors. Neutrons are now an important part of the science of heat. The "history of heat" is not finished. What if we could harness neutrinos?

This book is intended for all curious thinkers. While some aspects of Thermodynamics and Kinetics are highly mathematical, it is an area of natural philosophy that lends itself to visual representations. It has also been reduced to Laws of Nature that can be expressed in clear statements. The Science of Heat is also firmly grounded in observable phenomena. Knowing what can be observed in the laboratory is essential for understanding Thermal Science.

Pittsburgh, USA Gary D. Patterson
June 2025

Acknowledgements While the current book was written over the last 3 years, it reflects my educational history over the last 65 years. I benefitted from a good High School (Helix High School in La Mesa, California). I learned to love Chemistry from William Ramsey and Physics from Frank Watenpaugh. The ChemStudy approach prepared me to attend Harvey Mudd College and major in Chemistry. While a thorough training in mathematics is essential for a theoretical chemical physicist, learning to "think like a scientist" allowed me to actually work as a chemist immediately. The Chemistry Department at Harvey Mudd was the best in America in 1964, and remains so today. The thorough grounding in Thermodynamics and Statistical Chemistry obtained from J. Arthur Campbell and William Sly allowed me to attend graduate school at Stanford University.

I was able to start research immediately in the laboratory of Paul J. Flory (Nobel 1974). He set the highest standards for both research and writing. I taught Thermodynamics and Statistical Chemistry with Robert Pecora. Both the mathematical and physical aspects were covered. My thesis work involved both experimental and theoretical studies. I have followed this path ever since.

I was fortunate to join AT&T Bell Laboratories in 1972 in the Chemical Physics Department. This department contained both famous theorists, such as Frank Stillinger and Eugene Helfand, and world-renowned experimentalists, such as Mel Robin. Rather than being competitors, they taught me how to carry out research at the "cutting edge." Another benefit of Bell Labs was the existence of the best physicists and chemical engineers. They taught me the real meaning of Thermodynamics and Transport. The practical importance of physical and chemical phenomena must always be considered.

In 1984, I and around 1000 of my colleagues, became university Professors. I joined Carnegie Mellon University in Pittsburgh as Professor of Chemical Physics, and Polymer Science. For over 30 years I taught Thermodynamics, Chemical Kinetics, Transport, and Polymer Science. I had great colleagues, such as Edward Casassa, that taught me Theoretical Chemistry, and Bernard Coleman, that taught me Rational Mechanics. (Coleman was a member of the Rheological Trinity that included Walter Noll and Clifford Truesdell.) They stressed that Heat and Work were "processes."

I became a Chemical Historian in 2000. I was encouraged in this direction by John Hedley Brooke of Oxford University and Sy Mauskopf of Duke University. They also sponsored me as the 2004 Charles Price Fellow at the Chemical Heritage Foundation in Philadelphia. Eventually I served this institution as the Chief Bibliophile of the Bolton Society, the Chair of the Heritage Council, and as a member of the Board of Directors. I was tutored by the best Chemical Historians in the world as they spent time in Philadelphia.

Many of the members of the Bolton Society were also members of the Division of the History of Chemistry of the American Chemical Society. I soon joined them and was welcomed and tutored by colleagues such as Mary Jo Nye, Alan Rocke, Larry Principe, and Mary Virginia Orna. In addition to mentoring me as

a historian, friends like Ned Heindel taught me how to lead organizations. This allowed me to meet and strongly interact with most of the chemical historians in the world. On the subject of heat, I was treated to working with Robert Fox of Oxford and Hasok Chang of Cambridge.

No book of the present length and complexity is possible without a great editor. I have benefitted from two such experts. Carmen Giunta, the Editor of *The Bulletin for the History of Chemistry*, has often guided me towards a much-improved text. Seth Rasmussen has served, as either the lead editor or a joint editor, with me on many books. His contribution to the present book is extensive!

Writing books also requires the patience and support of my wife, Susan Patterson. She has provided both advice and companionship since 1967.

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About the Author

Gary D. Patterson is a Professor of Chemistry Emeritus at Carnegie Mellon University in Pittsburgh, PA USA. He received his Ph.D. in Physical Chemistry in 1972 from Stanford University. During his academic career, he published more than 100 articles in the chemical physics of amorphous systems, especially polymers. He is a Fellow of the American Physical Society and the Royal Society of Chemistry. He taught theoretical chemistry to students of chemistry and chemical engineering, especially Thermodynamics and Transport. He is the author of *Physical Chemistry of Macromolecules* (2007).

Patterson is the Historian of the Division of the History of Chemistry of the American Chemical Society. He has published three previous books with Springer: *A Prehistory of Polymer Science* (2012), *Polymer Science from 1935 to 1953: Consolidating the Paradigm* (2014), and *Chemistry in 17th Century New England* (2020). He is the author of *Paul John Flory: A Life of Science and Friends* (2016). He has edited three books based on HIST symposia: *Characters in Chemistry: A Celebration of the Humanity of Chemistry* (2013), *Preceptors in Chemistry* (2018), and *Modern Applications of Flory's "Statistical Mechanics of Chain Molecules"* (2020). Patterson has also been associated with the Science History Institute as the Charles Price Fellow (2004), the Chief Bibliophile of the Bolton Society, Chair of the Heritage Council, and member of the Board of Directors.

Introduction: The Concept of Heat and Boyle's *Natural History of Cold*

1

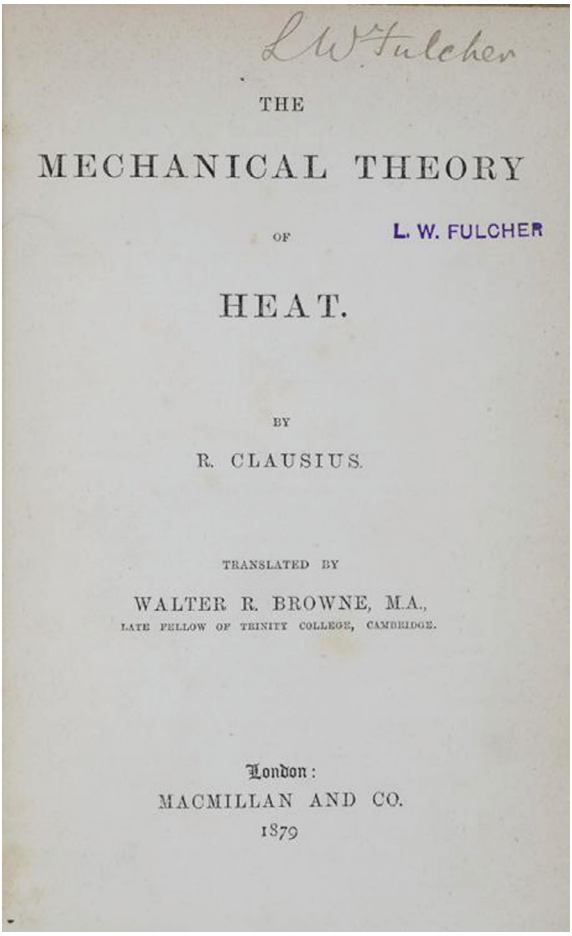
Abstract

The concept of heat is much more complicated than any Natural Philosopher imagined until the 19th century. However, in the 19th century, Rudolph Clausius knew enough to assert with complete confidence that: "Heat flows from a hot body to a cold body." Greek philosophers held many incoherent notions about heat and this body of Natural Philosophy is thoroughly discussed. Galileo introduced both better thoughts and a real device to quantitatively measure temperature. Francis Bacon wrote extensively on the notion of heat. Descartes both carried out seminal experiments and produced detailed theories of heat. The first major contribution to our understanding of heat is due to Robert Boyle and his monograph: *New experiments and observations touching cold, or, An experimental history of cold* (1665). This book is discussed in complete detail and reveals that Boyle knew more about heat and cold than anyone until the mid-19th century. The Introductory chapter (Chapter 1) sets the stage for the entire book.

Throughout human cultural history, people have referred to a particular phenomenon by using words like "heat". The German word for this phenomenon is *wärme,* and the French equivalent is *chaleur.* The Latin form is *calor* and the Greek equivalent is θάλπος. A common *Dictionary of Scientific Terms* [1] defines heat as: "A kind of energy that manifests in various ways." This definition makes it clear that, while it is a form of energy, it is NOT just "one thing." My favorite statement with regard to heat is: "Heat flows from a hot body to a cold body." This was articulated by Rudolph Clausius (1822–1888) in his classic treatise: *The Mechanical Theory of Heat* (1862, 1879) (Fig. 1.1) [2]. The Fourier "Heat Law" was formulated in 1807 and was initially presented to the Institute of France. But Isaac Newton (1642–1727) had studied the cooling of solid objects a century

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L. W. Fulcher

THE

MECHANICAL THEORY

OF

L. W. FULCHER

HEAT.

BY

R. CLAUSIUS.

TRANSLATED BY

WALTER R. BROWNE, M.A.,

LATE FELLOW OF TRINITY COLLEGE, CAMBRIDGE.

London:

MACMILLAN AND CO.

1879

Fig. 1.1 Title page of *The Mechanical Theory of Heat* (1879). (by permission of the Othmer Library, Science History Institute)

before [3]. They all knew that heat flows from a hot body to a cold body, but even Clausius did not know all the contributions to the observed "thermal conductivity".

1.1 Early Ideas About Heat

Early humans were greeted by a celestial object that projected warmth: the sun. Even today, our understanding of the sun is still evolving. The sun emits radiation over a very wide range of frequencies (energies). Visible light can be absorbed by matter and can be felt as heat, but most of the "warmth" of the sun is due to infrared radiation. One of the other terrestrial phenomena observed by early humans was "fire." It was also hot. An early conjecture was that the sun was a giant fire!

More formal discussion of heat and fire is found in the writings of Heraclitus (circa 500 B.C.) [4]. He proposed that all things are brought into being by fire, the true "αρχε". This notion has not disappeared, and one of the central processes in modern physics is the combination of two photons to produce an electron and a positron. Heraclitus is not the father of particle physics, but his speculation is a coherent response to the world in which he lived.

An interesting history of the development of the concept of heat was published in 1946 in *The Scientific Monthly* by Martin K. Barnett (1909–1958) [5]. Barnett notes that Heraclitus did not view fire as a substance but as a "transforming process." This concept will occur throughout the history of heat. Heat is one process of transporting energy from one place to another.

The "substantial" view of fire is attributed to Empedocles (450 B.C.) who postulated that all observable matter was composed of a mixture of four "elements." Empedocles was a student of Pythagoras (c. 570–c. 495). These entities could not be isolated by themselves. They were "imperishable," "homogeneous," and "unchangeable." Aristotle added more obfuscation to this story by introducing four underlying "properties," with each element represented by the combination of two properties. Fire was viewed as "hot" and "dry." Multiplication of explanations is one of the sure signs of incoherence. Democritus (460–360 B.C.) attributed causal power to "fire atoms."

Another Greek school of thought is associated with Parmenides (470 B.C.). He stressed that all "actual being" is eternal and cannot change. Democritus tried to create a synthesis of these ideas by proposing that "actual matter" was a large collection of "small bits" in constant random motion (Jean Perrin (1870–1942, Nobel 1926) and Albert Einstein (1879–1955, Nobel 1921) demonstrated that fluids are in constant random motion [6]). While the Greek philosophers had no idea whether their speculations were true, or even coherent, they do fall within the world of "possible ideas." Speculations about heat continued throughout the next 2500 years! Lucretius (first century B.C.), the author of *De rerum natura,* was more conservative about the ability of the "fire atoms" to ever change their velocity. Natural philosophy sometimes also displays a random trajectory through concept space.

The present treatise intends to examine both the historical development of the concept of heat and to present the current understanding of this quantity. Both the science and the scientists will be discussed in detail. The story of heat illustrates many of the issues that characterize the practice of science. It also reveals the connections between all of physical reality. While mathematics will be introduced as necessary, the history of heat can be appreciated by all scientifically curious people. While thermodynamics is a topic in the history of heat, the full science of heat is much richer and focuses more on actual situations in the physical world.

1.2 Temperature and Heat

The "modern period" with respect to the understanding of heat starts with attempts to "quantify" the measurement of "temperature**.**" Even ancient Babylon had a sense that there were degrees of temperature. "Then was Nebuchadnezzar full of fury, and commanded that they should heat the furnace seven times more than it was wont to be heated" [7]. Measuring the temperature in a furnace remained an issue that was partially addressed by the great pottery manufacturer, Josiah Wedgwood (1730–1795) FRS.

In order to understand heat, denoted Q, it is necessary to be able to measure temperature, T. One of my favorite books is *Evolution of the Thermometer, 1592–1743* (1900) by the famous bibliographer Henry Carrington Bolton (1843–1903) (Fig. 1.2) [8]. Bolton was a collector of all things bibliographic (The current Bolton Society is comprised of the worldwide community of chemical bibliophiles and is associated with the Science History Institute). He was able to trace the invention of a thermoscope by Galileo Galilei (1564–1642) (Fig. 1.3) [9]. It was composed of a glass bulb connected to a glass capillary, filled with wine. The level of the fluid was calibrated with snow and blood and marked on the capillary. It was of the inverted air type where the bulb is at the top and the fluid is contained in a vessel at the bottom of the capillary.

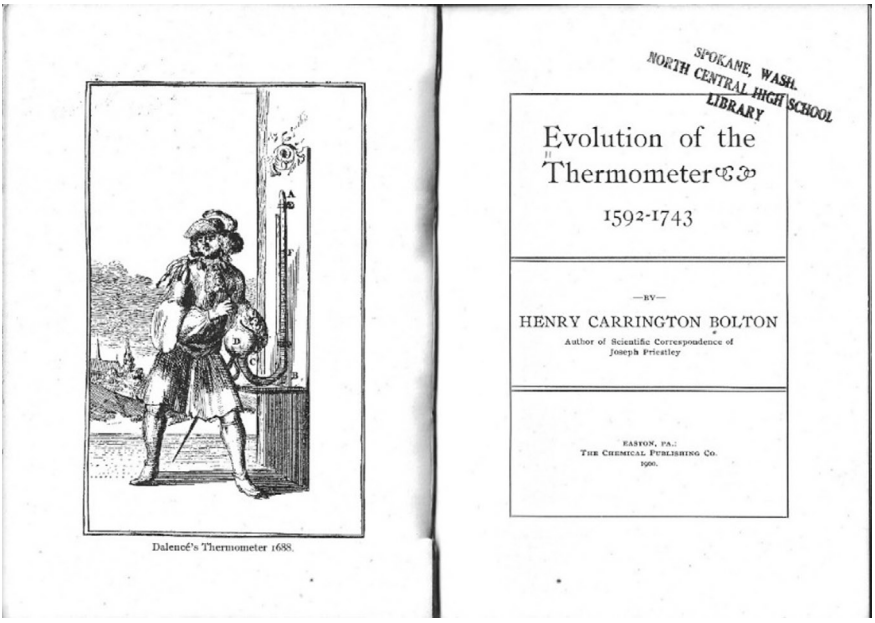


Fig. 1.2 Frontispiece and Title page of *Evolution of the Thermometer.* (scanned from my personal copy)

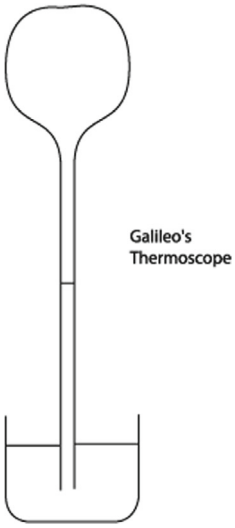


Fig. 1.3 A drawing of a thermoscope of the Galileo design [9]

The basic principle of the thermometer is that a measurable property of the system is sensitive to the temperature and can give a reliable and repeatable reading. The choice of the fixed-point system composed of snow and water remains as a standard today. In the time of Galileo, Italian physicians could reliably test for a human "elevated temperature." Fever thermometers have now become mostly electronic, but I was raised with a mercury version.

1.3 Francis Bacon and Heat

The 17th century was characterized by serious attempts to understand heat. Francis Bacon (1561–1626) discoursed extensively on heat over his lifetime. This intellectual story is beautifully told by Stephen Gaukroger in *Francis Bacon and the Transformation of Early-Modern Philosophy* (2001) [10]. Lord Verulam (Francis Bacon) was one of the deepest thinkers in England. Rather than trying to construct a tight useless system of false assertions, he focused on what could be done by humans in their own time. He knew that the future would produce new observations and new concepts, but that natural philosophers should not "wait for the future." His approach was grounded in two *programmes*: (1) The construction of a robust Natural History of repeatable observations, and (2) A coherent attempt to explain these observations in terms of both current concepts and potentially helpful speculations. He called this process "eliminative induction." One of Bacon's greatest disciples was William Whewell (1794–1866) who wrote *History of the Inductive Sciences from the Earliest to the Present Time* (1837) [11]. Whewell both knew and influenced all the English natural philosophers during his tenure at Trinity College, Cambridge (1812–1866) where he was Master from 1841–1866. The



Fig. 1.4 Title page of Bacon's *Novum Organum Scientiarum* (1620). (by permission from the Othmer Library of the Science History Institute)

details of Bacon's method are contained in his classic *Novum Organum Scientiarum* (1620) (Fig. 1.4) [12].

Although Bacon considered many human observations, he was especially concerned with color and heat. His goal was to discover the full phenomenological description of a material property and to fully explain it in terms of other material properties. Not surprisingly, Bacon considers gold [12]: "It is yellow, heavy, malleable, meltable, soluble in aqua regia, etc."

Bacon was also concerned with "changes" in substances. He knew that "heat causes changes in material bodies." (Chemistry is the science of matter and its changes.) Remarkably, Bacon is seldom mentioned in connection with chemistry. His contribution was not to laboratory practice but to the philosophy of knowledge creation. His extensive discussion of heat in the *Organum* serves as both a window into the value of Bacon's method, and a warning about the need to take experimental investigation seriously.

The discussion of heat occurs in Book II of *Novum Organum Scientiarum*. In Sect. 11 he presents a representative collection of observations that exhibit "heat." There are 27 entries. At the top of the list is the sun. Some philosophers considered the sun to be the sole source of heat on Earth. This stance produced some very

strange thoughts about heat! Bacon knew about "burning mirrors and lenses" and discussed their use in "concentrating heat."

One of the most dramatic terrestrial phenomena is "lightning." Bacon perceived that heat was associated with this event. (The physical system known as "The Earth" includes the atmosphere. It is a complicated system that exhibits highly heterogeneous distributions of both temperature and pressure. There is also a distribution of electric potential relative to the "ground." When the potential difference between the "clouds" and the ground exceeds the "breakdown potential" the phenomenon of "dielectric breakdown occurs." In the atmosphere this produces lightning.) Bacon had a notion that "energy that moves" was a key aspect of heat!

Many of the entries were associated with combustion and the appearance of "flame." (The combustion of hydrogen and oxygen to form water is "barely visible" in the laboratory. But if our eyes were sensitive to infrared radiation, we could not look at such "flames.") The appearance of a "burning system" depends on both the temperature of the system and the actual composition of the system as a function of location. Michael Faraday's *The Chemical History of a Candle* (1861) includes the flow pattern in the flame [13]. Heat is definitely associated with flames, but it would be many years before an understanding of flames was produced.

Bacon cites many examples of mechanical processes that raise the temperature of the system. Rubbing your hands together makes them "warmer." Extensive discussion of the conversion of "work" into "heat," both processes that involve the transfer of energy, will be found in the present book.

Bacon also cites many examples of "chemical processes" such as "sprinkling water on quicklime" or "dissolving iron in strong acid." Where does the energy that manifests itself as a rise in temperature of the system come from? Of even more interest is the phenomenon of "cooling" observed when saltpeter is dissolved in water. Is there a specific "thing" called "*cold*?" Since heat, Q, is a process, it can be either positive, 0 or negative. The value of the "energy" depends explicitly on the "frame of reference," the energy at which the arbitrary value of the energy is chosen to be 0.

Section 12 of the *Organum* is concerned with systems that "lack heat." The level of confusion is very high in this Table. There are 32 entries. When we look directly at the moon and stars, there is no sense of either an increase or decrease in "heat." (Since humans do not have an infinitely sensitive heat detector, many phenomena may seem to be neutral with respect to the flow of energy.)

One of the features of the Earth is "mountains." If they are tall enough, no snow is observed at the peak. At lower elevations, snow can be "perpetual." Since high mountains are "closer to the sun," why are they "colder?" Bacon recognizes that any actual location yields an average temperature that depends on the temperature at all other locations. The surface of the Earth also emits heat. The temperature "field" of the entire "Earth system" is very complicated. This will recur many times in this discussion.

Bacon viewed "heat" as having many of the properties of "light:" reflection, refraction, absorption, scattering. In the case of "infrared radiation," this is because

they are both electromagnetic waves. They are "energy in motion." It would be many years before the energy was determined as a function of wavelength (frequency). The "speed" of light in a vacuum is independent of frequency. All light is a form of heat, but some frequencies are absorbed much better by physical systems. The frequency spectrum of "thermal radiation" will be discussed in detail in Chap. 16.

To reach us at the surface of the Earth, sunlight must traverse the atmosphere. While some frequencies are absorbed by molecules in the atmosphere, all light is "scattered" by the polarizable atomic systems in the air. Bacon knew that the sun "feels" most intense at the point on the Earth where it traverses the least atmosphere. (This phenomenon was explained by Lord Rayleigh in 1899.) Blue light is scattered much better than longer wavelengths. Thus, infrared light is subject to much lower scattering losses.

Bacon was aware of the properties of human sensation: we do not detect temperature; we sense "rate of heat flow." If heat flows into an object grasped by us, we think it is "cold." But what it means is that it has a temperature lower than our hands. Since "normal" human temperature is 37 °C, objects that have a temperature lower than this appears cold to us. He also knew that "convection" increases the rate of heat flow, both warm and cold. ("Wind chill" has been known for millennia.)

Bacon continues in Sect. 13 by discussing cases where "Degrees of Heat" are manifested. Table III contains 41 entries. He distinguishes the difference between "inanimate bodies" that adopt the temperature of the surroundings, and "animate bodies" that can generate heat from within the substance. (Bodies that can increase their temperature without external assistance are far out of "equilibrium." Otherwise, they would violate the Second Law of Thermodynamics. The Philosophy of the Second Law is discussed in Chaps. 15, 17 and 20.)

Bacon identifies substances that can undergo processes that liberate heat (exothermic). For many years natural philosophers assumed that only exothermic processes would happen "spontaneously." Fortunately, endothermic processes (where the system cools) can occur without external assistance. (It would be late in the 19th century before this was explained!).

Many biological materials remain above the ambient temperature long after they are "dead." This is the "smoking gun" of either some form of life still present, or chemical reactions that are exothermic and are "fed" by the surroundings of the "corpse." The most important chemical theory for understanding biology is "Nonequilibrium Thermodynamics."

Bacon also discusses industrial processes. Combustion is a process of chemical reaction between some inflammable substance and oxygen. The production of "heat" is proportional to the "rate" of the chemical reaction. Active transport of the oxygen to the "reaction zone" increases the rate of the reaction, and hence the rate of the production of heat. Physical reality is much more interesting and much more complicated than we can imagine. While Bacon was hardly a chemical engineer, he anticipated the need for such people.

Bacon mistakenly attributed large thermal conductivity to gases. But he might have not understood the difference between "diffusion" of heat in an equilibrium gas and "convection" of the substance of the gas. The largest thermal conductivity of quiescent nonmetals is found in diamond (a form of crystalline carbon). (This will be discussed in Chap. 21.)

Bacon was aware just how ignorant natural philosophers were in the 17th century. But he was very optimistic that, if they would follow his "method," great progress would occur. In the long run his hope was justified, even if over shorter time periods the progress was negative.

1.4 Descartes and Heat

Because the phenomenon of heat is much more complex than most chemists can comprehend, many thinkers are required to formulate a coherent explanation. René Descartes (1596–1650) constructed a model of matter and heat that is not currently "in vogue." But a careful reading of his *Meteorology* (1637) reveals that he was a much more valuable source for important aspects of the current consensus than might have been predicted [14].

Descartes was a master geometer and easily "visualized" his thoughts. He viewed terrestrial material reality as a "plenum." There were no "empty" parts of "The Earth." Light and heat were everywhere, along with a collection of particles of a very wide distribution of sizes and shapes. An important figure from the book is presented in Fig. 1.5.

While Descartes had no "hard evidence" that matter was organized in this way, he did rely on valid observations. Solids are characterized by stable dimensions. Descartes concluded that the "constituent particles" of solids had ceased moving. This did not mean that "nothing" was moving inside the solid; light and heat could

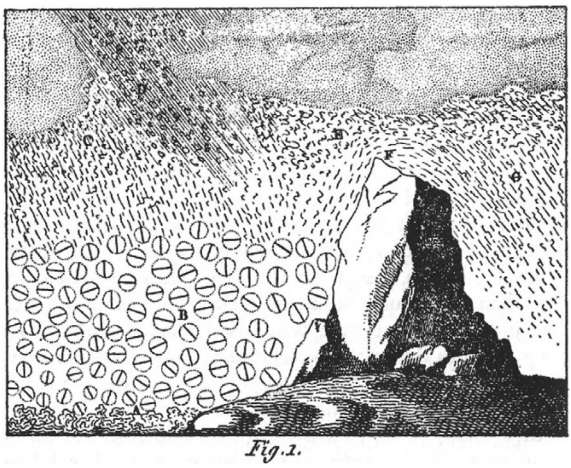


Fig. 1.5 Fig. 1 from *Meteorology* (scanned from personal copy) [14]

move through the "holes" in the solid structure. What he did not see was that the light and heat were characterized by wavelengths that were large with respect to the microscopic structure of solids.

Descartes was the greatest "optician" of the early seventeenth century. His *Dioptrique* (Optics) (1637) is still worth reading [14]. He explained many meteorological phenomena in terms of reflection and refraction. He understood just how complex the atmosphere really was and explained rain and hail as thermal phenomena. He knew that the "specific gravity" of ice was lower than that for water. He discussed this in both structural and thermal terms.

Descartes' greatest contribution to future thought about the thermal properties of matter was his insistence that, at the microscopic level, all matter was dynamic. He envisioned local fluctuations in the evolving structure of both liquid and gaseous media. He also thought in fully three-dimensional terms. He described matter in terms of the full possible symmetries of space. He included both vibrational and rotational motions, and he envisioned chiral symmetries. One of the pillars of chemical thought is geometric structure: Descartes was the Father of Chemical Structure. It would take 250 years to refine the picture, but the sketches found in his *Meteors* (Meteorology) can be understood today [14].

1.5 Boyle and Heat

Robert Boyle (1627–1691) FRS is a central figure in seventeenth century thought about heat. He interacted with most of the chemists during his lifetime and produced a massive *oeuvre.* One useful collection of his writings with commentary is *Robert Boyle on Natural Philosophy* (1965) by Marie Boas Hall [15]. The latest contribution to the understanding the Natural Philosophy of Robert Boyle is *The Chemical Philosophy of Robert Boyle* (2020) by Marina Banchetti-Robino [16].

Robert Boyle put into practice the *programme* outlined by Francis Bacon. During his lifetime, Boyle joined forces with master experimentalists, like Robert Hooke (1635–1703) FRS, and carried out "quantitative" measurements of material properties. His most famous induction was codified as "Boyle's Law:" In a dilute gas, the product of the gas pressure and the gas volume is a constant at constant temperature and amount of gas. (Of course, it fails at higher gas densities and lower temperatures.)

Boyle's overall stance on heat is contained in Hall [15].

> "The nature of heat seems to consist mainly, if not only, in that mechanical affection of matter we call local motion mechanically modified, which modification, as far as I have observed, is made up of two conditions. The first of these is, that the agitation of the parts be vehement, by which degree of rapidness the motion proper to bodies, that are hot, distinguishes them from bodies that are barely fluid. The second is this, that the determinations be very various, some particles moving towards the right, some to the left hand, some directly upward, some downwards, and some obliquely."

The technology of the "blacksmith" greatly impressed Boyle. Hammered iron became hot. Macroscopic energy was converted to microscopic energy.

One of the enduring goals of the Royal Society of London was to construct "Natural Histories" of terrestrial phenomena. One of their first requests was for a Natural History of Cold. Robert Boyle published this in 1665: *New experiments and observations touching cold, or, An experimental history of cold* (Fig. 1.6). There are three preliminary "Discourses" and 21 chapters, denoted as "Titles," covering a wide range of thermal processes [17].

The first Discourse is entitled "New Thermometrical Experiments and Thoughts." For this series of experiments Boyle employs a well-known maritime device: the "weather glass." The weather glass responds to both pressure (a barometer) and temperature. Boyle is fully aware of this fact. He warns his reader to use a true thermometer, sealed "hermetically" and filled with highly rectified spirit of wine and tinged with "Cochinele." Boyle was acutely aware of the need for a

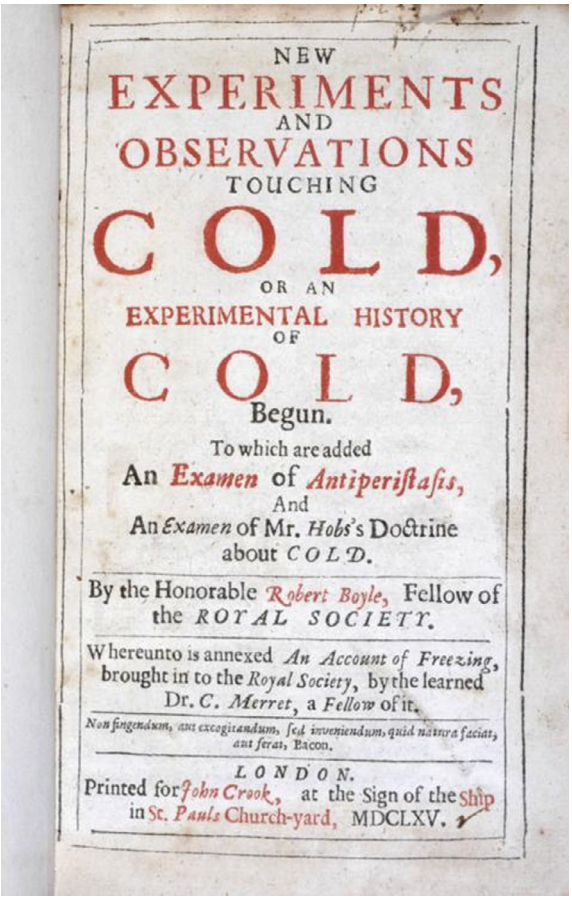

NEW
EXPERIMENTS
AND
OBSERVATIONS
TOUCHING
COLD,
OR AN
EXPERIMENTAL HISTORY
OF
COLD,
Begun.
To which are added
An *Examen* of *Antiperistasis*,
And
An *Examen* of Mr. *Hobs*'s Doctrine
about COLD.
By the Honorable *Robert Boyle*, Fellow of
the *ROYAL SOCIETY*.
Whereunto is annexed *An Account of Freezing*,
brought in to the *Royal Society*, by the learned
Dr. *C. Merret*, a *Fellow* of it.
Non fingendum, aut excogitandum, sed inveniendum, quid natura faciat, aut ferat, Bacon.
LONDON.
Printed for *John Crook*, at the Sign of the Ship
in St. *Pauls* Church-yard, MDCLXV.

Fig. 1.6 Title page of Boyle's *New Experiments and Observations Touching Cold* (1665) (By permission of the Othmer Library of the Science History Institute)

"Standard" for the measurement of temperature that could be used everywhere. This issue will remain throughout the book.

Boyle addresses the temperature dependence of the gas pressure in the next Discourse. He constructs two glass systems terminated with a small glass "tip." He "heats" one of the systems and then breaks the tip under water: Bubbles exit from the tip revealing that the pressure inside the glass is higher than ambient. He then cools the other system and submerges it: When he breaks the tip, water enters the vessel, since the pressure inside the cooled gas is less than the pressure of the water. Boyle also discusses the fact that, at constant volume, the gas fills the whole volume at all available pressures. Throughout this project, Boyle is evolving a theory of gases. He did much more than produce Boyle's Law.

Boyle then constructs a system containing two vessels: An outer cylindrical vessel containing approximately half its volume of water, and an inner vessel completely full of water. The inner vessel is sealed at one end and inverted into the outer vessel, which is then closed with cement so that no air could enter the system. The outer vessel was immersed in a mixture of snow and salt until the water began to freeze. The air in the outer vessel was assumed to adopt the same temperature as the water. This would create a pressure differential between the top of the inner vessel and the surface of the water in the outer vessel, but the water in the inner vessel did not fall. Boyle is learning about the ability of heat to flow until thermal equilibrium is obtained. The initial gas(air) pressure in the outer vessel is 1 atmosphere. The initial "gas" pressure above the water in the inner tube is 0, since there is no gas. The difference in pressure keeps the inner vessel full of water. After lowering the gas pressure in the outer vessel, the pressure difference is still much larger than necessary to support the excess height of water in the inner vessel.

Boyle also constructs a system containing "glass bubbles" with variable volumes of water inside. When the density of the water is matched by the density of the bubble, the bubble achieves neutral buoyancy. While not invented by Galileo, it is now called a Galileo Thermometer. It was also independently invented by the geniuses at the Accademia del Cimento of Florence in 1666 [18].

In Title I of the "History," Boyle carried out a series of experiments touching "Bodies capable of Freezing others." He discusses the mixture of snow and salt that was widely employed during this century. He discovered that many "solutes" would produce the effect, in addition to "sea salt." Even sugar was effective. One of Boyle's favorite words was "frigorifick," the ability to induce cold. One of the best substances to mix with the snow to produce "cold" was rectified spirit of wine (95% ethanol). Common views of this substance focused on its "heat" and called it a "vegetable sulphur." Another remarkable solution was created with *"Sal Armoniack"* (ammonium chloride). As this solution was cooled, remarkable crystals formed as collections of needles. These solutions are currently used as "weather predictors." One of the limitations in experimental practice in the mid-17th century was the limited range of temperatures below ambient.

In Title II, Boyle chose to focus on pure substances and when they were able to freeze. Freezing or melting point remains a useful property of a pure substance.

He also subjected solutions to the action of "deep-winter cold." One of the most important phenomena was the "phase separation" that often occurs. In addition to ice crystals, both solutions of varied compositions and nearly pure liquids were observed. (A *programme* to fully understand binary and ternary liquid mixtures continued well into the 20th century.) The indigenous people of New England strengthened "maple syrup" during the winter by crystallizing out the pure ice. Not only was this effective, but it did not require the use of precious wood to drive off water by heating the syrup.

In Title III Boyle discussed bodies that were "not disposed to be frozen." Many liquids do not become "crystalline solids" when cooled. With sufficient cooling the viscosity increases until it is so large that it becomes a "non-equilibrium glass." The phenomenology of the liquid-glass transition was still being debated in the 20th century. Of course, Boyle tried to freeze liquid mercury. He could not achieve a low enough temperature to do this ($T_m = -38.87$ °C). He also tried to freeze a concentrated solution of common salt, and was unable to do it. He had discovered the phenomenon of "freezing point depression." More dilute solutions eventually separate into an ice layer on top and a more concentrated solution below. Boyle carried out enough experiments to baffle many generations of experimental chemists. His results are carefully described and have been verified many times.

In Title IV, in order to make the concept of "cold" more precise, Boyle invented new devices filled with rectified wine. Rather than the Galileo style "thermoscope," (Fig. 1.3), he places the "test bulb" at the bottom and then, after removing the air, seals the top. The vertical tube is also constructed with a fine bore. Boyle also used rectified and dried turpentine as the "thermometric fluid." He then etched the stem with a diamond at various "fixed points." Of course, one of them was the temperature of a solution of ice in water.

In Title V, Boyle compares heat and cold with regards to their tendencies to go upwards or downwards. Up and down on Earth is a question of buoyancy in the gravitational field. Boyle cites the general opinion of "Philosophers" that heat tends upwards. He also tentatively asserts that cold tends downwards. (Alas. All bodies radiate infrared in all directions. In a famous experiment carried out by Marc-Auguste Pictet (1752–1825), a piece of ice can influence a thermometer above it by employing two parabolic reflectors [19].) Boyle is treading new ground in these experiments. He knows that "heat flows from a hot body to a cold body." If the experimental setup consists of a hot body of metal placed on top of a cold body of the same metal, heat flows "down" (and correspondingly, "cold" flows up). (Since heat, Q, can be either positive or negative, dQ/dt can also be either positive or negative, depending on the state of the system.) It was too early for Boyle to grasp all the complexities of heat and heat flow, but he was brave enough to try many actual experiments.

In Title VII, Boyle carries out precise measurements of the volume of ice, water and aqueous solutions. In the 17th century, many Natural Philosophers denied that Ice was "frozen water." After Boyle, no literate Natural Philosopher could conscientiously assert such a thing. The volume of the same mass of ice exceeds that of water at the same temperature. Characterization of the full phase diagram for a

pure substance is essential for a proper understanding. Boyle used the opportunity to please the Royal Society to advance our understanding of the phases and phase changes of ice and water. He also measured the tremendous pressure created by the freezing of ice. Reciprocally, he discovered that ice can be melted by pressure, because its molar volume exceeds that of water at the ordinary melting point. True measurements remain true, but until they are routinely known by the full chemical community, utter nonsense can occur. Boyle is still worth reading today.

Title XIII discusses the "sphere of activity" of cold. Boyle is aware that heat is conducted differently in different substances. He is also aware that the interface between different regions in the system affects the transmission of heat (or cold). Title XIV considers the various mediums through which Cold(Heat) may be diffused. There is no such thing as a perfect "insulator." But there is a wide range of thermal conductivities. Once again, Boyle is measuring important thermal properties of matter. He also constructed coherent notions for the mechanism for thermal transfer. He envisions matter to be in constant motion: hotter regions can communicate this motion to colder regions.

Boyle was able to create good "vacuums." He carried out experiments designed to measure the thermal conductivity of a vacuum. He suspended a small vial of water in his vacuum chamber and pumped out the residual air. He then surrounded the chamber with a mixture of ice and salt. The water in the vial crystallized. Apparently, heat does not "require a medium" to flow. If heat was a material body of finite size, it could not have penetrated the vacuum chamber. The clear demonstration by Boyle was often forgotten by later "thermal scientists."

Boyle also surveyed the literature of explorers and verified that "ice bergs" are quite pure water. Another important observation of explorers is that pure ice bergs appear blue. This is due to light scattering by the ice. Like Descartes, Boyle was fascinated by Meteorology. The Natural History of the Earth remains an active area of research in the present.

Title XVII introduces an important concept for the entire History of Heat. Natural Historians proposed that there existed a "*Primum Frigidum*," a substance that was naturally completely "cold." Just as there was a substance that was naturally completely "hot." Boyle argues against such a notion with both experiments and logic. Boyle views "cold" (and "heat") as just a sign of "agitation." It is not a substance itself. He calls the notion that cold and heat are "primary qualities" an "unwarranted conceit."

Boyle addresses the ancient philosophers who thought that The Earth was the *primum frigidum.* Boerhaave knew that the Earth was hotter the farther underground the temperature was measured. Boyle cites volcanoes and other phenomena that produce hot water or lava from the "bowels of the Earth." He also quotes mine owners that knew that after the region closest to the surface, the temperature rises as the mine descends. He visited such places and confirmed this for himself. Other ancient philosophers nominated water as the *primum frigidum.* Boyle immediately dismisses this notion by observing that lakes freeze from the top! When the air is colder than the freezing point of water, ice forms. Also, since saltpeter can "cool" water, how could water itself be the frigid "form?" This valid observation led some

philosophers to claim that "nitre" was the *primum frigidum* and to talk about the "aerial nitre." Boyle dismisses this idea since it is "special pleading" that is almost never applicable.

Title XVIII considers "air." If "heat" is a sign of agitation, and gases are the most agitated bodies, how could it be the *primum frigidum!?* Ancient philosophers cited the ability of "cold air" to freeze water. Boyle reminds them that air can be as hot as anything on Earth and can melt any crystalline solid or boil any liquid. Whatever air is, it is not a form of cold itself.

Boyle liked to "argue," but he preferred to "demonstrate!" He filled a "weather glass" with well-rectified wine and placed it in a glass "receiver" connected to a vacuum pump. As he "drew out the air," he noticed that the liquid level in the weather glass decreased. He also examined the volume of air at constant pressure as a function of temperature. Remarkably, it changed very little near room temperature. This was a hint that an absolute measure of temperature was needed, not just a differential measure.

Boyle was very interested in global meteorology. He understood just how complicated the temperature profile of the Earth really was. He knew that "convection" (wind) was extremely important. He carried out an experiment with "laboratory wind" (bellows) and discovered that he could heat a weather glass with "cold air." The energy of the moving air can be dissipated on the glass because air is "viscous."

Boyle anticipated one of the central experiments of Thermal Science. He wondered whether all bodies emit thermal "particles" at all times. He did not yet know what these particles were, but he could envision both the movements of individual particles within the body of the air and the net motion of that body. If air was composed of particles, just like heat" and "cold," how much did the thermal particles weigh? He knew that air had a measurable mass density. Careful measurements of the mass of a physical system as a function of temperature revealed no change in the mass. Whatever heat and cold were, they were massless.

Robert Boyle both thought deeply and explored extensively the subject of heat and cold. If his book had been widely read in the 18th century, much of the nonsense would have been avoided. It is the faith of the Natural Philosopher that, in the long run, there will be an increase in understanding physical reality. But, the history of heat demonstrates that the actual trajectory is quite tortuous. Before much progress could occur, it was necessary to develop a standard, reliable quantitative scale of temperature. This issue is discussed further in the following chapter.

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2 Temperature and Thermometers: The Development of the Concept of Temperature and the Invention of Laboratory Thermometers

Abstract

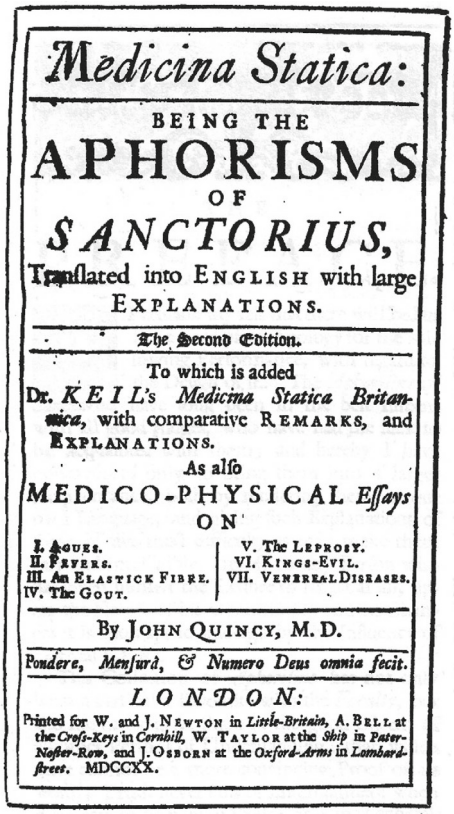
In order to become a true science, the measurement of temperature needed to be made both quantitative and reproducible. The first dramatic increase in the range and accuracy of the measurement of temperature was reported by Isaac Newton in 1701. He followed the cooling of an iron bar from the hottest temperature obtainable with his furnace until it achieved the ambient temperature. Newton's Law of Cooling is discussed in detail. A modern recreation of this experiment demonstrated that Newton had succeeded far beyond expectations. The Fahrenheit mercury thermometer is also illustrated and discussed. It has remained a standard tool in the practice of Thermodynamics!

The scientific study of the temperature of a material body was introduced above. Galileo's invention of a good thermoscope was immediately put to good use by his friend, Santorio Santorio (1561–1636), better known as Sanctorius of Padua. Sanctorius was a well-known physician and his book of aphorisms is still in print (Fig. 2.1). He used a Galilean thermoscope to measure the body temperature of his patients. Body temperature was one of the "fixed points" used in the calibration of early devices for the measurement of temperature.

Many famous scientists in the seventeenth century contributed to the progress of the understanding of temperature. The Accademia del Cimento carried out many experiments on thermoscopes. Marin Mersenne (1588–1648) described a unique thermoscope in his 1644 treatise *Cogitata Physico-mathematica* [1]. In 1667, the Accademia published an extended treatise on thermometers. Unlike previous instruments, that focused on the volume of the gas in the instrument, the Florentine thermometer depended on the volume of the spirit of wine in contact with the body being tested. The bore of the capillary tube was carefully ruled (Fig. 2.2).

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Medicina Statica:

BEING THE

APHORISMS

OF

SANCTORIUS,

Translated into ENGLISH with large EXPLANATIONS.

The Second Edition.

To which is added

Dr. KEIL's *Medicina Statica Britannica*, with comparative REMARKS, and EXPLANATIONS.

As also

MEDICO-PHYSICAL *Essays* ON

I. AGUES.
II. FEVERS.
III. An ELASTICK FIBRE.
IV. The GOUT.
V. The LEPROSY.
VI. KINGS-EVIL.
VII. VENEREAL DISEASES.

By JOHN QUINCY, M. D.

Pondere, Mensurâ, & Numero Deus omnia fecit.

LONDON:

Printed for W. and J. NEWTON in *Little-Britain*, A. BELL at the *Cross-Keys* in *Cornhill*, W. TAYLOR at the *Ship* in *Pater-Noster-Row*, and J. OSBORN at the *Oxford-Arms* in *Lombard-street*. MDCCXX.

Fig. 2.1 Title page of the English translation of *De Medicina Statica* (Venice 1614) (scanned from my personal copy)

The top of the thermometer was sealed by fusing the glass, so that the temperature indicated by the device was independent of the external pressure. The alcohol was colored to make it easier to read the height.

Once high-quality thermometers could be manufactured, the issue became one of attaining universality, so that any scientist anywhere could certify that the temperature that she measured was the same as that measured elsewhere. Robert Boyle (1627–1691) discussed this issue at length in his treatise *New Experiments and Observations Touching Cold* (1665) (See Chap. 1).

One of Boyle's chief concerns was the lack of a universal standard for temperature. This issue was addressed by Robert Hooke (1635–1703) [3]. Hooke was a genius at constructing scientific instruments and produced a precise capillary tube to be used in his large spirit of wine thermometer, sealed as shown above. Hooke chose the beautiful red insect dye, cochineal, as his colorant. He used distilled water at its freezing point as the standard temperature and marked this location on the stem. In his monumental treatise, *Micrographia* (1665), Hooke discusses the issue of expansion with heat [3]. Hooke tested the expansion of metals such as lead, tin, silver, antimony and brass, and glasses such as ordinary silicate glass

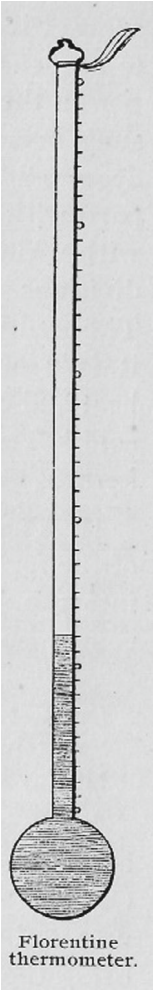


Fig. 2.2 Florentine thermometer from the Accademia del Cimento in Florence. (scanned from my copy of Bolton (1900) [2])

and antimony oxide glass. Hooke asserts that "Heat is a property of a body arising from the motion or agitation of its parts."

2.1 Newton's Law of Cooling

Isaac Newton (1642–1727) made a serious attempt to provide an extensive scale of fixed points for temperature. It was published anonymously in the Philosophical Transactions of the Royal Society of London in 1701 [4]. An outstanding recent paper has made Newton's work accessible to a universal audience [5]. The overall goal of Newton's work was the elucidation of the phenomenon of ballistic cooling of metals: Newton's Law of Cooling [6].

For the discussion of temperature, Newton created a scale that went from the freezing point of water (0 °Newton) to the heat of his coal stove (192 °N). Maruyama and Moriya drafted a Table with his results [5]. It includes the conversion to modern Celsius values and a description of the basis for the fixed points.

This monumental effort, both on the part of Isaac Newton and of Maruyama and Moriya, required a bootstrapping procedure and a speculative theory of cooling. Newton prepared an iron slab of 4.25 lb. In the recreation of the experiments a slab 4×4x1 inches was cast. In the modern experiment, the temperature of the slab was measured with a thermocouple inserted in the center of the slab. Newton needed to be more creative. He chose his 0 °N as the freezing point of crushed snow and used a standard thermometer of the Hooke design. The next important point was human body temperature, also verified with the thermometer. Newton chose to call this temperature 12 °N. This sets the size of the Newton degree.

Newton proposed that the heat flux from the cooling slab was linearly proportional to the temperature difference between the sample and ambient: $\Gamma \propto (T - T_{ambient})$. In more modern dress, this corresponds to the differential equation:

$$c\rho V \frac{dT}{dt} = -\kappa S(T - T_{amb}) \tag{2.1}$$

where c is the specific heat,ρ is the mass density, V is the volume, S is the surface area and κ is the heat transfer coefficient. The solution to this equation is:

$$T(t) = (T_0 - T_{amb}) \exp\left(-\frac{\kappa St}{c\rho V}\right) + T_{amb} \tag{2.2}$$

Newton then conducted experiments on the slab as a function of time after heating to its maximum temperature: T_0. Along the way he tested the slab with various materials. At the start the iron was glowing intensely. Eventually Newton concluded that this temperature was 192 °N. One of the more interesting points was the temperature at which one could "just see the glow:" 114 °N. Newton had access to regulus of antimony, pure Sb. It crystalizes at 146 °N. The modern value for the melting point of antimony is 630.6 °C. No "thermometer" in 1701 could register such a temperature (Mercury boils at 356.7 °C). Newton also used lead (96 °N) and tin (72 °N). Maruyama and Moriya investigated the time dependence by working far from the ambient temperature. Under these conditions the equation can be simplified to:

$$\ln\left(\frac{T}{T_0}\right) = -\left(\frac{\kappa S}{c\rho V}\right)t \tag{2.3}$$

They concluded that Newton had done an especially careful job.



Fig. 2.3 Original Fahrenheit thermometer and painting of Fahrenheit (Image in the public domain)

2.2 Fahrenheit and His Thermometer

The design and manufacture of the classic mercury thermometer is associated with Daniel Gabriel Fahrenheit (1686–1736). He made especially uniform capillary tubes. He also modified the design of the test bulb to be a cylinder, instead of the earlier globes (Fig. 2.3).

The zero of this device was determined with a mixture of ice, water and salt. The height at 32° was determined with ice and pure water. The point at 96° corresponds to normal human body temperature. Fahrenheit established himself as a maker of "philosophical instruments" in Amsterdam. He worked closely with Herman Boerhaave, the famous physician and chemist at the University of Leyden (Detailed discussion of the work of Boerhaave will occur in Chapter 3). When Fahrenheit traveled to London in 1724, he was warmly received and elected as a Fellow of the Royal Society.

An essential source for the understanding of temperature is *Inventing Temperature: Measurement and Scientific Progress* (2004) by Hasok Chang [7].

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Herman Boerhaave: The Natural History of Fire (Heat)

3

Abstract

One of the key documents in the History of Thermodynamics is a chapter in Herman Boerhaave's *Elementa Chemiae* (1732): "The History of Fire." It is the first section of the discussion of the "Instruments of Chemistry." A thorough discussion of this entire document is presented in Chapter 3. Boerhaave concludes that: "Heat(fire) consists of corporeal bodies." They are very small, heavy, hard, and move very fast. Both the assertions and the arguments are discussed. While Boerhaave was not "correct" in his conclusions, he featured actual experiments, cogent analysis, and coherent conclusions.

One of the high points in 18th century chemistry was the publication of Herman Boerhaave's (1668–1738) *Elementa Chemiae* (1732) (Fig. 3.1) [1]. (My own copy is actually a pirated English translation of the notes taken during Boerhaave's lectures in Latin and published by Peter Shaw in London (1727).) Boerhaave considered "fire" to be one of the six chemical "instruments." The other five are air, water, earth, menstruums, and vessels. A public domain image of Boerhaave is shown as Fig. 3.2.

Two essential sources for the life and work of Boerhaave are *Herman Boerhaave: The Man and his Work* (1968) by G. A. Lindeboom [2] and *Inventing Chemistry: Herman Boerhaave and the Reform of the Chemical Arts* (2012) by John C. Powers [3].

Boerhaave was a master of the furnace and kept many in operation for many years. He believed that it was fire that allowed substances to explore their full potential. Without fire all substances would be solids! He believed that "fire" could be added to any substance. He wrote an entire chapter on "The History of Fire."

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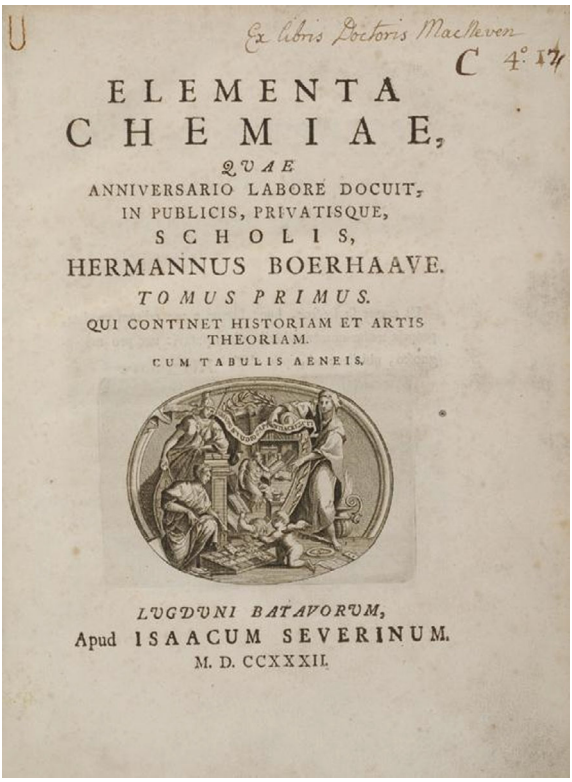


Fig. 3.1 Title page of Boerhaave's *Elementa Chemiae* (1732) (by permission of the Othmer Library of the Science History Institute)



Fig. 3.2 Herman Boerhaave, University of Leyden (public domain)

3.1 Detailed Discussion of "The History of Fire"

Boerhaave was not a wild speculator. He carried out an enormous number of experiments, some lasting 30 years. While the "ancients" considered "fire" to be either a "gift from the gods" or even divine itself, Boerhaave viewed it as the "source" of all movement in the universe. He also identified it as the cause of all changes in Nature. (In order for this to be true, it would be necessary to label as fire many kinds of energy. Mechanochemistry was known in the 18th century, as was Photochemistry.) Boerhaave lists 2 considerations:

1. Solids were commonly viewed as passive, with no changes taking place. Boerhaave cited the thermal expansion of solids as evidence of mobility. He viewed fluids as active with constant changes taking place. (Many chemists, including Newton, thought fluids were also passive.) Boerhaave distinguished between "common fire," which included light and many other substances, and the "heat" that was the true "fire."
2. One of the "royal" instruments that was well-known in the early 18th century was the "burning glass." It was a large lens that could focus sunlight to a very small volume. (Even the "ancients" used concave mirrors to produce intense sunlight and melt metals.) Boerhaave considered the energy contained within the focal volume to be "pure fire." (Light is indeed a form of heat: energy that moves!)

Boerhaave launched into an extended essay on the relationship between light and heat. Light can be separated into different colors. When metals are heated, they emit light of many colors. He cites one of the most intriguing artifacts known in antiquity. If mercury is shaken in a glass container, it soon emits light. (This experiment must be carried out in total darkness in order to see the effect.) It is clear that Boerhaave realized that there is more going on here than exchange of heat.

Boerhaave is also aware of the effect of friction on solid bodies. Friction (a mechanical process) produces heat in the bodies. This heat can even be large enough to produce combustion in air and to render crystalline substances liquid, after which rapid cooling yields a glass. The example is steel and flint (polycrystalline silica). (Robert Hooke reported the appearance of the surface of a broken flint in *Micrographia* [4].) Microscopic examination of the "spark" produced by the interaction of a steel plate and a flint reveals a "globule" of "glass."

Boerhaave concluded that "fire" is a "body" (substance) *sui generis*. It can be manipulated and employed in industrial processes, but it has existed from the Creation. This is not a speculation based on too much wine; it is a reasonable induction from his extensive experiments. He cites Newton as believing that light is a particle with both energy and momentum. It would be several centuries before physicists finally agreed with Newton. But, is "heat" always equivalent to "light?"

The universe was a constant source of observation for Boerhaave. He did not know why the sun was hot, but the light that arrives from the sun is strong evidence

that it is. He also knew that the center of the earth was much hotter than the surface. One evidence was the high temperature deep in mines. Another is the existence and eruption of volcanoes.

One pure speculation was that, since heat is a substance, and since there is more heat as we approach the center of the earth, heat must have weight. Boerhaave also believed that heat flows so as to equalize the temperature in any region. He promulgated a dicta that: "all heat depends on fire." He summarizes his speculations as:

1. Heat(fire) consists of corporeal bodies. Such objects must have both weight and extension. (Phonons have momentum and wavelength. Classically momentum implies mass.) (Photons also have momentum and wavelength, but are not classical particles.) Boerhaave cites the ability of focused light to move a metal needle balanced on a pivot.
2. Heat expands gases. Boerhaave argues that since an expanded gas, at constant pressure, has more motion, it is the heat that supplies the motion. (This is an early recognition that energy can be transferred from one form to another.)
3. Every physical substance is characterized by a thermal conductivity: κ. Since heat "penetrates" all bodies, it "must be very small!" (The discussion of actual thermal conductivity was not possible in 1732.) Boerhaave envisioned the internal structure of a material body as an obstacle course. (Helium gas can diffuse through some metal films.)
4. Boerhaave also reasoned that, since fire particles could not be separated into smaller parts, that they were the "hardest" bodies.
5. Since Boerhaave is thinking of fire as light, he proposes that it moves with the greatest of all velocities. (Alas, heat can move as sound. And, even sound eventually is scattered and undergoes a random walk through the sample.)

The discussions in *Elementa Chemiae* are at the highest level for 1732. They are rooted in actual observations and argued cogently. It is small wonder that Lavoisier continued to view heat as a substance.

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4 Joseph Black: Towards an Experimental Foundation of Thermodynamics

Abstract

Major progress in the understanding of the thermal properties of matter in the 18th century was made by Joseph Black and his friends and colleagues. One of the key concepts that was developed was the heat capacity; the amount of heat per unit substance required to raise its temperature one degree. Another concept was the latent heat associated with changes in the phase of the material. With the new understanding of both heat and work, James Watt and his friends were able to produce "steam engines" that used the vapor phase to produce useful work. The magisterial *Lectures on the Elements of Chemistry, Delivered In the University of Edinburgh* (1806), edited by John Robinson, is still worth reading. Chapter 4 brings this work to life in the 21st century.

Joseph Black (1728–1799) was one of the most influential English chemists of the 18th century (Fig. 4.1). He was Professor of Medicine and Chemistry at both the University of Glasgow (1756–1766) and Edinburgh (1766–1799). After his death, John Robison (1739–1805), the Professor of Natural Philosophy at the University of Edinburgh, edited Black's *Lectures on the Elements of Chemistry* and published a coherent and literate two volume work in 1803 [1]. (My copy is an American Edition of 1807.)

Black was a brilliant natural philosopher and both carried out extensive experiments on heat and organized the results into clear statements. His primary observation of heat is that: "it can be communicated from one body to another." Black reported one of Isaac Newton's most famous experiments employing two bell jars and two thermometers (From *Optics, Qu. 18*) [2]. One bell was kept at atmospheric pressure, while the other one was evacuated with an air pump. The two jars were thermally equilibrated indoors. The thermometers read the same temperature. The two jars were then taken outdoors in winter. The evacuated jar

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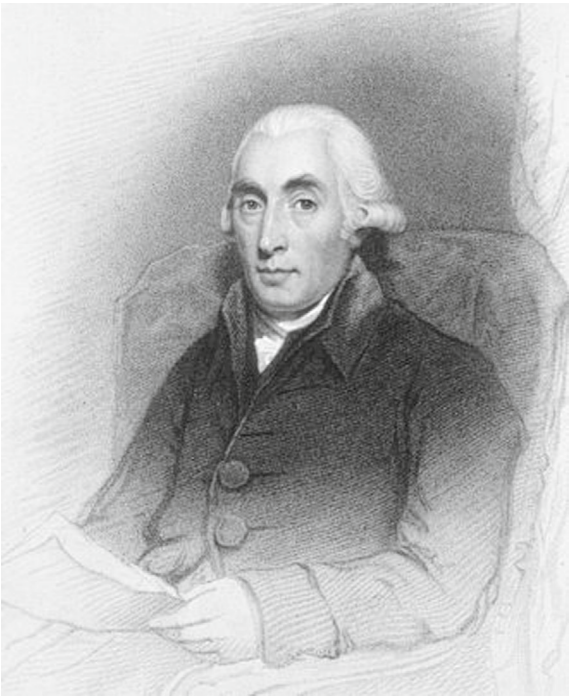


Fig. 4.1 Joseph Black, University of Edinburgh (with permission of the owner, Robert Anderson)

cooled at almost the same rate as the air-filled jar. After a short while, the temperatures were again the same. The jars were then brought back indoors and were soon equilibrated as before. Black summarized many such experiments with the observation that "heat penetrates all space and all matter." Neither Newton nor Black knew what heat was, but they were not confused about its ubiquitous presence. Similar experiments were carried out by Benjamin Franklin (1706–1790) and by Sir Benjamin Thompson (Count Rumford) (1753–1814).

Black asked the obvious question: What has been transferred when heat flows from a hot body to a cold body? Was heat a form of "matter?" Since it penetrates everything, it must be very small, or a tenuous fluid. Was there another substance known as "cold?" Some natural philosophers believed in frigorific particles (See Chapter 1). Black rejected this notion as "groundless imagination." Black correlates the experience of heat with the presence of the sun. He considered the sun as the primary source of heat on the earth. He explained the sensation of "cold" as an artifact of physiology: when heat flows from us to the object, we sense cold. When heat flows from the object to us, we sense heat. But, if we warm our hands by another source, placing them in otherwise warm water produces the sensation of cold.

Joseph Black explored the conditions under which matter can be either warmed or cooled. Mixing with another substance can produce both effects. He discusses the additional cold produced in snow by the addition of salt. The mixture can

become a salt solution, but its measured temperature is lower than 0 °C. Even more dramatic cooling can be produced by mixing snow with nitrous acid or vitriolic acid. Henry Cavendish (1731–1810) was very active in exploring the full range of possible temperatures.

4.1 Formulation of the Heat Capacity as an Important Thermodynamic Quantity

With an extended range of experimental temperatures and the best thermometers in England, Joseph Black began a program of detailed investigations of the amount of heat needed to raise the temperature of a substance. He called this ratio the "heat capacity**."** The numerical value depended on the size of the unit of temperature, the chosen measure of heat, and the chosen measure of matter. Modern heat capacities are expressed as Joules/mol K. (The "mole" is the current standard measure of substance and is equal to Avogadro's number of units: $N_A = 6.023\,x\,10^{23}$) In Black's era heat was measured in calories and matter was more likely to be expressed in terms of mass. The calorie is the amount of heat needed to raise the temperature of one gram of pure water by one degree. By using water as his "standard," Black was able to determine that the heat capacity varied greatly for different substances. This effort by Joseph Black is one of the foundational experiments in the History of Thermodynamics. Much more will be said about heat capacity below.

The basic experiment, as envisioned both then and now, is to choose a sample, weigh it, measure its initial temperature, add heat Q, wait, measure the final temperature. Then calculate the heat capacity $C = Q/(T_{final}–T_{initial})$. Nevertheless, this is not what Black, or anyone else, actually did in 1760. There was no clear way to measure absolute heat, Q. Another important issue is that heat capacity is an "extensive property of matter." Twice as much matter requires twice the heat in order to produce the same temperature change. Black's solution was to employ a system that included both the sample and a surrounding amount of liquid water of equal mass. The temperature of the heated sample, T_s, and the initial temperature of the water, T_0, were measured. The heated sample was added to the water and the combined system was allowed to come to thermal equilibrium. The final temperature, T_f, was then measured. The "relative specific heat," c_{rel}, was then calculated as

$$c_{rel} = \frac{T_f - T_0}{T_s - T_f} = \frac{c}{c_{water}} \tag{4.1}$$

The relative specific heat, c_{rel}, has no units. It is a pure number ratio. The heat lost by the sample has the same magnitude as the heat gained by the water. This is an early recognition of the conservation of energy in a closed system. The two masses are equal.

In addition to the capacity for heat, Black considered the "conductivity of heat." The discussion of this phenomenon largely occurs in the appended Notes provided

by John Robison. While individual substances do have different thermal conductivities, the detailed structure of the macroscopic material also influences how the heat moves through the sample. The concept of "insulation" is clearly presented. Materials with lots of isolated voids retard the spread of heat. This applies to snow as well, which insulates the ground from the bitter cold above.

Black also discusses "convection." When a hot piece of metal is in contact with air, the gas is heated quickly and expands. This material then becomes buoyant relative to the ambient air and rises. The convection of the air brings in new colder air and the cycle continues. The refractive index of the air depends on its density, so that the convection can be "seen" as fluctuations of the light from the sun or any bright source. Black understood that radiant heat was not influenced by gravity in a vacuum. (It was long before the general theory of relativity.)

4.2 Invention of the Concept of Latent Heat

Joseph Black carried out many experiments on liquids. Most of them could be solidified by cooling. He naturally reasoned that solids "melt" because of the heat added to them. It would be many years before a more accurate theory of liquids was formulated. Even a century after the seminal work of Josiah Willard Gibbs (1839–1903), most popular presentations discussed melting as "shaking apart." But Black also considered the many ways that water could be prevented from freezing by mixing it with other substances.

One class of experiments earned lasting fame for Joseph Black. He discovered that when snow and water are mixed, adding heat does not produce a change in temperature! As heat is added, snow melts and becomes liquid water. Eventually all the snow has melted and the addition of heat produces new increases in the temperature of the pure water. The amount of heat needed to melt all the ice was christened "latent heat." During a "phase transition" both phases may be present at the same time.

Another way to melt ice is to subject it to higher pressure. This strange phenomenon occurs because the specific volume of ice exceeds that of water at the same temperature. Although it would be many decades before Le Chatelier's Principle was perfected, matter responds to external forces by changing in such a way as to reduce the stress.

Another of Black's experiments studied supercooled water. Heat could be withdrawn from the liquid by using a bath with ice, water and salt. Eventually the liquid water crystallized. The temperature of the newly crystallized ice and water mixture rose during crystallization! The heat liberated by the formation of the ice caused the system to warm. The heat of melting, the negative of the heat of crystallization, reflected the difference between the crystalline ice and the liquid water. The full explanation of this fact needed to wait a century.

Black knew that a salt solution could be cooled well below the freezing point of pure water. He also knew that snow could be melted by adding salt to produce a cold salt solution. He tried to explain this phenomenon by invoking cohesive

attraction between the salt and the water, but this was before the atomic theory of matter and long before the theory of dissociated salts in water. His explanation was not incoherent, but it involved invoking a connection between Thermodynamics and Transport. The salt was invoked as an agent that increased the"fluidity" of the water. Actual experiments of the dependence of the viscosity of salt solutions lead to an increase with concentration.

4.3 Development of the Concept of the Phases of Matter

During the 18th century, there was always a temptation to revert to a hylomorphic view of matter. Bare matter had no distinctive properties. All observable aspects of material reality needed to be added. In this world, light is matter that does not have mass. Light was viewed as an element by many 18th century scientists. Heat was an "additive" that could change bare matter into some observable form, such as a crystal, liquid or gas. Chlorine would then be bare matter that had received some "green" (chloros). This conceptual world is not incoherent, but it makes it very difficult to achieve any sort of universal understanding.

One of the triumphs of 18th century chemistry was the manipulation and study of the vapor state. Many unique gases were isolated and named. Joseph Black is usually cited as the discoverer of "fixed air" (carbon dioxide). He produced this by treating chalk ($CaCO_3$) with vitriolic acid (H_2SO_4). He noted that this gas would extinguish a candle. From a hylomorphic perspective, fixed air needed to be composed of bare matter, heat (it was a gas) and "anti-inflammability" (a quality just the opposite of what made inflammable air (H_2) such a potent explosive). As more and more gases were identified (oxygen, nitrogen, sulfur dioxide, ammonia, hydrogen sulfide, nitrous and nitric oxide), it became necessary to invent more and more specific qualities that yielded the observed gas. Nitrous oxide (N_2O) would then be composed of bare matter, heat, and "hilarity." It was a great game while it lasted, but it was a degenerating paradigm, not a progressive one. The future became only more complicated; there was no unifying principle.

Joseph Black carried out many experiments on "vapours." The simple definition of a vapour (British spelling) was a gas produced by heating a liquid or solid. The observable quality of a vapour was that it was elastic (just as the spring of Boyle). A vapour exhibits pressure and a highly variable volume. When heat is added to the gas, the pressure increases at constant volume. If sufficient heat is added, the gas can burst the containment vessel.

4.4 Mechanical Work and Steam Engines: The Role of Black and Watt

One of Joseph Black's best friends was James Watt (1736–1819). Watt was very interested in the potential of using vaporization as a method of producing useful "work." When a liquid is heated at constant pressure, the temperature rises until

the vapor pressure of the liquid is equal to the applied pressure. Further heating leads to a large increase in the volume of the system, but no increase in temperature until all the liquid is converted to gas. This additional heat is called the heat of vaporization. It is a form of "latent heat," similar to the heat of melting. One of the secrets of Watt's engine was to use the latent heat of recycled (liquified) vapour rather than waste it. (A time-honored principle in business is that "time is money." After Watt, another principle was established: energy is money.)

While the full thermodynamic theory of work was not yet complete in the 18th century, Black knew that if work was done by a system, its energy was reduced. Work requires a change in the system. One sort of work that mattered to Black and Watt was PV work. At constant pressure, the work of volume change is W = PΔV. If the pressure varies during the change, P(V), the work is obtained by integration:

$$W = \int_{V_1}^{V_2} P(V)dV \tag{4.1}$$

Thermodynamics is an important part of Mechanical Engineering.

Joseph Black gave real meaning to chemical words like "volatile." A volatile liquid can easily be converted into a gas. (In hylomorphic terms, a liquid must acquire "volatility." Black would claim that volatility was an intrinsic property of the liquid state.) The development of a real theory of material phases is one of Black's greatest achievements. He knew that the temperature at which a liquid converted to a gas was an explicit function of pressure, $T_{vap}(P)$. And while the melting point was also a function of the applied pressure, the change in boiling point with pressure was much larger. (A thermodynamic discussion of this phenomenon is contained below.) One of the commercial devices that depends on the pressure dependence of the boiling point is Papin's Bone Digester (Fig. 4.2).

Denis Papin (1647–1713, FRS) was a French Huguenot natural philosopher, physician and inventor. He worked with Huygens in Paris, Leibniz in Marburg and Robert Boyle in London. This device is the forerunner of the autoclave and the "pressure cooker." Papin also invented steam engines and should be remembered in the history of heat.

4.5 Black's Brilliant Disciples

Black's ideas about "latent heat" were not universally accepted in the 18th century. John Robison made a spirited defense of this idea in the "Notes" to the "Lectures." The big question was: Where is this latent heat stored? Let us consider one of the systems discussed by Robison: a droplet of mercury between two glass plates. A single volume of mercury will spontaneously form a drop on a single plate. Gravity would drive the system to a thin film. Isaac Newton placed a single drop of oil on the surface of a lake. It spread until it covered the surface. What creates

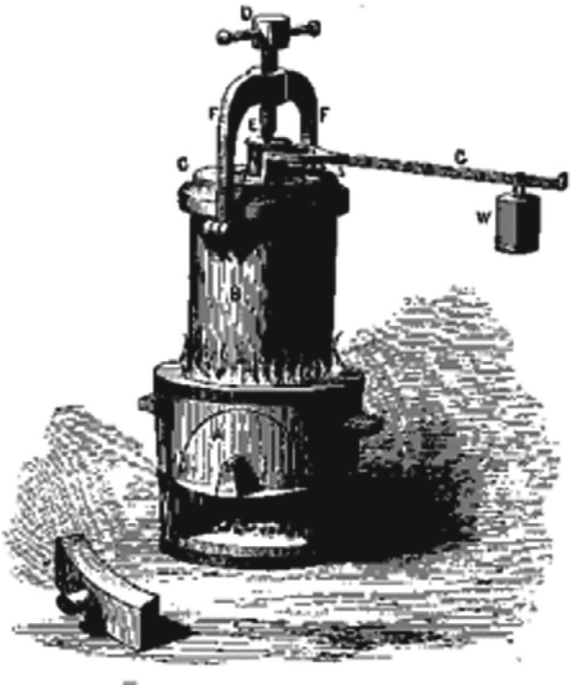


Fig. 4.2 Denis Papin's "bone digester." (public domain)

the difference? Robison considered the influence of a second plate of glass. The droplet will "deform" under the force of the upper glass, but upon removal the droplet recovers its initial shape. The relative stability of a liquid drop had to be due to "internal pressure." This phenomenon required an "attractive force" inside the drop.

The 18th century answer to this question was provided by Roger Boscovich (1711–1787) (Fig. 4.3). He was thoroughly Newtonian and adopted a model of matter that started with "particles." Boscovich proposed that the complex properties of actual materials arose from the complicated interparticle potential, u(r). In order for droplets to form at all, the particles must have an attractive part to the potential. While Newton might have suggested an inverse squared dependence of the attractive potential, Boscovich knew that this would not explain the observations. First, simple liquids are, to a reasonable approximation, incompressible. This means that the repulsive part of the potential is very steep. (Modern "ideal" liquid potentials contain a $1/r^{12}$ repulsive component.) For liquids that form droplets, the attractive part of the potential must also be steep, but not as steep as the repulsive part. (Modern "ideal" liquid attractive potentials contain a $-1/r^6$ attractive part.) This attractive potential allows the collection of particles to maximize the negative potential energy as a sphere. The repulsive part restrains the collapse to a well-contained size.

The secret to understanding latent heat is the concept of "microscopic potential energy." When a high kinetic energy particle leaves the surface, it is slowed down

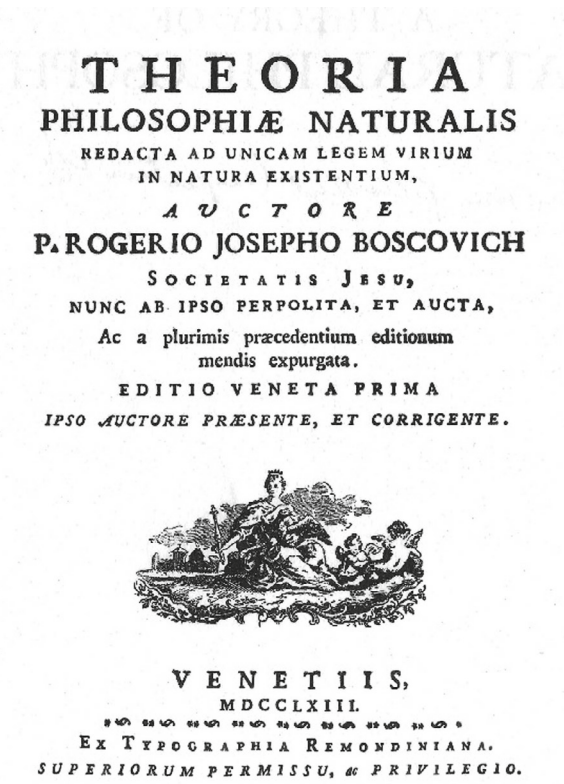

THEORIA
PHILOSOPHIÆ NATURALIS
REDACTA AD UNICAM LEGEM VIRIUM
IN NATURA EXISTENTIUM,
AUCTORE
P. ROGERIO JOSEPHO BOSCOVICH
SOCIETATIS JESU,
NUNC AB IPSO PERPOLITA, ET AUCTA,
Ac a plurimis præcedentium editionum
mendis expurgata.
EDITIO VENETA PRIMA
IPSO AUCTORE PRÆSENTE, ET CORRIGENTE.
VENETIIS,
MDCCLXIII.
EX TYPOGRAPHIA REMONDINIANA.
SUPERIORUM PERMISSU, ac PRIVILEGIO.

Fig. 4.3 Title page of Boscovich's *Theoria Philosophiae Naturalis* (1763). (scanned from personal copy)

by the attractive potential of the remaining liquid particles. It soon has virtually no potential energy, and less kinetic energy than it started with. In a closed system, the temperature of the drop decreases as high energy particles join the gaseous state. Some of the energy of the drop is restored as particles return to the surface.

Eventually the system reaches either phase equilibrium with a liquid and a gaseous phase, or the droplet evaporates to all gas. In the extreme case of complete vaporization, the temperature of the gas is lower than the starting temperature of the drop. The total energy of the system must be constant. Kinetic energy has been converted to a decrease in negative potential energy. When a gas condenses, the particles are accelerated and the potential energy is converted to kinetic energy of the liquid.

Robison presented a listing of "facts" that transcended mere speculation. He asserted that fluids must consist of "particles." (In fact, no coherent theory of chemistry based on hylomorphic principles has ever been demonstrated.) His theory of solids left much to be desired. In the 18th century, Abbé René-Just Haüy (1743–1822) constructed a completely coherent (and actually correct) theory of crystalline solids, *Traité de Mineralogie* (1801) [4]. The observed faces of the crystals revealed the underlying symmetry of the solid. Crystals were composed

of real “unit cells” with unique geometry that could pack perfectly to produce the observed macroscopic crystal shape. (In fact, crystals do not “shake themselves apart.” They melt long before the microscopic vibrations render the crystal structure unstable. Crystals melt “at the surface.”).

Black was well aware of the phenomenon of sublimation. Solids can sublime directly to gases. He also knew that such solids could be melted under higher pressure. Once again, a real explanation of this phenomenon required either a microscopic model of the solid or a full thermodynamic theory of phase transitions. Both will be presented below.

Joseph Black represented a serious attempt to understand real phenomena based on repeatable experiments on well-characterized materials. He was conservative in his speculation but clear about both the assumptions and the arguments. Further work could build on his foundation. He was also blessed with a community of mathematicians, natural philosophers and engineers.

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5 Antoine Lavoisier: *Mémoire Sur La Chaleur* (1780) Presented and Critiqued by Clifford Truesdell's *The Tragicomical History of Thermodynamics 1822–1854* (1980)

Abstract

One of the most important scientific programmes of the 18th century was the work by Lavoisier and Laplace. Lavoisier published a general "textbook," *Traité elementaire de Chimie* (1789). The part on Caloric is discussed. Lavoisier and Laplace published the monumental *Mémoire sur la Chaleur* (1780). This careful analysis of heat from their perspective dominated discussion until the middle of the 19th century. The original volume is discussed in exhaustive detail. A complete and coherent critique of the *Mémoire* by Clifford Truesdell, *The Tragicomical History of Thermodynamics 1822–1854* (1980), is also discussed in detail and employed to conclusively debunk the notion of the conservation of heat. Heat is a process, not a substance.

One of the seminal chemical events of the late 18th century was the publication of Antoine-Laurent Lavoisier's (1743–1794) *Traité elementaire de Chimie, presente dans un ordre nouveau et d'apres les decouvertes modernes* (1789) [1]. It was quickly translated into English by Robert Kerr (1755–1813), *Elements of Chemistry, in a new systematic order, containing all the modern discoveries,* and published in Edinburgh in 1790. Joseph Black enthusiastically accepted these advances and immediately taught them to his students.

The book starts off by acknowledging the work of the "celebrated Boerhaave." According to Lavoisier, all pure substances expand when heated. They do this by inserting more *caloric* between the characteristic particles of the body. (Alas, water can expand when cooled below 277 K. It continues to expand until its density approaches that of ice near 233 K.) Boerhaave viewed "fire" as a collection of very small, hard particles. Lavoisier viewed caloric as a continuous fluid that repelled ordinary material particles. In order to have solids, these material particles needed to have intrinsic attractions. In order to have fluids, these attractive forces needed to be of short range. He acknowledges the existence of a unique gaseous

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phase (aeriform fluid), but his theoretical model does not allow for a first order phase transition between liquids and gases. (Indeed, above the critical point there is no distinction between dense and expanded fluids!) For Lavoisier, caloric is a continuous elastic fluid, not a collection of particles. But, in his seminal *Mémoire sur La Chaleur* (Memoir on Heat, Fig. 5.1), written with Pierre-Simon Marquis de Laplace (1749–1827) in 1780, they state that [2]: "Heat (Chaleur) is a widely distributed fluid in all of Nature that penetrates all bodies." (Since Boerhaave's heat particles are "very small," we cannot distinguish between a fluid composed of a continuous substance (a truly fictive notion) and a fluid composed of very small particles.) Laplace also expressed his own ideas about the microscopic world [3]:

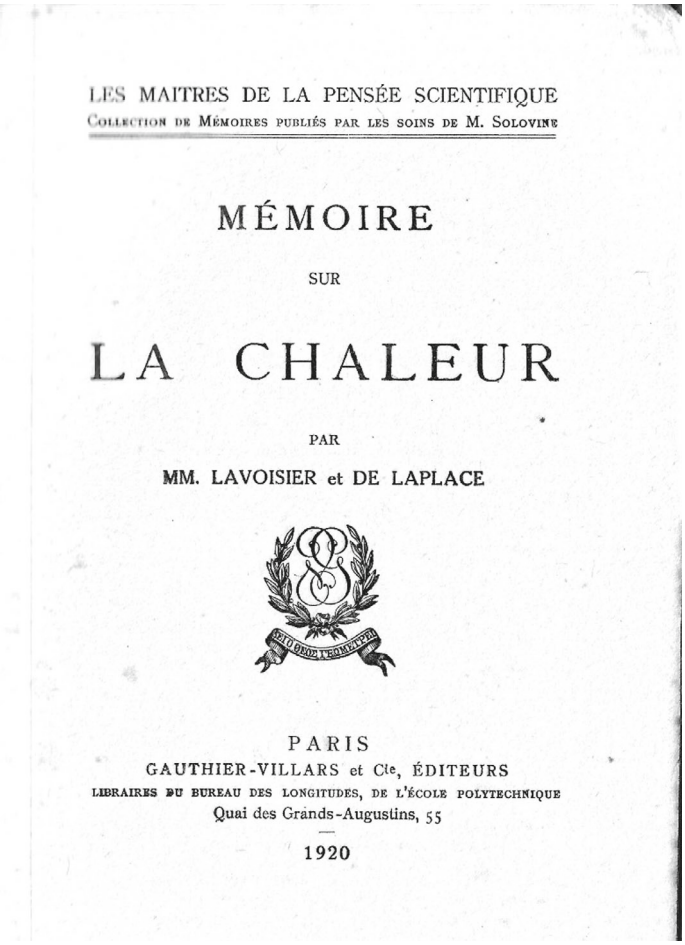
> "In bodies of a small size, the attractive force of matter is negligible. It reappears in its parts in an infinity of forms and with a vitality so prodigious that it is difficult to believe it is the same force that makes heavenly bodies gravitate about each other.
>
> The hardness of bodies, their crystallization, the refraction and diffraction of light, the raising or lowering of the level of fluid in capillary tubes, and generally all the chemical combinations are the result of attractive forces whose laws have not yet been determined."

This is in the spirit of Newton and Roger Boscovich. While the collaboration between Lavoisier and Laplace was both fruitful and successful, Lavoisier was a "chemist" while Laplace was a "physicist." They combined the best of both worlds.

Lavoisier and Laplace acknowledge the existence of another model of matter. This model is grounded in the theory of solids. Solids also contain many "holes." The particles that compose the solid are continually in motion in this structure. Eventually, this motion "shakes apart" the solid and it melts in this model.

While this "fictive" substance, *calorique*, helped Lavoisier to think about matter, it could never be prepared in a pure form. Boerhaave, on the other hand, considered light to be a pure form of heat! And, a blackbody cavity can be viewed as "heat in a bottle." Sound is also a form of heat, but it requires a material medium. Sound can be injected into a condensed medium, but it is then absorbed by the system and raises the temperature. The energy of the sound is distributed into all the thermal channels available in the system. One of the reasons that Boerhaave adopted a more "modern" view of heat is that he was a Newtonian. Lavoisier was more of a Cartesian. Lavoisier discussed so-called "free caloric," not associated with any other body, but asserted that it was impossible to obtain it. He also asserted that all actual bodies are compounds of some "base" and caloric. Following Black, he discussed "specific caloric," the amount of caloric needed to raise the temperature of the body one degree of temperature.

The goal of Lavoisier's *Traité* was to give a complete system of chemistry. He compiled a "Table of Simple Substances." The first item in the list was Light. The second item was Caloric. Oxygen gas was a compound of a dephlogisticated base and caloric. (All gases must contain caloric.) Lavoisier also alludes to work by Claude-Louis Berthollet (1748–1822) that asserts that oxygen combines readily with light. Oxygen does absorb ultraviolet light, leading to dissociation and


LES MAITRES DE LA PENSÉE SCIENTIFIQUE

COLLECTION DE MÉMOIRES PUBLIÉS PAR LES SOINS DE M. SOLOVINE

MÉMOIRE

SUR

LA CHALEUR

PAR

MM. LAVOISIER et DE LAPLACE

PARIS

GAUTHIER-VILLARS et Cie, ÉDITEURS

LIBRAIRES DU BUREAU DES LONGITUDES, DE L'ÉCOLE POLYTECHNIQUE

Quai des Grands-Augustins, 55

1920

Fig. 5.1 Title page of my copy of *Mémoire sur la Chaleur*

eventual formation of ozone. But ozone was not known in 1789. Nitrogen (Azote) and Hydrogen (Inflammable Air) were also listed. In 1789, none of these simple diatomic gases had been liquified by pressure and removal of the heat generated before decompressing. And the theory of the gaseous state was still awaiting the work of Maxwell and van der Waals.

Laplace was a master of classical mechanics. He stated the general principle of the "conservation des forces vives." He clarifies this statement by including his formula for *vis-viva*: mv^2. The total for the body is the sum of the *vis-viva* of each of the particles of which it is composed. While the heat was a continuous fluid, the material body was a collection of particles. In the "caloric" theory the particles were driven by the heat, while in the Hookean theory the particles themselves were in motion due to their own momentum.

Laplace now addresses the contact between a solid body at temperature T_1, placed in contact with another solid body at $T_2 < T_1$. Heat will flow from the hotter body to the colder body until $T_1 = T_2$. They next discuss the effect of solar radiation on solid bodies. Since the mass of the light is so small, it cannot have much *vis-viva.* And solids can reflect or refract the light rather than absorbing it. Even a black solid cannot be heated much!

While Lavoisier and Laplace are often careful to honor experimental facts, they are also occasionally willing to make bold speculations: "La quantité de chaleur libre reste toujours la meme dans le simple mélange des corps." Free heat is conserved, because it "must be!" They also assumed that mass is conserved, because it must be.

They expand on this approach:

> *Si, dans une combinaison ou dans un changement d'état quelconque, il y a une diminution de chaleur libre, cette chaleur reparaitra tout entire lorsque les substances reviendront a leur premier état, et, reciproquement, si, dans la combinaison ou dans le changement d'état,il y a une augmentation de chaleur libre, cette nouvelle chaleur disparaitra dans le retour des substances a leur état primitive.*

During a chemical reaction or a phase change, heat can flow to places outside the system under consideration. When the system is returned to its original condition, the heat must be fully restored to the system. As we will see, Carnot treated this assertion as a Law of Nature. Alas, it was not.

5.1 Article II Measurement of Heat and Specific Heat

One of the most vexing questions at this point in time was the appropriate quantitative measure of the amount of substance for comparisons of different chemicals. Lavoisier was focused primarily on the mass. He could measure mass as well as anyone in1780. He could measure heat better than anyone in 1780. And he had good thermometers. Many "specific heats" were measured. Each unknown could be compared with the same mass of water at the freezing point temperature. Lavoisier also developed a precision ice-water calorimeter (Fig. 5.2).

Lavoisier measured the mass-based specific heat for many pure substances and mixtures. The following table was published (Fig. 5.3).

Pure water is the standard for these measurements. Mercury has a very small value because the atomic weight of mercury is 11 greater than that for water. But, even taking this into account, it is much lower than expected in 1780.

Lavoisier also employed his calorimeter to study chemical reactions, including combustions. Had he lived, he might have discovered many of the effects that were only achieved by scientists like Victor Regnault (1810–1878).

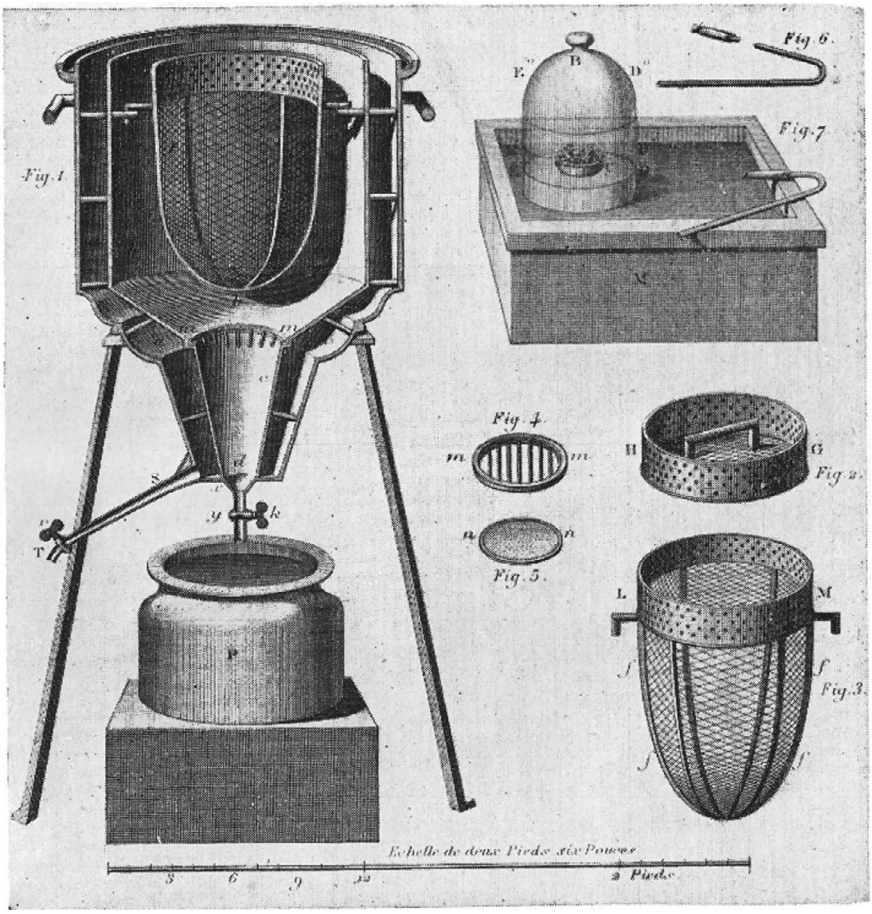
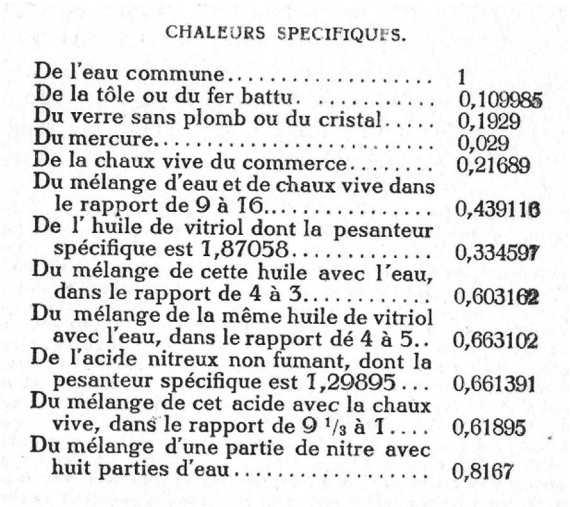


Fig. 5.2 Lavoisier style ice-water calorimeter. The outer jacket ensured that the active ice-water mixture was thermally insulated. Heat from the sample "basket" flowed into the ice-water mixture producing either more ice or more water (scanned from my personal copy)

5.2 Article III: The Mistaken Law of Conservation of Heat

Laplace acknowledges that in order to create a universal theory of heat it would require having a much larger data set. Both much lower and much higher temperatures would be helpful. He also seems to equate the "thermodynamic energy" of an equilibrium substance with its "total heat." This perspective, now viewed as less than helpful, created confusion in 1780 as well. In the scientific world of the "*Mémoire*," one of the goals was to create a "Law of Nature" that expressed the "heat" for a particular substance as a direct function of temperature. The experimental procedure required "heat" to flow through the surface of the body.



CHALEURS SPECIFIQUES.

De l'eau commune.....	1
De la tôle ou du fer battu.	0,109985
Du verre sans plomb ou du cristal.....	0,1929
Du mercure.....	0,029
De la chaux vive du commerce.....	0,21689
Du mélange d'eau et de chaux vive dans le rapport de 9 à 16.....	0,439116
De l' huile de vitriol dont la pesanteur spécifique est 1,87058.....	0,334597
Du mélange de cette huile avec l'eau, dans le rapport de 4 à 3.....	0,603162
Du mélange de la même huile de vitriol avec l'eau, dans le rapport dé 4 à 5..	0,663102
De l'acide nitreux non fumant, dont la pesanteur spécifique est 1,29895...	0,661391
Du mélange de cet acide avec la chaux vive, dans le rapport de 9 1/3 à 1....	0,61895
Du mélange d'une partie de nitre avec huit parties d'eau.....	0,8167

Fig. 5.3 Table of "chaleurs specifiques" from "Memoire" (scanned from personal copy)

Measured specific heats varied over a wide range, especially when compared at constant mass.

The burden placed on "chaleur" eventually proved to be too much. Even here, "free heat" needed to be created to distinguish energy that could flow in and out of the body of the sample and heat that could not. Eventually there were as many kinds of chaleur as there were phenomena. This is the "smoking gun" of a degenerating paradigm.

The thermodynamics of single component systems is complicated enough, but Laplace wished to comprehend all thermal phenomena. This included mixtures and chemical reactions. He cites many things about terrestrial matter that he believes to be true. He believes that particular bodies of matter "contain heat." Clifford Truesdell (1919–2000) emphasizes that "heat" is a process, not a thermodynamic quantity. No flow, no heat [4]. (Truesdell was the leading engineer in the construction of Rational Thermodynamics. His work will be discussed in more detail in Chapter 7.) The elephant in the room is the other "process" that is associated with changes in matter: work. Do substances "contain" work? (More "modern" perspectives acknowledge the existence of "potential energies" that could produce either heat or work under the right process.) Laplace was stuck treating potential energy as "latent heat." It was the "only game in town." The distilled form of this discussion is: *"dans les changements causes par la chaleur a l'état d'un systeme de corps, il y a toujours absorption de chaleur; en sorte que l'état qui succede immediatement a un autre, par une addition suffisande de chaleur, absorbe cette chaleur sans que le degree de temperature de system augmente."*

5.3 Article IV Combustion and Respiration

The discussion now turns to combustion and respiration. In 1780 combustion was often linked to the presence of the "matter of fire:" *phlogiston.* Apparently, it adhered to the surface of the combustible body. Joseph Priestley (1733–1804) coined the name "dephlogisticated air" for the element we now call oxygen. It facilitated combustion, respiration and calcination. "Fixed air" was envisioned as a compound of dephlogisticated air and a "base." Ordinary terrestrial air was now viewed as more than a merely physical substance. The theory that composed a "new systematic order, containing all modern discoveries" was hailed in 1777 as "verité demontreé."

There is no need to disparage the advances made by Lavoisier. His goal was to produce a theory that truly comprehended all that was known about matter. Oxygen does play a major role in many terrestrial phenomena. The heat liberated by combustion is much larger than that observed in simple thermal processes. Where did the heat come from? The caloric theory required that all gases contain "calorique." Was there another source of heat associated with oxygen? There was no way for chemists in 1777 to comprehend the internal structure and energetics of molecules. Laplace does battle with Adair Crawford (1748–1795) FRS, FRSE. Crawford carried out many of the same experiments as Lavoisier. He was respected in England and Scotland. He was a practicing physician and Professor of Chemistry in London. Lavoisier's work was subjected to verification by the Acadèmie des Sciences and reproduced by Berthollet. Laplace summarizes the results: "la chaleur degageé par l'air pur, lorsqu'il est absorbe par le phosphore, est a peu pres deux et un tiers plus grande que lorsqu'il est change en air fixe."

Lavoisier was sensitive to the fact that the product of combustion for phosphorus was $P_2O_5(s)$, while fixed air (CO_2) is a gas. Tremendous progress was being made until the French Revolution put an end to its most famous tax farmer. He also made clear that saltpeter reacted with powdered carbon to produce fixed air. The oxygen was stored in the "nitrate."

Animal physiology was also a subject of investigation. Even "Guinea pigs" were used as test subjects. They were forced to breathe pure oxygen. Fixed air was produced and weighed. After many experiments with different species of animals, they confidently asserted that "respiration is a form of combustion." They also conceived of animals in chemical engineering terms: The blood allows gas transport as well as "heat transport."

5.4 Reflections and Discussion of Truesdell's Analysis of the *Mémoire*

The historical evaluation of the concept of "calorique" has been blessed with two classic works. Robert Fox produced an annotated version of his doctoral dissertation as *The Caloric Theory of Gases: From Lavoisier to Regnault* (1971) [5]. All the highways and byways of the caloric delta have been explored. From a highly

technical perspective, Truesdell, the Father of Rational Thermodynamics, has presented in gory detail all the advances and errors of the tale: *The Tragicomical History of Thermodynamics (1822–1854)* (1980) [4]. Truesdell constructed a form of Thermodynamics that attempts to fully describe macroscopic material reality in a mathematically rigorous form that agrees with all known facts about matter. He answered the question, in a historically nuanced way: What if Laplace had done it right? He also made clear that, after Rudolph Clausius (1822–1888), it was no longer acceptable to insist that heat was conserved. Both of these books are challenging and are not suitable for "beach reading." But the rewards for the serious historian of science and teachers of Thermodynamics are massive.

Laplace continued to think about heat during his successful career as Citizen Laplace. Much of his work was focused on sound and its description. What does sound have to do with heat? Everything! Laplace realized that sound was an adiabatic process. (Actually, for Laplace, no heat flow. The term "adiabatic" was coined by Rankine in 1859.) The local regions of compressed and expanded matter were hotter or colder than the surrounding body. But there was not enough time for heat to fully flow before the wave had passed. A detailed hydrodynamic theory must include heat as well as pressure, temperature and density. Laplace knew that the heat capacity of matter depended on the conditions of measurement. One of the most important measurable quantities in the theory of sound is the ratio of specific heats:

$$\gamma = \frac{c_P}{c_V} = \frac{K_p}{K_V} \tag{5.1}$$

The second notational form is due to Laplace. The squared speed of sound is then:

$$c^2 = \gamma \left(\frac{\partial p}{\partial \rho} \right)_T \tag{5.2}$$

This produces good agreement with the measured speed of sound in air. Buoyed by this success, Laplace constructed a detailed mathematical theory of heat.

Laplace proposed the existence of a "heat function:" $H_L(p, \rho)$. Truesdell strongly objects, because heat is not a state function at all! He demonstrates conclusively that if heat is conserved, and if the system chosen "for simplicity" is the perfect gas, the heat capacities cannot be constant!

Another famous French scientist of this era is Simeon-Denis Poisson (1781–1840). His contributions to mathematics and physics earned him recognition as one of the 72 immortals inscribed on the Eiffel Tower. Poisson was both a consummate mathematician and an extremely creative physicist. His work was known by Sadi Carnot (1796–1832) and reveals both the physics and the mathematical structure of the theory.

Notation is always an annoying factor in the history of heat. In, at least vaguely familiar form, the amount of heat that has flowed, ΔQ, between the beginning and the end of a process is:

$$\Delta Q = \int_{t_1}^{t_2} \left(\frac{\delta Q}{dt} \right) dt = \int_{t_1}^{t_2} \dot{Q}\,(t) dt \tag{5.3}$$

Heat is always the definite integral of the process of heat flow over the process interval. (The dot above a quantity indicates the time derivative.)

Modern textbooks bravely talk about δQ, the inexact differential of the heat, as if that was enough. Poisson tried to construct an actual mathematical quantity that was a function of observable variables. Heat flow requires a gradient in the temperature. (Chapter 6 discusses heat flow and the theory of Fourier.) Poisson chooses the two observables as the time rate of change of volume and temperature.

$$\frac{\delta Q}{dt}(\dot{V}, \dot{T}) = \left(\frac{\partial \dot{Q}}{\partial \dot{V}} \right) \dot{V} + \left(\frac{\partial Q}{\partial \dot{T}} \right) \dot{T} \tag{5.4}$$

In an isothermal process, the heat flow is entirely due to the volume change. For an adiabatic process, Laplace and Poisson derive three relationships for an ideal gas:

$$p\rho^{-\gamma} = const. \tag{5.5}$$

$$pT^{\frac{\gamma}{1-\gamma}} = const. \tag{5.6}$$

$$T\rho^{(1-\gamma)} = const. \tag{5.7}$$

These relationships remain true today. Poisson also analyzed the consequences of assuming that the heat function, H_L, was a state function, independent of the path. For an adiabatic process:

$$\rho \left(\frac{\partial H_L}{\partial \rho} \right) + \gamma p \left(\frac{\partial H_L}{\partial p} \right) = 0 \tag{5.8}$$

The expression for the heat flow is now given in terms of pressure and density:

$$\frac{\delta Q}{dt} = \left(\frac{1}{\frac{\partial p}{\partial T}} \right) \left(K_V \dot{p} - K_p \dot{\rho} \right) \tag{5.9}$$

Further derivation demonstrates that the constant volume heat capacity can be expressed as:

$$K_V = M\left(\frac{1}{\gamma T}\right)\left[\left(\frac{p^{\frac{1}{\gamma}}}{\rho}\right)\psi\left(\frac{p^{\frac{1}{\gamma}}}{\rho}\right)\right] \tag{5.10}$$

where the function Ψ is identical to H_L. Truesdell shows conclusively that if the ratio of specific heats for a perfect gas is constant, and the measured constant pressure heat capacity is also constant, then the constant volume heat capacity cannot be a constant in the caloric theory. This result was published only almost 200 years after the "*Mémoire*." While experimental evidence finally doomed the caloric theory, it was always incoherent physically and mathematically.

The detailed mathematical discussions in Truesdell are at a level well beyond a typical historian, or even a chemist. Nevertheless, for those able to both read and understand this book, it is conclusive proof that "heat" is not a conserved quantity.

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6 Joseph Fourier: *The Analytical Theory of Heat* (1822) and the Foundation of the Science of Heat Flow

Abstract

Jean-Baptiste Joseph Fourier (1768–1830) derived the modern phenomenological theory of heat flow in his classic *Théorie Analytique de la Chaleur* (1822). The background to this mathematical theory is presented and the full theory is described. Several actual laboratory situations are discussed in detail. The mathematical level of this chapter is Calculus in Three Dimensions. The physical principles of actual heat flow are also discussed in detail at the phenomenological level. This work is the basis for all modern books on heat flow and is worth the effort to read and understand it for all practitioners and teachers of Transport.

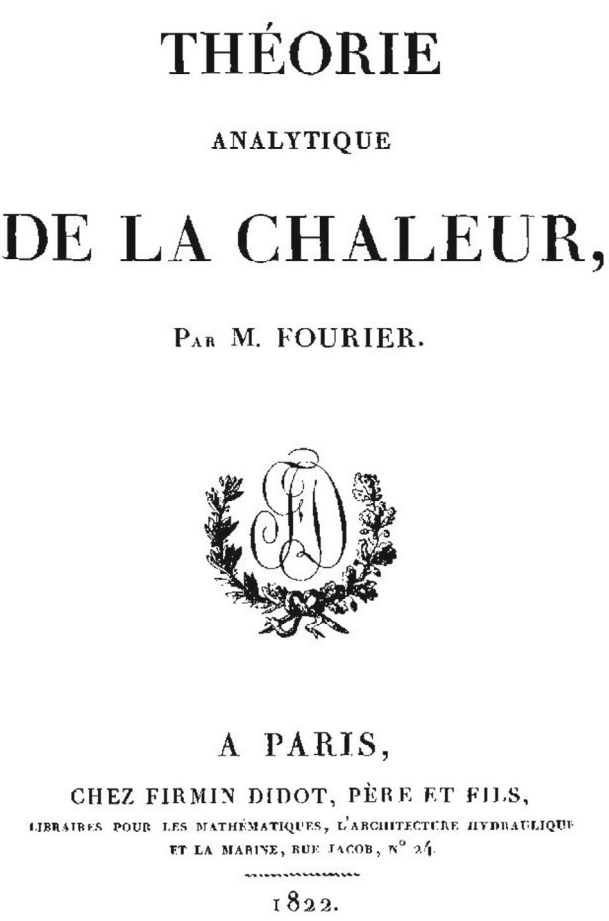
France was blessed with some of the best mathematicians in the world in the period 1750–1850. Jean-Baptiste Joseph Fourier (1768–1830), one of the very best, was interested in the problem of "heat" and developed mathematical tools to precisely characterize the wealth of experimental observations being obtained in this period. The results are summarized in the monumental *Analytical Theory of Heat* (1822) (Fig. 6.1) [1]. (My copy is the 1878 English translation by Alexander Freeman.)

The basic physical world for Fourier is the continuous distribution of mass, pressure and temperature in the sample. The sample is presumed to be homogeneous in composition, but capable of supporting variation in the local state. He considers the temperature field: $T(\vec{r}, t)$. If there are variations in the temperature in the sample, heat will flow until the average temperature of the sample, $\langle T \rangle$, is uniform.

Fourier was also quite aware of the interaction of the sample with its "environment." One classic case is a solid surrounded by a vacuum. The sample will "radiate" heat until it reaches its limiting temperature range. In the actual laboratory, the vacuum will be bounded by a containing vessel. The sample will

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THÉORIE

ANALYTIQUE

DE LA CHALEUR,

PAR M. FOURIER.

A PARIS,

CHEZ FIRMIN DIDOT, PÈRE ET FILS,

LIBRAIRES POUR LES MATHÉMATIQUES, L'ARCHITECTURE HYDRAULIQUE ET LA MARINE, RUE JACOB, N° 24.

1822.

Fig. 6.1 *Théorie Analytique de la Chaleur* (1822) (image in common domain)

then radiate heat until it reaches the temperature of the containing vessel. The containing vessel also radiates heat into the vacuum.

The concept of "radiant heat" is not a fictive speculation; hot objects emit radiation into the vacuum and the study of infrared radiation was well advanced by 1822. Heat also flows within solid objects. The thermal conductivity, κ, is reported in units of Watts per meter per K (W/m K). Copper has a thermal conductivity at standard temperature (273.15 K) of 401 W/m K. Diamond has a much higher value (1000 W/m K). There was no way for Fourier to explain these empirical values, but he could measure them! (Science does not require explanations or theories

for quantities that can be measured. A partial explanation for the difference noted above is the speed of sound in these two materials. Diamond exhibits a speed of sound of 12,000 m/s, while copper exhibits 4760 m/s.)

Fourier was a master geometer. Descartes' may have been the shoulders on which the French giants stood, but there were dozens of geometrical geniuses in France in the century in question. Fourier considers samples of many geometries, not just "bars" and spheres. The most important task for a French scientist (and for me too) was often to determine the best "frame of reference" in which to solve the problem. Fully three-dimensional questions needed to be addressed by fully three-dimensional mathematics.

In order to calculate the time dependence of the temperature at each point in the sample, three measurable quantities were needed: the specific heat of the sample, the thermal conductivity of the sample, and the thermal conductivity of the surrounding medium (taken to be effectively infinite in extent). Fourier was also aware that the nature of the "surface" also mattered. A "rough" surface is effectively larger since the fluid medium can interact with the full extent of the sample surface, not just its two-dimensional projection. There can also be a "surface resistance" caused by the mismatch of thermal conductivities. And infrared rays can reflect from a polished surface.

Fourier's goal was to take the required measurable properties of the sample, determine the "initial conditions" of the system, and solve the partial differential equations governing heat flow. This is paradigmatic phenomenological Science. In addition, Fourier carried out many experiments to check his mathematical results. The job is not done until the "experimental spiral" has converged.

6.1 Fourier and Experimental Thermodynamics

In addition to being a Mathematician, Fourier was a Natural Philosopher. He knew intimately the observations of Nature that involved heat. He immediately addressed the issue of the fixed points of the temperature scale. He chose zero as the melting point of ice. He denoted the normal boiling point of water as $T = 1$.

He discussed the measurement of the amount of heat necessary to melt a standard mass of ice. He also considered the change in temperature associated with a pure phase after absorbing a standard amount of heat. Every measurable property needed to be "standardized" so that any natural philosopher anywhere could discuss the same phenomena. (Fourier was the Perpetual Secretary of the French Academy of Sciences [2, 3].

Fourier desired to discover "universal behavior" for matter, but he was fully aware of the wide range of actual equations of state observed in the laboratory. Adding heat does not "always" cause an increase in volume. Adding pressure does not always lead to an increase in melting temperature.

Fourier was careful to consider all geometric issues with regard to matter and its surfaces. How is heat absorbed by a solid in contact with a vacuum, a gas,

a liquid or a solid? A highly polished metal surface reflects heat, while a rough blackened surface absorbs heat very well.

Fourier discusses "rays of heat" that propagate in a vacuum. While not mentioning Pictet by name, (Marc-Auguste Pictet (1752–1825) FRS was a Swiss natural philosopher that reported the reflection of heat.) he notes that heat can be focused and reflected by polished conical mirrors. He also comments that this form of heat can travel long distances at great speed. When the medium of transmission is a gas, the radiant heat does transfer some of its energy to the gas. When the medium is a transparent solid, the rays can be refracted. (There is no such object as a "perfectly transparent solid at ambient temperature." Heat is "scattered" by static imperfections in the solid and by sound waves.)

Fourier considers the "equilibrium state" of a material body. The average local temperature is equal everywhere. If it were not so, heat would flow from regions of higher temperature to regions of lower temperature. (He lived too soon to be considering the constant fluctuations that occur in an equilibrium body. It is these fluctuations that defeat Zeno's paradox.)

Fourier identifies this behavior as similar to "light." When a small body is heated to a high temperature, it emits visible light. It also emits "radiant heat." (Infrared radiation) One principle of such radiation clearly understood by Fourier is that there is a direct relationship between emission and absorption of radiant heat. The equilibrium temperature depends on a dynamic process of emission and absorption.

While the full microscopic theory of thermal conductivity could not be presented by Fourier in 1822, he knew all the physics that had been discovered by that date. He knew that all waves are attenuated as they travel through a material medium. He considered the consequences of waves produced at particular locations within the solid. If the wave propagated in a direction perpendicular to the surface, it would have more intensity at the surface than if it had traveled further, due to its direction being more tangential. This exact geometric conclusion was verified in the laboratory!

Fourier clearly understood the principle of the thermal black body cavity. The closed container is maintained at an average temperature T by some external process. The interior of the cavity is devoid of all matter. But if a thermometer is placed within the cavity, it will indicate the cavity temperature, independent of its location within the cavity. The radiant heat pervades the cavity and is absorbed by the thermometer.

Fourier was not above speculating about the "true nature of heat." He stated that "Heat is the origin of all elasticity." His microscopic model is the one where the intrinsic, or occupied, volume of the solid is determined entirely by the size of the "molecules" and their packing. Heat produces a higher volume which can be opposed by increasing the pressure. He presents heat as a "repulsive force." While it is nice to know the thoughts of such a genius, he is careful to remind the reader that none of the mathematical analysis in this work depends on the microscopic model that he favors!

6.2 The Fourier Heat Flow Equation

Fourier uses words like "molecule," but it is easier to understand what he is doing if the more modern language of "continuum mechanics" is employed. The medium is measured by a three-dimensional field: $(\vec{r}, t)$. There exists a small region centered at each point: $d\vec{r}$. If at time $t = 0$ the temperature at $(\vec{r}_i, 0)$ is different than the temperature at $\left(\vec{r}_j, 0\right)$, a quantity of heat, dQ_{ij}, will flow between i and j. The essence of Fourier's theory of heat is the assertion, inspired by Newton, that:

$$dQ_{ij} \propto \left(T_i - T_j\right) \phi\left(\vec{r}_i - \vec{r}_j\right) dt \tag{6.1}$$

Fourier starts his detailed considerations using the model of an infinite slab (thickness e) of the solid between two heat baths at temperatures T_1 and T_0. The goal is to establish the temperature profile of the slab: T(z). (Fourier still worries about Xeno's paradox!) The result is:

$$T(z) = T(0) + \frac{(T(e) - T(0))}{e} z \tag{6.2}$$

He then calculates the flux of heat, F, through any plane in the slab.

$$F = -\kappa \frac{dT}{dz} \tag{6.3}$$

where κ is the thermal conductivity. Many measurements of the thermal conductivity of solids had been made in Fourier's time. Diamond is the champion.

Another classical geometry is the infinite parallelopiped. In this section it is heated at one end. Each side of the square cross-section is of length 2 l. The "bar" is immersed in a heat-bath of air at $T = 0$. The problem is to calculate the steady-state temperature profile of the bar, $T(x)$. Fourier considers a random "slab" of thickness dx at location x. The external surface of the slab is of area $8ldx$. This surface radiates an amount of heat per unit time: $hT(x)8ldx$, where h is the emissivity of the metal bar. Heat is also conducted along the bar. The flux of this heat is:

$$-4l^2\kappa \frac{dT}{dx} \tag{6.4}$$

This leads to the second Fourier Heat Law:

$$\left(\frac{d^2T}{dx^2}\right) = \frac{2hT}{\kappa l} \tag{6.5}$$

Fourier then integrates these equations to yield the steady-state temperature profile:

$$T(x) = T(0) \exp\left(-x\sqrt{\frac{2h}{\kappa l}}\right) \tag{6.6}$$

This result is fully modern because the mathematics are correct. The surface emissivity and the bulk thermal conductivity are different.

The system considered in this section consists of a closed container with air inside. The interior is heated by a surface element maintained at temperature, T_s. The container is surrounded by air maintained at a lower temperature, T_a. The container has two surfaces that both emit and absorb heat. The thermal conductivity of the metal of the container enters the expressions as well. For Fourier, this is merely a math problem to be done while smoking a cigar.

While textbooks adore one-dimensional problems, and they are helpful for teaching the basics of the subject, Fourier is delighted to proceed to the general three-dimensional case. There are surfaces, such as the six faces of a cube or the boundary of a sphere, and there are interior locations as before. Proofs are given that the mathematics of heat flow are fully capable of dealing with such systems. Finite element analysis allows appropriate planes to be defined and the flux perpendicular to these planes calculated.

Fourier constructs a space and time dependent function for the temperature field: $T(\vec{r}, t)$. The medium is characterized by a known thermal conductivity: κ. If there is a temperature gradient at the chosen point of interest, heat will flow proportional to the direction and magnitude of the gradient at a rate determined by the conductivity. The other measurable quantities needed in practical problems are the heat capacity, C, and the density of the material, ρ. Fourier's equations contain the ratio: $(3\kappa/C\rho)$. Temperature changes exponentially as: $\exp(-(3\kappa/C\rho)t)$.

Chapters II through IX consist of elegant mathematical treatises on the movement of heat in solid objects of particular shape. This material may have been Fourier's favorite part, but it does not add anything to our understanding of heat itself. New experiments and new concepts were needed to make further progress. But no one needed to re-invent the phenomenological theory of heat flow.

Truesdell does point out one great need. Fourier did not produce a clean, rigorous presentation of the mathematics of heat flow. Sir George Stokes (1819–1903) was perhaps the best Irish mathematician of the 19th century. Any student of fluid mechanics is in awe of the Navier–Stokes equation [4]. It reveals the underlying physics of the phenomenon of fluid flow in a mathematically rigorous form, just as Maxwell's equations do for electricity and magnetism. Stokes provided the full tensor form for the equation for heat flow in a crystalline solid [4]. (The paper following Stokes is a contribution by Rankine!).

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7 Sadi Carnot: *Réflexions sur la Puissance Motrice du Feu et sur les Machines Propre a Développer Cette Puissance* (1824)

Abstract

A true science of Thermodynamics required both a physical and a mathematical foundation. This was provided by Sadi Carnot in his classic "Motive Power of Heat." This book is discussed in complete detail, including a transparent presentation of the mathematics. However, Carnot adopted Lavoisier's false assertion that "heat is conserved." Clifford Truesdell constructed a complete and correct theory of Rational Thermodynamics. In this book he critiqued the work of Carnot in complete detail. The essential ideas and important mathematical expressions are presented and discussed. Truesdell praised Carnot for providing a sound basis for Thermodynamics, while also correcting the fatal flaws.

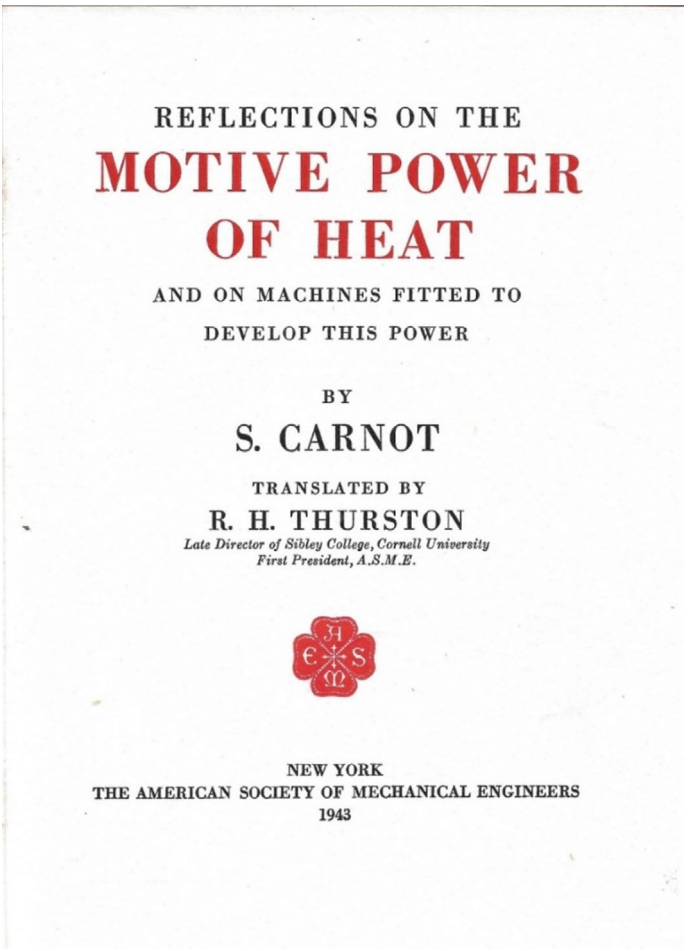
One of the most important books on the nature of heat was published by Nicolas Leonard Sadi Carnot (1796–1832): *Réflexions sur la Puissance Motrice du Feu et sur les Machines Propre a Développer cette Puissance* (1824) [1]. My copy is the memorial edition translated by R.H. Thurston (President of the American Society of Mechanical Engineers) (Fig. 7.1) [2].

Carnot came from a famous French family, both then and now. A later Sadi Carnot served as President of France from 1887–1894. His father, Lazare Carnot, was a well-known mathematician and a leader of the French Revolutionary Army. Sadi was highly precocious and was admitted to the École Polytechnique at the age of 16. He became an officer in the Army Corps of Engineers. Eventually he was able to obtain a position on the General Staff in Paris. He devoted his time to "private intellectual pursuits of an engineering nature." The scientific world has benefitted ever since. Sadi Carnot died young, but bequeathed to Science his masterpiece.

A working "steam engine" was invented by Thomas Newcomen (1664–1729) in 1712. It consisted of a furnace (to provide energy), a movable piston in contact with the steam produced by the furnace, a source of cold water to condense the

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REFLECTIONS ON THE

MOTIVE POWER

OF HEAT

AND ON MACHINES FITTED TO

DEVELOP THIS POWER

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THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS
1943

Fig. 7.1 Title page of my copy of *Reflections*

steam, and valves to control the flow of steam and water. It was used to pump water out of mines. Improvements were made to the design of a steam engine by James Watt (1736–1819) FRS, FRSE in 1776.

When Carnot devoted his genius to analyzing the underlying principles of the steam engine, he was able to use a real object of technology that had well-measured properties. He reduced the basic principles to clear mathematical expressions. These insights became the foundation of the whole field of Thermodynamics.

In 1824 the predominant "theory of heat" in France was still associated with the fictive material substance, *calorique.* It was believed that "heat was conserved." Rumford had clearly shown that work could be converted into heat. Now, Carnot

showed how heat could be converted into work. Eventually the concept of the conservation of a new quantity, energy**,** was established, but not by Carnot.

Scientists in 1824 knew that "heat flows from a hot body to a cold body." After Fourier, they had a correct mathematical theory of heat flow. The true significance of the work of Carnot is the creation of a correct mathematical framework for discussing heat and work. He had a superior knowledge of both the technological aspects of heat engines and the mathematical aspects of natural philosophy. (Great chemical and mechanical engineers still do!).

While the goal in this book is the explanation of heat, Carnot needed to start with work. A complete discussion of work requires an understanding of force. When a material system undergoes displacement in response to force, work is done. For a heat engine, the work is produced by changes in volume and pressure. The mathematical expression of this physical fact is:

$$W = \int_{V_0}^{V_1} P(V)dV \tag{7.1}$$

Carnot also knew that when a physical quantity changed in response to a gradient in potential, energy was flowing. He understood the difference between isothermal and adiabatic. He recognized the true significance of temperature. Although I have never seen it called this in a textbook, Carnot's Law is that: "*Wherever there exists a difference of temperature, motive-power can be produced."*

Carnot also understood that motive-power could be employed to produce differences in temperature. He cites "percussion" and friction as examples of the production of heat by purely mechanical means. He also understood "adiabatic compression and rarefication." No heat can flow across the boundary, but the temperature changes during these processes. He constructed the concepts of "the furnace" and the "refrigerator." A furnace is a "source" of heat, and a refrigerator is a "sink." This is real engineering science.

Carnot describes his conceptual water-based heat engine:

1. The system, initially composed of liquid water, is exposed to a source of heat at temperature $T_A > T_{boiling}$ until equilibrium is reached at constant pressure, P. The volume changes from V_A to V_B.
2. The system is then allowed to change freely without any heat flow (adiabatic). The pressure is now an explicit function of the volume, P(V), and the temperature is also an explicit function of the volume, T(V). In his ideal system, the adiabatic expansion is continued until the temperature is equal to the value provided by the refrigerator, T_B.
3. The system is then compressed at T_B until the water is completely liquified. Heat flows from the system to the sink at T_B.

Carnot is fully aware that work has been done and heat has been transferred. He formulates Carnot's Second Law: *The maximum of motive power resulting from the*

employment of steam is also the maximum of motive power realizable by any means whatsoever. The Corollary of this dictum is: *That in the bodies employed to realize motive power of heat there should not occur any change of temperature which may not be due to a change of volume.*

These two laws are called "fundamental" by Carnot, but are rarely enunciated in modern textbooks. All actual processes in Nature achieve less than the theoretical maximum due to "losses." Carnot understood the difference between "reversible" processes that occurred without loss, and "irreversible" processes where loss occurred.

Carnot is also aware that the initial charge of liquid water requires heat to raise its temperature to T_A. This initial loss of heat would need to be "recovered" by a process that returns the water to its initial condition at T_A and atmospheric pressure. This means that all heat engines are "inefficient" in a mechanical sense. "There are no perpetual motion machines."

The growing realization that there are many forms of energy and that they can be converted into one another is evident in *Reflections*. He discusses the motive-power of a waterfall, a classic source of energy. He does not yet know the relationship between the temperature difference between the two heat reservoirs and the motive power, but he is thinking about it.

In order to simplify and clarify the discussion, Carnot chooses a purely gaseous system and adiabatic changes of volume. A bare fact is that adiabatic compression of a gas leads to an increase in temperature. He constructs a simple system composed of the gas contained in a volume limited by a piston. He also requires two heat baths at temperatures T_A and T_B. He proposes the following protocol:

1. Bring the gas in the piston into contact with the source of heat at T_A.
2. The gaseous volume will increase, cooling the gas at constant P. The heat source will transfer heat to the gas to keep the system at T_A.
3. The system is then removed from the heat source and thermally isolated. The gas will continue to expand adiabatically, but the temperature is now not maintained and adiabatic cooling occurs. He chooses to allow this to continue until the gas temperature is T_B, the value of the second source.
4. The system is now placed in thermal contact with the second heat bath. The piston is used to compress the gas until it achieves a lower volume. Heat flows from the gas into the heat bath at temperature T_B.
5. The system is now disconnected from the heat bath and insulated from heat sources. The piston is used to compress the gas until its temperature attains the initial value, T_A.

This is the classic "Carnot Cycle" found in any good Thermodynamics text and, of course, in *The Mechanical Theory of Heat* (1875) [3]. Another major assertion could be called Carnot's Third Law:

TABLE OF THE SPECIFIC HEAT OF GASES

Names of Gases	Specific Heat under Const. Press.	Specific Heat at Const. Vol.
Atmospheric Air	1.000	0.700
Hydrogen Gas	0.903	0.603
Carbonic Acid	1.258	0.958
Oxygen	0.976	0.676
Nitrogen	1.000	0.700
Protoxide of Nitrogen	1.350	1.050
Olefiant Gas	1.553	1.253
Oxide of Carbon	1.034	0.734

Fig. 7.2 Table of specific heats from Carnot [2]

The motive power of heat is independent of the agents employed to realize it; its quantity is fixed solely by the temperatures of the bodies between which is effected, finally, the transfer of caloric.

Carnot was also interested in the fundamental measurable properties of matter. The practical heat capacity, C, is equal to the heat absorbed divided by the change in temperature: $C = \Delta Q/\Delta T$. He was also aware that the heat capacity depended on the full conditions of change. During an adiabatic process, the practical heat capacity is 0. During an isothermal process, such as a phase change, the practical heat capacity is infinite. During a constant volume process, no PV work can be done. During a constant pressure process, the volume can change. The energy lost to work is not then available to increase the temperature and the heat capacity is increased.

Quantitative measurements of the relative specific heat were available for many gases under both constant volume and constant pressure conditions. Carnot noticed that the difference between these two quantities was the same for all the gases that he knew (Fig. 7.2).

The observed difference was explained for a gas that obeyed the Marriotte Law: $P\overline{V} = RT$ (the bar above the V indicates one mole or whatever quantity is used to determine R, the gas constant). France was blessed with a wealth of scientists studying the mechanical and thermal properties of gases. Simeon Denis Poisson was another Polytechnicien who made calculations of the changes in gases due to changes in the temperature, pressure and volume. The modern version of his result is:

$$\overline{C}_P - \overline{C}_V = P\left(\frac{\partial \overline{V}}{\partial T}\right)_P = R \tag{7.2}$$

Another approach to understanding this result is provided by the conditions of adiabatic compression:

$$C_V \ln T + R \ln V = const. \tag{7.3}$$

Rearranging this expression yields:

$$T^{\frac{C_V}{R}} V = const. \tag{7.4}$$

All the numerical calculations of Carnot reflect this fact.

A thorough discussion of the heat associated with isothermal changes in volume is also given. Carnot's Law of isothermal volume changes is:

> *When a gas varies in volume without change in temperature, the quantities of heat absorbed or liberated by this gas are in arithmetic progression, if the increments or decrements of volume are found to be in geometric progression.*

For example, if a gas is reduced isothermally to half its volume, the amount of heat set free is equal to the amount of heat set free by reducing the volume further to one quarter of its initial volume. Carnot then immediately considers that, when the gas is rapidly (adiabatically) compressed, this amount of heat is available to heat the gas and such devices can be used to start fires.

The experimental situation for the thermal properties of gases was yet to be improved by the work of Regnault. One of the most vexing situations for a mathematical theorist is bad data. A great mathematician can envision a mathematical form that fits almost any pattern. If the experimental pattern is corrupt, the mathematician becomes an accessory.

One of the goals of the *Reflexion* was to calculate the temperature dependence of the motive power due to the flow of heat. Carnot formulated two dicta:

1. The quantity of heat due to a change of volume of a gas is greater as the temperature is higher.
2. The fall of caloric produces more motive power at inferior than at superior temperatures.

The modern expression for the "efficiency" of a heat engine is:

$$\frac{T_1 - T_2}{T_1} \tag{7.5}$$

For the same temperature difference between the higher source temperature, T_1, and the lower sink temperature, T_2, the efficiency is larger for lower T_1. Carnot demonstrates this fact for two cases of his cycle differing by 100 °C.

Carnot was fully aware that the full empirical foundation needed for a complete theory of Thermodynamics was not yet available. He does discuss the fact that

solids and liquid do not have enough dynamic range for their volumes to make good heat engines.

Since he was a practicing engineer, he also discusses the technological limitations of actual heat engines. The upper temperature is set by the furnace. The lower temperature is set by the available cooling water. In order to achieve the largest temperature drop in the adiabatic expansion, the initial pressure should be high and the vessel should be large. These are competing conditions. Many new designs for heat engines were introduced in the 19th century. But Carnot had already shown that any of them produced only a small fraction of the energy released by the burning of coal.

While the work of Carnot was only a start along the path to Thermodynamics, he introduced clear concepts and quantitative methods. Rather than being of merely historical interest, *Reflexions* is the solid ground on which it was eventually constructed.

7.1 Truesdell's Critique of Carnot and His Cycle

Clifford Truesdell admired the work of Carnot (See Chap. 5) [4]. It contained errors that were a consequence of its place in history, but most of the fundamental axioms were both new and correct. Truesdell constructed a "rational thermodynamics" based on the verbal text of the *Reflexions.* (Of course, he also constructed the Thermodynamic Temple in the late 20th century.) Truesdell associates the central equation of heat flow with the intent of Carnot.

$$\frac{\delta Q}{dt}(\dot{V}, \dot{T}) = \left(\frac{\partial \dot{Q}}{\partial \dot{V}}\right)\dot{V} + \left(\frac{\partial Q}{\partial \dot{T}}\right)\dot{T} \tag{7.6}$$

He credits Carnot with a clear engineering approach to the "process" of heat flow. He also assigns the essential notion of a "heat function" to Carnot.

$$\Delta Q(path) = H_C(V_2, T_2) - H_C(V_1, T_1) \tag{7.7}$$

Truesdell acknowledges that Carnot has a sound concept of work as a path integral:

$$W(path) = \int_{t_1}^{t_2} P(V(t), T(t))\frac{dV}{dt}\, dt \tag{7.8}$$

As Truesdell's analysis proceeds, the deleterious consequences of assuming the "Caloric Theory of Heat" becomes clear.

Truesdell presents an enlightening discussion of the concept of a "thermodynamic cycle." The "Carnot Cycle" remains a part of every engineering Thermodynamics text. What Carnot assumed, in addition, is that the reverse of

a Carnot cycle is also a Carnot cycle. What Truesdell proved was that this is not true. If the adiabatic expansion occurs first, it follows a different adiabat than in a traditional Carnot cycle. And the final adiabatic compression in the reverse cycle also follows a different adiabat. Yes, path does matter.

Carnot chose to state his fundamental axioms in words. Emile Clapeyron (1799–1864) attempted to clothe them in both graphs (diagrams) and equations. Truesdell succeeded in using both diagrams and equations to show that Carnot was required to assume the Caloric Theory of Heat in his theory: hence, it is false.

Nevertheless, not all of the theory is false. Truesdell derives the rigorous form of Carnot's main theorem for the heat associated with an isothermal change of volume of an ideal gas:

$$\Delta Q\,(isothermal) \;=\; \frac{R}{\mu(T)} \int_{V_1}^{V_2} \frac{dV}{V} \tag{7.9}$$

where μ(T) is Carnot's function. Truesdell employs a generic cycle diagram in TV space (Fig. 7.3).

Truesdell references the work of Clapeyon that showed that the area signified by A is equivalent to the work in the cycle:

$$W \;=\; \int_{path} PdV \;=\; \int_{A} \left(\frac{\partial p}{\partial T}\right)_V dVdT \tag{7.10}$$

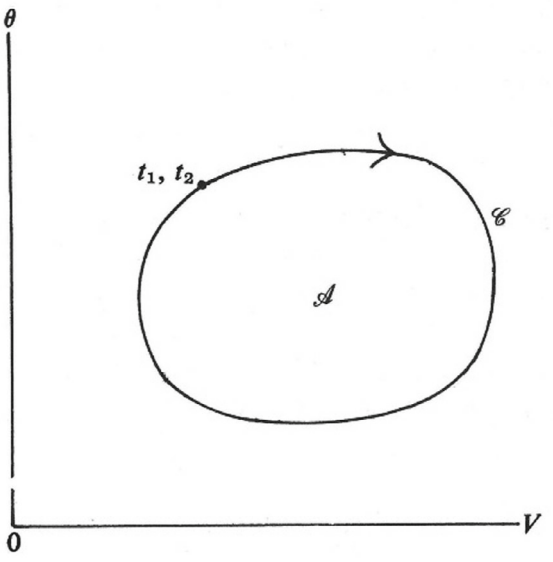


Figure 2. Cycle

Fig. 7.3 Generic cycle from Truesdell (1980) ($T = \theta$) [Truesdell C (1980) The Tragicomical History of Thermodynamics (1822–1854). Springer-Verlag, New York, USA, p 86, adapted with permission from Springer Nature]

This trick shows up many more times in Thermodynamics. Truesdell is fond of two partial derivatives that appear in the general expression for heat flow. He denotes them as:

$$\begin{aligned} \Lambda_V &= \left(\frac{\partial H_C}{\partial V}\right)_T \\ K_V &= \left(\frac{\partial H_C}{\partial T}\right)_V \end{aligned} \tag{7.11}$$

The first quantity is called the "latent heat with respect to volume." We shall discover later that it is related to the entropy. The second quantity is the "heat capacity at constant volume. An immediate mathematical consequence is:

$$\left(\frac{\partial \Lambda_V}{\partial T}\right) = \left(\frac{\partial K_V}{\partial V}\right) \tag{7.12}$$

Once the proper forms of the mathematical equations that truly instantiate Thermodynamics are constructed, many relationships can be derived in minutes.

(Truesdell was a master at this.)

In addition to being a master mathematician and rheologist (Truesdell won the Bingham Medal of the Rheology Society), he was a sensitive historian of science. It is worth quoting his parting eulogy to Carnot [4]:

> "It is now obvious to the spectator that Carnot founded thermodynamics, founded it not only in physical concept but also in program and schema. Of more lasting importance than any specific calculation is his having perceived that a theory of work effected by heat necessarily restricts the class of constitutive relations allowed, and it was he himself who obtained in principle the central restriction, the Carnot-Clapeyron Theorem: $\mu\Lambda_V = \left(\frac{\partial p}{\partial T}\right)_V$."

Truesdell also quotes another observer from the 19th century that understood the significance of the work of Carnot: Gabriel Lippmann (1845–1921, Nobel 1908):

> "He observed that while the physicists and chemists of the early 19th century might now seem to have stood but a short step from the creation of thermodynamics, in fact they were far away from it; they lacked one idea. They would have had to introduce into physics in place of the conception of molecular motion, *mechanical work,* which is a quantity measurable by experiment. Only the geometers used the notion of work: Sadi Carnot devised how to introduce it (work) into physics; that was the start of modern physics."

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James Joule: The Foundation of the Experimental Science of Energy

8

Abstract

Thermodynamics is a classical phenomenological theory; it is based on a demonstrably reproducible set of measurements. The greatest advance in this science is associated with James Prescott Joule. He showed experimentally that different forms of energy can be converted into one another. He also joined forces with many of the other natural philosophers in the mid-19th century, such as William Thomson, William Rankine and Victor Regnault. This is a great story and the details are discussed in both physical and mathematical terms. Chapter 9 presents the precise experimental work of Regnault. After a sufficient set of experiments established the "Laws of Thermodynamics" in verbal form, the time had come for a complete mathematical theory. Chapters 10, 11 and 12 present and discuss the evolution of the mathematical theory associated with Rankine, Thomson (Kelvin) and Clausius.

James Prescott Joule (1818–1889) was so important in the history of heat that the SI unit of energy (and hence heat) is the Joule. He is also an example of a wealthy scientist that used both his money and his time to advance our understanding of nature. One of his best friends, William Henry (1774–1836), and one of the leading chemists in the Manchester Literary and Philosophical Society, also benefitted from the family firm. While Joule was not part of the academic community, he was in personal contact with all the leading figures in the history of heat.

Joule was tutored by one of the brightest minds of the early 19th century, John Dalton (1766–1844). He learned both experimental skills and mathematical rigor. Natural Philosophy (Science) is "like a disease:" but you must catch it from someone who has it. (Dalton was infected by John Gough (1757–1825), the blind philosopher of Kendall. Gough also influenced William Whewell.) Joule adopted a practical attitude towards physical reality: wasted energy was wasted money. Joule's intellectual world centered on the Manchester Literary and Philosophical

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Society, of which he was the Secretary and President. The essential biography of Joule was written by Osborne Reynolds (1842–1912) FRS, President of the Manchester Literary and Philosophical Society, in 1892 [1]. The present chapter is based on *The Scientific Papers of James Prescott Joule* (1883). It was edited by Lord Lyon Playfair (1818–1898) and William Thomson (1824–1907) [2].

Joule created a laboratory equipped with the latest and best apparatus. He knew that heat, Q, was evolved from a wire conducting electricity. He carried out extensive measurements and produced Joule's First Law: $Q = I^2 Rt$, where I is the current, R is the electrical resistance of the wire, and t is the elapsed time. This was the first large step towards formulating the principle that heat is a form of energy, and that it can be created by mechanical and electrical means. One of the "dicta" associated with the French "*calorique"* was that it could be neither created nor destroyed. Since Joule could create heat and Carnot could transmute it into work, the scientific basis of the concept of caloric was destroyed. Joule also considered the heat generated by the passage of current through an electrolytic cell (battery). The form of the law adduced from purely metallic conduction was verified for purely electrolytic conduction.

Joule did not work in an intellectual silo. He was completely familiar with the work of Faraday, Davy, and Rumford. He constructed his own precision galvanometer. He used the best thermometers, good to 0.01 °F. He had access to every item of metal available in England or the Continent. He was an electrochemist, as well as a "brewer."

Joule would have been vaguely amused at 21st century political pontifications. He knew from laboratory experience that more energy per pound sterling was produced by burning coal than by consuming zinc in an electric battery! Not all energy is created economically equal.

While energy is energy, the measurement of energy depends on the physical process involved. Different communities chose different measures of energy. One of Joule's favorite measures was the foot-pound: the energy needed to raise a mass weighing one pound to a height of one foot. Engineers of heat engines and natural philosophers of thermochemistry preferred the calorie: the amount of heat needed to raise the temperature of one gram of water one degree celsius. British engineers preferred the BTU (British thermal unit). (The bane of every student of science is the proliferation of units.)

Joule's Law states that: "Wherever mechanical force is expended, an exact equivalent of heat is always obtained" (1843). This revolutionary truth was resisted by English academic scientists in the 1840s, but more and more evidence was presented by Joule and by 1850 he was elected as a Fellow of the Royal Society.

While Joule was capable of carrying out the most sophisticated experiments possible in the 1840s, he knew that clear and simple experiments that demonstrated the equivalence of mechanical energy and heat were the most convincing. He constructed a machine that used gravitational potential energy to drive a paddle wheel immersed in water (Fig. 8.1). Careful insulation produced an essentially adiabatic environment. Using this apparatus, he measured that the mechanical equivalent of

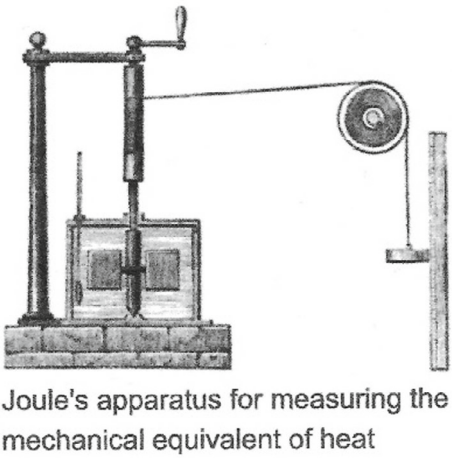


Fig. 8.1 Drawing of Joule's "paddle-wheel" apparatus demonstrating the equivalence of work and heat. (Public domain)

heat was 772.692 foot-pounds per BTU (4,150 J/Cal) (Modern value: 4,186 J/Cal) [3].

While many scientists worked on the relationship between heat and work, it was Joule in 1847 that fully expressed the truth that energy is conserved in his address to the Mancusians, reproduced as Chapter 1 of his biography: "On Matter, Living Force and Heat" [1]. One by one, the objectors became promotors of the conservation of energy. When William Thomson joined the team, the final outcome was greatly strengthened. (This is the signature of a progressive truth.)

Electric current can be produced in many ways. A chemical battery transfers the energy of oxidation to flowing electrons. Flowing electrons produce heat due to metallic resistance. The magneto-electric effect transfers mechanical energy to electric current. Electric current produces heat, just like in the case of electrochemistry. Joule was both a great believer in the universality of physics and a great demonstrator of this fact. Discussions of heat often ignore the magnetic field, but some of the greatest experiments in the history of heat involve magnetic effects.

One of the most common sources of heat is due to mechanical friction. Benjamin Thompson (Count Rumford, 1753–1814) carried out experiments on the boring of cannon barrels by measuring the rise in temperature of a bath of surrounding water. Joule followed up this line of inquiry by forcing water through small holes where the heat is due to the viscosity of the water.

8.1 Joule and His Scientific Community

Science is a collective enterprise and part of the obligation of a "scientist" is to contribute his results to the full community. One outcome of this activity is the rapid exposure of error. The sooner an error is both revealed and explained, the sooner time and money will cease to be wasted. But even when no error can be

demonstrated, the conservative character of human communities provides intellectual "resistance" to the flow of information. New facts require new concepts and new words.

Scientific communication can take many forms. Local talks can expose the work to like-minded scientists. If the work is favorably received it can be presented at national meetings, such as the British Association for the Advancement of Science, founded in 1831. (The classic history of this group is *Gentlemen of Science* (1981) [3].) Scientific journals are another channel for communication. The *Philosophical Transactions of the Royal Society* constituted one of the most important documentary records. If an article was published there, it had been reviewed by members of the Royal Society. Joule presented a paper to the Royal Society, "On the Production of Heat by Voltaic Electricity," on December 17, 1840. It was rejected for publication! It was then submitted to the *Philosophical Magazine* and published in 1841 as "On the Heat evolved by Metallic Conductors of Electricity and in the Cells of a Battery during Electrolysis" [4]. Joule's local community, The Manchester Literary and Philosophical Society, immediately elected him a member in January, 1842. Joule's next paper was also published in *Philosophical Magazine*: "On the Calorific Effects of Magneto-Electricity, and on the Mechanical Value of Heat" (1843) [5]. Finally, Joule was able to publish a short paper in the *Proceedings of the Royal Society of London* in 1844: "On the Changes of Temperature Produced by the Rarefaction and Condensation of Air" 5, 517–518 (1844) [6]. The long version was published the following year in *Philosophical Magazine*: 26, 369–383 (1845) [7]. Joule's work on the mechanical equivalent of heat was presented to the British Association in 1845 and published in full in *Philosophical Magazine*: "On the Existence of an Equivalent Relation between Heat and ordinary Forms of Mechanical Power" 27, 205–207 (1845) [8].

Osborne Reynolds (1842–1912) FRS was both a great engineer and scientist and a great scientific statesman. In Chapter VI of his biography of Joule, he paints a picture of the English scientific landscape in 1845 [1]. The Rock on which this community was anchored was Michael Faraday (1791–1867). (Joule emulated Faraday in so many ways.) Other critical figures in this vibrant community included John Frederick Daniell (1790–1845) FRS, a master electrochemist who invented the Daniell Cell battery. Sir William Robert Grove (1811–1896) FRS was also an electrochemist and a strong supporter of the concept of the conservation of energy. Thomas Graham (1805–1869) FRS was one of the English founders of physical chemistry and one of the founders of The Chemical Society in 1841. Reynolds also cites John Herschel, William Allen Miller, Sir Charles Wheatstone, William Whewell, James David Forbes and William Henry, all FRS. The Royal Society, like the Académie des Sciences, was a worthy referee in matters scientific.

Joule was not a clairvoyant, and had to find words to describe his new results. His friends in the Royal Society were a great help. He was also not a university-trained mathematician. Whenever he found himself hindered by his background, he both read the best books and talked to the best people.

In addition to his electrochemical and mechanical experiments, he constructed a set of vessels, pumps and valves that allowed him to explore the behavior of

gases as a function of temperature and pressure. He achieved precision at the level of Victor Regnault (1810–1878) of France. Regnault received the Rumford Medal of the Royal Society in 1848 "For his experiments to determine the laws and the numerical data which enter into the calculation of steam engines." One of the results of his measurements was the realization that at some temperature, the pressure of the gas was expected to reach 0. His calculated value for this temperature was −461 °F. (Modern value: −459.67 °F).

Joule continued to expand the reach of his investigations. Musical sound has fascinated scientists since antiquity. Isaac Newton calculated an estimate for the speed of sound, but failed to realize that longitudinal sound waves depend on the adiabatic longitudinal modulus. Laplace corrected this mistake. Joule used his measurements of the mechanical equivalent of heat to calculate the ratio of the specific heat at constant pressure to that at constant volume.

In addition to mechanical and electrical heat, Joule measured "chemical heat." This work was first published in *Comptes Rendus* (1846). It was reprinted in *Philosophical Magazine* in 1852 [9].

One of the significant events in the life of Joule was the 1847 meeting of the British Association for the Advancement of Science held at Oxford. After his talk on the mechanical equivalent of heat, William Thomson made some observations that provoked good discussion. After the session, Thomson approached Joule and they discussed the work in detail. This led to a lifelong friendship and collaboration. Another Fellow impressed by Joule's work was Sir George Gabriel Stokes (1819–1903) FRS.

Joule was also not content to merely "make measurements." He considered the possibility that a permanent gas was composed of "small" particles in rapid motion. As an approximation, he assumes the ideal gas law for the pressure in terms of particles with momentum and kinetic energy. His calculation of the velocity for gaseous hydrogen was remarkably accurate. He also calculated the specific heat of many gases and noted that translational energy was not sufficient to reproduce the measured heat capacities. (Hydrogen, oxygen and nitrogen are diatomic molecules and exhibit rotational contributions to the heat capacity.)

8.2 Joule and the Mechanical Equivalent of Heat

In 1850 Joule published his work on the mechanical equivalent of heat in the *Philosophical Transactions of the Royal Society of London* [10]. Since he was not yet a member of the Royal Society, the paper was "communicated" by Michael Faraday. This paper led to his immediate election as a Fellow of the Royal Society. Joule recounts the careful work of Count Rumford and his explanation of the heat produced by boring cannon barrels. Rumford used horses to provide the "horse-power" for his experiment. The thermal fluid was water, which was the standard for specific heat. And he had access to good thermometers. While Rumford's actual value for the mechanical equivalent of heat was not very "accurate," the concept

1st. *That the quantity of heat produced by the friction of bodies, whether solid or liquid, is always proportional to the quantity of force expended.* And,

2nd. *That the quantity of heat capable of increasing the temperature of a pound of water (weighed in vacuo, and taken at between 55° and 60°) by 1° Fahr., requires for its evolution the expenditure of a mechanical force represented by the fall of 772 lbs. through the space of one foot.*

Oak Field, near Manchester,
June 4th, 1849.

Fig. 8.2 From "On the Mechanical Equivalent of Heat" (1850) [10]

was clear. He also discusses the contributions of Davy, Dulong, Faraday, Grove and Mayer.

Joule had been faithful in communicating his prior results to the Royal Society over a period from 1840–1849. He recounts these former experimental results. Over the decade he had employed many different mechanical and electrical effects to raise the temperature of water and other liquids. In the present paper he gives his next estimate for the mechanical equivalent of heat. He used the best thermometers available in both England and France. He was in constant communication with Victor Regnault. His "paddle-wheel" mechanism was designed to minimize both losses due to friction and due to the conduction of heat. It was described at a level that brought smiles from Regnault. After presenting all his results and fully discussing the corrections and calculations, he stated his conclusions as given in Fig. 8.2.

8.3 The Joule–Thomson Coefficient

In 1851 William Thomson was also elected as a Fellow of the Royal Society. Joule formed a scientific partnership with Thomson that produced four landmark papers published in the *Philosophical Transactions of the Royal Society of London.* The first one appeared in 1853: "On the Thermal Effects of Fluids in Motion," [11]. Actual gases are not ideal. One evidence of this is deviation from the Boyle Law. Newton and Boscovich proposed that atoms and molecules interact through complex potentials that include both a repulsive part and an attractive part. If the potential was purely repulsive, as originally proposed by Newton, expansion into an empty container would convert potential energy into kinetic energy and raise the temperature. If gases are allowed to "leak" out of a container at higher pressure through a small hole, the temperature of the escaping gas is higher than the bulk temperature. Explanation of this effect needed to wait for James Clerk Maxwell (1831–1879). Thomson and Joule explored the consequences of forcing gas through a "porous plug." They developed the technology to allow the gas to flow between a region of higher pressure to a region of lower pressure while

maintaining local equilibrium. The temperature of the gas upon exiting into the lower pressure region was lower than the high-pressure side. This is now called the Joule–Thomson effect. They defined a coefficient that can be measured, and that indicates the nonideality of the gas. The full thermodynamic discussion of this effect was yet to be produced, and the microscopic explanation was years away.

The appearance of the 1850 paper by Joule and other papers by Thomson had stimulated work in many other countries. One of the foundational papers was published by William Rankine (1820–1872): "On the Mechanical Action of Heat, especially in Gases and Vapours," (1850) [12].

Part II of the work by Joule and Thomson was published in 1854 [13]. Not only was this paper much longer, but included two new gases: carbon dioxide and hydrogen. An extended study of well-dried atmospheric air demonstrated that the extent of cooling was proportional to the pressure difference. The makings of a valid transport law were now evident. There was also evidence for a true thermodynamic definition of the Joule–Thomson coefficient: $\mu_{JT} = \Delta T/\Delta P$ at constant enthalpy. (The more modern form is given as Eq. 8.1 below.) The numerical value obtained for μ_{JT} was 0.0176.

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H \tag{8.1}$$

Extensive experiments on "carbonic acid" (CO_2) yielded a value of 0.0793, much higher than for atmospheric air. (Indeed, precision measurements of the equation of state for carbon dioxide later in the 19th century revealed the full extent of "nonideality" associated with CO_2.) On the other end of the range, the measured Joule–Thomson coefficient for hydrogen gas was 0.0058.

While the Joule–Thomson coefficient was essentially independent of pressure over the measured range, it did depend on the temperature of the initial bath (Fig. 8.3).

In order to convert to a common set of conditions, an actual theoretical expression for the equation of state was necessary. The "dream team" is revealed in this discussion. Rankine sent Thomson (another Glasgow Professor!) the results of some of his calculations, based on the experimental results obtained by Regnault.

Temperature of bath.	Excess of pressure.	Cooling effect.	Cooling effect reduced to 100 lbs. pressure.	Theoretical cooling effect for 100 lbs. pressure.
12°·844	60·601	5°·049	8°·33	8°·27
19·077	37·248	2·938	7·89	8·07
91·516	74·938	3·586	4·78	4·96

Fig. 8.3 Results of Joule and Thomson for the effect of temperature and pressure on the Joule–Thomson coefficient [13]

The exact form for "low pressure" is:

$$\frac{PV}{P_0V_0} = \frac{T}{T_0} - \frac{\alpha V_0}{TV} \tag{8.2}$$

where the empirical constant $\alpha = 1.9$ for carbonic acid gas. The "standard" absolute temperature is the melting point for ice: $T_0 = 273$ K. (The team of Joule, Thomson, Rankine and Regnault are all-in on absolute temperatures.) The standard pressure is $P_0 = 1$ atm. The standard volume, V_0, is calculated for a "perfect gas." The final empirical quantity is the specific heat at constant pressure, K_p. A closed-form expression for the decrement in temperature observed in the Joule–Thomson experiment is then:

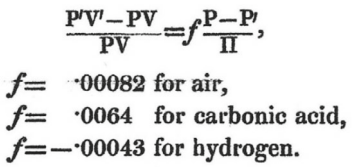
$$\Delta T = \frac{3P_0V_0\alpha T_0}{K_pT^2} \tag{8.3}$$

This form produced good agreement with the observed decrements. (Over a wider range in pressures and temperatures, the Joule–Thomson coefficient eventually vanishes. This is called the "inversion point, since the Joule–Thomson coefficient becomes positive above this temperature.)

After this triumph, Joule and Thomson proceed to derive thermodynamic relations from sound experiments and valid theory. The first Section discusses isothermal compression of a real gas. Following the work of Regnault and Rankine, Joule and Thomson express the deviation from the Boyle Law as that given in Fig. 8.4 [13].

The Boyle temperature for hydrogen (the temperature at which the second virial coefficient, $B_2(T)$, equals 0) is 110 K. Thus, the value of the coefficient above is negative for hydrogen. The inversion temperature for hydrogen is 293.7 K, so that the Joule–Thomson coefficient is very small, as observed. Nonideality is manifested differently for different measures of the thermal properties of gases. The Joule–Thomson coefficient depends on the first and second temperature derivatives of $B_2(T)$. Rankine was especially sensitive to the conversion of interparticle potential energy into heat.

In Section II, the remarkable properties of saturated steam are considered. Small changes in pressure or temperature led to large changes in the system. Thomson explicitly advises the reader that new measurements and calculations have been made since the paper published in the *Transactions of the Edinburgh Royal Society*


$$\frac{P'V' - PV}{PV} = f\frac{P - P'}{II},$$

$f =$ ·00082 for air,
$f =$ ·0064 for carbonic acid,
$f =$ —·00043 for hydrogen.

Fig. 8.4 Equations and results for the deviation of gases due to nonideality and the quantity "f" is an empirical deviation from the Boyle Law [13]

in 1849 [14]. A simple expression for the absolute temperature of a system is derived to be:

$$T = J/\mu \tag{8.4}$$

where J is the mechanical equivalent of heat and μ is the Carnot function.

8.4 Joule and the Thermodynamics of Solids

One of my favorite papers by Joule was published in 1859 in the *Philosophical Transactions*: "On some thermodynamic properties of solids" [15]. While studies of gases are often featured in discussions of the history of thermodynamics, many key phenomena are observed in solids. Joule, with help and advice from Thomson, constructed a differential thermometer with a sensitivity of 1/8800 of a degree Celsius. Electromagnetic elements and a large graduated circle made this possible (Fig. 8.5).

In addition to metallic substances, Joule studied two organic materials: Gutta-Percha and Natural Rubber. These two substances have the same empirical chemical formula: C_5H_8. Gutta-percha is a solid at room temperature. When a classical solid is subjected to tensile stress it dilates as well as extends. This dilation leads to a decrease in the temperature of the solid, since work has been done against the potential energy of the crystal lattice. Similar examination of rubber yields an increase in the temperature. The sample does not dilate, since it is more like a liquid. The adiabatic extension of the sample caused by the tensile force produces substantial work which is available to be converted to heat.

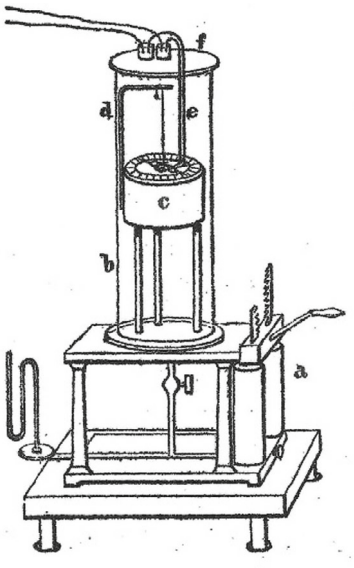


Fig. 8.5 Joule's apparatus for the thermoelasticity of natural rubber [15]. (The figure is scanned from my copy of *The Scientific Papers* [2])

The astonishment increases when the stretched sample is heated. The sample retracts! Although a cross-linked rubber sample might be expected to exhibit a maximum extension due to the actual solid character created by the crosslink network, the observed extension is much smaller than this. Even more astonishment occurs when the extension is increased by increasing the tensile force. The sample becomes much warmer and becomes hard!

The hardening of natural rubber can be understood by cooling a sample "at rest." It will crystallize spontaneously. The heat of crystallization is consistent with the temperature rise observed during hardening under tensile force. But, why does extension lead to a sharp rise in the melting point? The answer can be observed by measuring the refractive index of the sample both parallel and perpendicular to the strain: stretched natural rubber becomes birefringent. This is a sign of orientation of the polymer chains, but in 1858 the notion of rubber as a collection of chain molecules was not known. The source of the retractive force in cross-linked natural rubber is entropic. But the detailed thermodynamic understanding of entropy was decades away. A statistical mechanical theory of rubber elasticity needed to wait until the 20th century.

Truesdell understood the true significance of the work of Joule [16]:

> Joule's stage was grander than Thermodynamics. The thermodynamics of 'reversible' processes in fluids cannot be regarded as more than a small part, and the simplest, of a general science of heat, a science which concerns mainly irreversible processes and which embraces the effects of electric and magnetic fields. It is that greater science, not classical thermodynamics, that gave man a grasp, even if often at first uncertain and sometimes partly incorrect, of a new concept that has reshaped his whole view of the phenomena of nature: *energy* and its conversions. That greater science Joule's experiments, conceived with brilliant insight and presented to the reader in easy clarity of colloquial English, helped to found.

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Victor Regnault: Quantitative Science of the Thermodynamics of Gases

9

Abstract

Victor Regnault was the greatest French experimentalist of the mid-19th century. His measurements of the specific heat of many gases allowed later theorists to both test their theories and to be inspired by what he observed. He devised the precision apparatus that allowed these measurements. He also studied the specific heat of solids and revealed that the limiting law presented by Dulong and Petit did not apply to all metals and was badly in error for other elements and compounds. While this chapter does not dwell on the microscopic details of his apparatus, it does reveal just how important Regnault was for the progress of Thermodynamics.

Henri Victor Regnault (1810–1878) was at the center of the study of heat in the center of the 19th century. He was educated at the École Polytechnique and the École des Mines. He visited Justus von Liebig (1803–1873) at Geissen. In 1840 he was appointed to the Chair of Chemistry at the École Polytechnique, replacing the recently retired Joseph Gay-Lussac (1778–1850). He also took over the Chair of Physics at the Collège de France in 1841. He was one of the greatest experimental chemical physicists of the 19th century and was most famous for his studies of gases.

The Académie des Sciences in Paris continued to produce outstanding progress in Chemistry and Physics in the mid-19th century. Regnault was elected to the Académie in 1840. The experimental tradition established by Lavoisier and maintained by Gay-Lussac was continued by Regnault and in 1847 he published extensive tables of the properties of steam as a function of temperature and pressure [1]. He was rewarded with the Rumford Medal of the Royal Society in 1848 for this work.

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Upon Regnault's death, Jean-Baptiste Dumas (1800–1884) wrote his Éloge for the *Mémoires de l'Académie des Sciences de l'Institut de France* [2]. A fond memoire by Paul Langevin (1872–1946) was delivered and written in 1911: *Un célèbres physician Francais: Victor Regnault* [3]. While Regnault was conversant with all the work on gases and heat in 1840, he was devoted to determining in the laboratory what the actual physical situation was. Only by establishing the true relationships between the measurable properties of the substances could a useful theory be constructed. He was true to his "faith." A helpful modern biography is "Henri Victor Regnault: Experimentalist of the Science of Heat," published in *Physics in Perspective* [4].

One of his greatest achievements as a teacher was his mentoring of William Thomson (later Lord Kelvin). The concept of a lowest temperature was explored by Joule, Regnault and Thomson. Regnault's estimate for the lowest absolute temperature was −459.67 °F. Actually, exploring the properties of matter near this temperature needed to wait for another 60 years. But only by establishing the essential positive nature of temperature could Thermodynamics be constructed as a consistent system.

Dumas described Regnault as an experimentalist. He never assumed that measuring a real physical property was "simple." He worked until he fully understood all the variables that influenced the result. He either invented experimental means of minimizing errors or carefully calculated their effect. Regnault realized that higher precision could be obtained if the measurements were "differential." Temperature differences could be measured with a precision of 0.001 °C. Absolute temperatures are much less precise. (This is still true today. Precision has been improved to one part in 10^6, but absolute temperatures are not so accurate.) Regnault also insisted that any other scientist in the world could obtain the same results by following the complete description of the experiment. Like Faraday, Regnault's results have "stood the test of time."

Heat capacities of gases are difficult to measure with precision, but Regnault achieved good results (Fig. 9.1) [5]. Theorists needed to know that this property is a function of temperature. It would be many years before a full explanation of the results was given, but naïve notions, inaccurate even for beginners, were no longer possible.

9.1 Specific Heat of Solids

Another of Regnault's major achievements was the precise measurement of the heat capacity of solids. The early work of Pierre Louis Dulong (1785–1838) and Alexis Thérèse Petit (1791–1818) established that the specific heat capacity of 13 metals could be favorably compared when multiplied by the newly proposed atomic weights for these elements (Fig. 9.2) [6].

The concordance of these results is stunning for 1819. It would be many years before it could be explained, but the only thing needed was greater precision in the specific heats and the relative molar masses.

ON PERFECT GASES. 59

I. Name of the Gas.	II. Chemical Composition.	III. Density.	IV. Specific heat at constant Pressure: compared weight for weight with Water.	V. Specific heat at constant Pressure: compared volume for volume with Air.	VI. Specific heat at constant Volume: compared weight for weight with Water.	VII. Specific heat at constant Volume: compared volume for volume with Air.
Atmospheric Air		1	0·2375	1	0·1684	1
Oxygen	O_2	1·1056	0·21751	1·013	0·1551	1·018
Nitrogen	N_2	0·9713	0·24380	0·997	0·1727	0·996
Hydrogen...	H_2	0·0692	3·40900	0·993	2·411	0·990
Chlorine	Cl_2	2·4502	0·12099	1·248	0·0928	1·350
Bromine	Br_2	5·4772	0·05552	1·280	0·0429	1·395
Nitric Oxide	NO	1·0384	0·2317	1·013	0·1652	1·018
Carbonic Oxide.....	CO	0·9673	0·2450	0·998	0·1736	0·997
Hydrochloric Acid.....	HCl	1·2596	0·1852	0·982	0·1304	0·975
Carbonic Acid.....	CO_2	1·5201	0·2169	1·39	0·172	1·55
Nitric Acid.	N_2O	1·5241	0·2262	1·45	0·181	1·64
Steam	H_2O	0·6219	0·4805	1·26	0·370	1·36
Sulphuric Acid.....	SO_2	2·2113	0·1544	1·44	0·123	1·62
Hydro-sulphuric Acid.	H_2S	1·1747	0·2432	1·20	0·184	1·29
Carbonic di-sulphide.	CS_2	2·6258	0·1569	1·74	0·131	2·04
Carburetted Hydrogen	CH_4	0·5527	0·5929	1·38	0·468	1·54
Chloroform	$CHCl_3$	4·1244	0·1567	2·72	0·140	3·43
Olefiant Gas.....	C_2H_4	0·9672	0·4040	1·75	0·359	2·06
Ammonia	NH_3	0·5894	0·5084	1·26	0·391	1·37
Benzine.....	C_6H_6	2·6942	0·3754	4·26	0·350	5·60
Oil of Turpentine.....	$C_{10}H_{18}$	4·6978	0·5061	10·01	0·491	13·71
Wood Spirit	CH_4O	1·1055	0·4580	2·13	0·395	2·60
Alcohol.....	C_2H_6O	1·5890	0·4534	3·03	0·410	3·87
Ether.....	$C_4H_{10}O$	2·5573	0·4797	5·16	0·453	6·87
Ethyl Sulphide.....	$C_4H_{10}S$	3·1101	0·4008	5·25	0·379	6·99
Ethyl Chloride.....	C_2H_5Cl	2·2269	0·2738	2·57	0·243	3·21
Ethyl Bromide.....	C_2H_5Br	3·7058	0·1896	2·96	0·171	3·76
Dutch Liquid.....	$C_2H_4Cl_2$	3·4174	0·2293	3·30	0·209	4·24
Aceton.....	C_3H_6O	2·0036	0·4125	3·48	0·378	4·50
Butyric Acid.....	$C_4H_8O_2$	3·0400	0·4008	5·13	0·378	6·82
Tri-chloride of Silicon	$SiCl_3$	5·8833	0·1322	3·27	0·120	4·21
Tri-chloride of Phosphorus.....	PCl_3	4·7464	0·1347	2·69	0·120	3·39
Tri-chlorideof Arsenic	$AsCl_3$	6·2667	0·1122	2·96	0·101	3·77
Tetra-chloride of Titanium.....	$TiCl_4$	6·6402	0·1290	3·61	0·119	4·67
Tetra-chloride of Tin.	$SnCl_4$	8·9654	0·0939	3·54	0·086	4·59

Fig. 9.1 Regnault's table of the specific heats of gases [5]

	Specific heats	Relative weights of the atoms	Products of the weight of each atom by the corresponding capacity
Bismuth	0,0288	13,30	0,3830
Lead	0,0293	12,95	0,3794
Gold	0,0298	12,43	0,3704
Platinum	0,0314	11,16	0,3740
Tin	0,0514	7,35	0,3779
Silver	0,0557	6,75	0,3759
Zinc	0,0927	4,03	0,3736
Tellurium	0,0912	4,03	0,3675
Copper	0,0949	3,957	0,3755
Nickel	0,1035	3,69	0,3819
Iron	0,1100	3,392	0,3731
Cobalt	0,1498	2,46	0,3685
Sulphur	0,1880	2,011	0,3780

Fig. 9.2 Table compiled by Dulong and Petit of the specific heats, relative atomic masses and the product of these two quantities [6]

Regnault was the assistant to Dulong in his course on physics at the École Polytechnique. He also benefitted from many discussions with Dumas and Biot. He was in the right place at the right time and took full advantage of this opportunity. Langevin summarized Regnault's philosophy of experimental research as follows [3]:

In establishing the fundamental data of physics, we must resort, so far as possible, to direct methods. It is necessary that the adopted procedure is, so to speak, the *material realization* of the definition of the element one seeks. But this material realization, under conditions that offer every guarantee of exactitude, frequently presents great difficulties. It is to overcome these difficulties that the experimenter must apply his effort, rather than to seek, by theoretical considerations, to attain knowledge of the element under study by easier observation of complex phenomena.

Dumas suggested to Regnault that he pursue the preliminary results of Dulong and Petit and extend it to many elements and compounds. This he did! While "universal laws" were attractive to Regnault, he insisted that experimental reality trumped any theoretical speculation. Regnault's apparatus for measuring the specific heat of solids is a model, even today (Fig. 9.3) [7].

Later work has established that the "Law" of Dulong and Petit is a limiting result for monatomic solids. A modern compilation of results in the format of Dulong and Petit is given in Fig. 9.4.

A thorough discussion of the heat capacity of solids needed to wait until the 20th century and is presented in Chaps. 20 and 21.

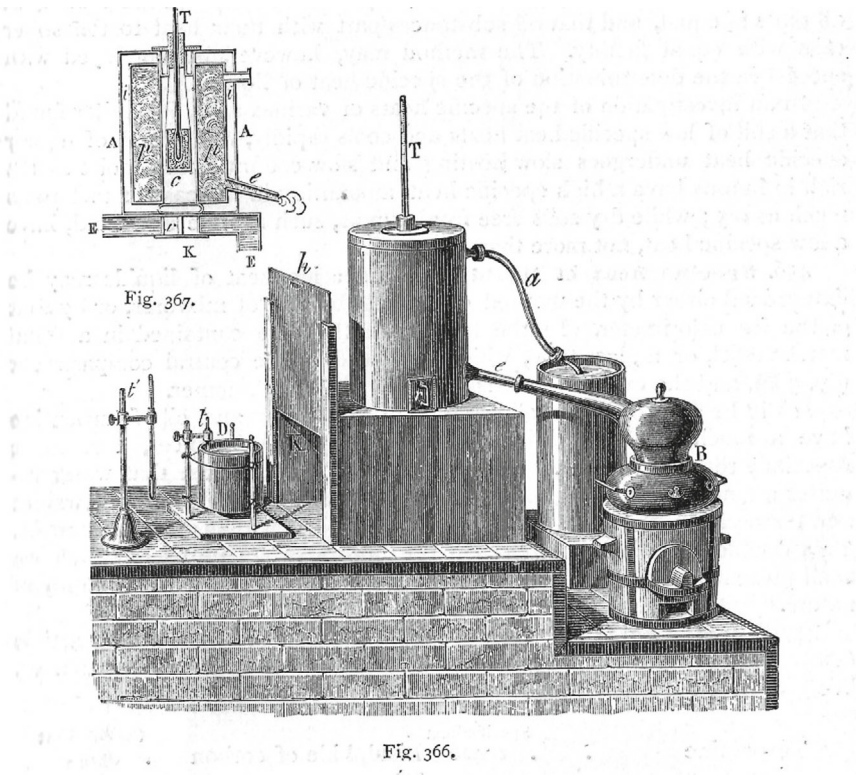


Fig. 9.3 Drawing of Regnault's calorimeter scanned from my copy of Ganot's *Elementary Treatise on Physics, Experimental and Applied* [7]

9.2 Ganot's Elementary Treatise on Physics, Experimental and Applied

A remarkable book was produced in France, starting in 1851, that was updated through 20 editions and translated into more than 10 languages [9]. (My copy is an English translation from 1881 (Fig. 9.5)).

Almost 200 pages are devoted to a discussion of Heat (Book VI). Rather than an advanced treatise on the mathematical theories of heat, Ganot chose to exhaustively present what was known from laboratory and industrial practice. It was intended for students preparing for entrance examinations to schools like the École Polytechnique, but it was widely read by everyone from elite researchers to interested intellectuals in France and England. It was inspired largely by Regnault!

Ganot acknowledges the current state of discussion of heat (chaleur). One view was that heat was an imponderable fluid that pervaded all of space, including all matter. Another view was that heat consisted of the vibratory motions of matter at the atomic level. (Remarkably, these two views are complementary, and for

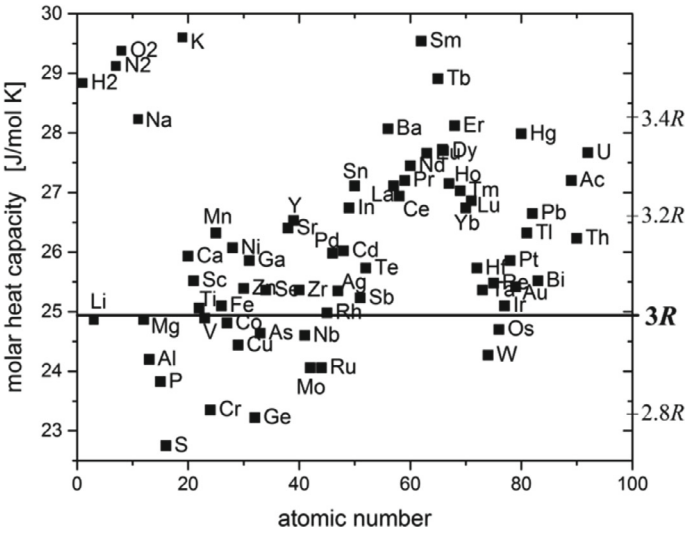


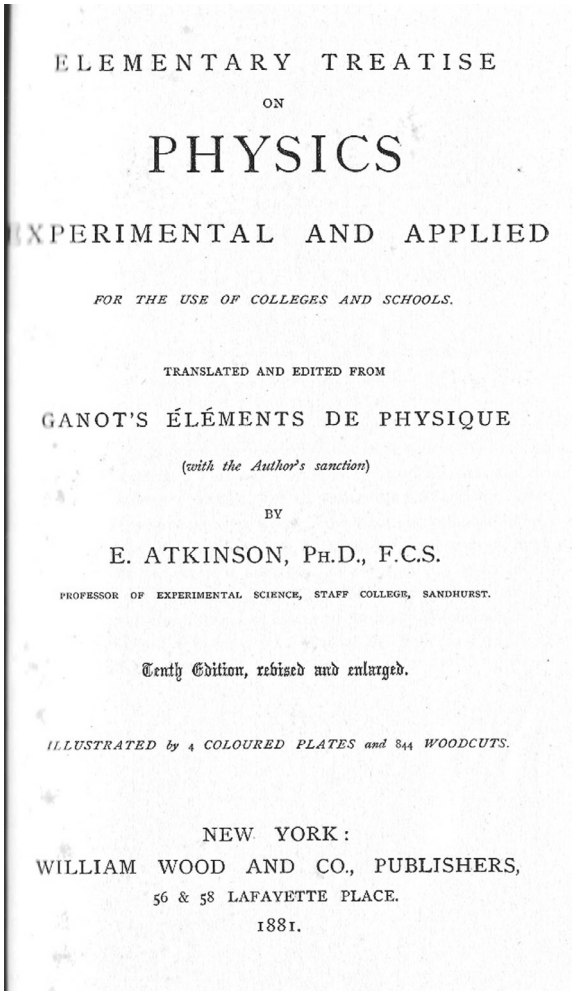
Fig. 9.4 Molar heat capacity as a function of atomic number for many elements [8]

1851, allowed students to think about what they were reading.) The second view is often called the *vis viva* view of heat. In the first view, the pervasive heat fluid was joined by a pervasive "elastic ether." (The pervasive ether view of material reality remains as a part of modern physics. It is now called the "vacuum field.") Ganot also recognizes that "sound" is a form of heat that allows heat to be transported. (Rather than being an incoherent approach to heat, the views of Boerhaave and Lavoisier emphasized the pervasiveness of heat. Heat flows. There are many possible channels. But there is no known place that is devoid of heat.)

Ganot discusses the elementary notions of motion in solids, liquids and gases. He presents an extended discussion of the dynamic theory of gases. When heat is added to a material system, the temperature is raised, or in a multiphase system, it can remain the same. Heat can be produced by friction (or any generalized loss process) and work can be produced by the flow of heat. Ganot still misunderstands that material bodies can exhibit negative thermal expansion coefficients.

The book is rich with instructive figures. The technical details of the construction of a mercury thermometer are given. Regnault was famous for his differential thermometers. Ganot discusses them in detail and illustrates the actual devices that make them possible.

Chapter 2 discusses the expansion of solids. By the mid-nineteenth century, accurate micrometers were being manufactured and these allowed precision of 0.1 mm. Ganot also discusses optical methods for many solids. Enough precision was obtained to produce mathematical virial expansion of the coefficient of linear expansion to quadratic terms. With such detailed knowledge, horologists were able to design clock pendulums that compensated for the change in temperature.



ELEMENTARY TREATISE

ON

PHYSICS

EXPERIMENTAL AND APPLIED

FOR THE USE OF COLLEGES AND SCHOOLS.

TRANSLATED AND EDITED FROM

GANOT'S ÉLÉMENTS DE PHYSIQUE

(*with the Author's sanction*)

BY

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Tenth Edition, revised and enlarged.

ILLUSTRATED by 4 COLOURED PLATES and 844 WOODCUTS.

NEW YORK:

WILLIAM WOOD AND CO., PUBLISHERS,

56 & 58 LAFAYETTE PLACE.

1881.

Fig. 9.5 Title page of my copy of Ganot's Physics

Chapter 3 discusses the expansion of liquids. This subject relies on the work of Dulong, Petit and Regnault. The thermal expansion coefficient of mercury was determined to six places (0.01543 /K) with a special apparatus. The thermal pressure coefficient was also determined and is very large (60 atm/K). In this chapter Ganot does discuss the maximum density of water. No explanation is given, nor could it have been in 1881.

Chapter 4 discusses the expansion of gases. The work of Gay-Lussac and Regnault is presented. The thermal expansion of air is found to be 1/273. This precision work allowed an air thermometer to be used for a much-extended range. Regnault was also able to measure the density of many gases at standard temperature (0 °C) and pressure (760 mm Hg).

Chapter 5 discusses the relations between phases. Ganot is confused about the cause of melting, but that does not stop him from accurately discussing the phenomenon. By 1881 he had read the work of Rudolph Clausius and William Thomson. But he missed the reality that ice contracts when it melts. The melting point of ice decreases as the pressure is increased. Ganot knows about so-called freezing mixtures, but he has no idea what they are or why they form. Liquids contained in a closed volume reach equilibrium with their associated vapor phase. Regnault carried out extensive measurements of the vapor pressure as a function of temperature. Ganot also presents an important example of the equilibrium between two vessels containing the same liquid at different temperatures. Heat and mass flow from the vessel at higher temperature, and hence higher vapor pressure, to the vessel at lower temperature. The Laws of Transport were known in 1881 and heat can flow due to convection. Ganot presents a thoroughly modern discussion of a liquid in equilibrium with its vapor, both in a non-equilibrium state and when the system has achieved equilibrium. Perhaps he underestimates the frequency of particle ejection far from the normal boiling point, but his picture of both dynamic ejection and re-integration is sound. Ganot also discusses the critical point of a liquid in equilibrium with its vapor. He references the work of Andrews on carbon dioxide.

One of the industrial procedures that became popular in the later 19th century was refrigeration. Many schemes were employed, but ammonia refrigerators became common. As techniques for producing cold were improved, the so-called permanent gases were liquified. Michael Faraday was a pioneer in this area. Auguste Pictet developed an apparatus for liquifying gases that can be explained using pure Thermodynamics. The gas is subjected to great pressure under isothermal conditions. A great deal of heat is removed from the system under these conditions. Eventually, the cold gas is allowed to return rapidly to a low pressure. The temperature of the sample plummets and a very cold liquid is obtained.

Chapter 7 discusses thermal conductivity. Whatever else heat is, heat flows from a hot body to a cold body. Ganot cites the ability of some sources of heat to pass through some bodies without much loss. He calls this “radiant heat.” (Substantial discussion of radiant heat is found in Chapter 17.) Heat can also flow within a body. Ganot calls this “conducted heat.” Metals are good conductors of heat. Ganot notes that there is a proportionality between the electrical and thermal conductivity (See chapter 23).

Chapter 8 discusses the radiation of heat. Ganot focusses on the work of Macedonio Melloni (1798–1854). He was the Director of the Vesuvius Observatory in Naples. His “thermomultiplier” (Fig. 9.6) was invented in 1831 and is still an important part of experimental physics.

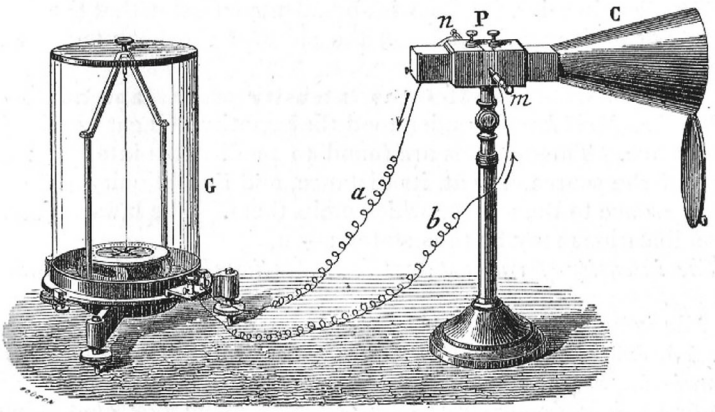


Fig. 338.

Fig. 9.6 Melloni Thermomultiplier. The device on the left is a precision galvanometer. It is attached to the two electrodes of a thermopile. The concentrator cone focuses the thermal rays onto the thermopile. (Further discussion of the thermopile is contained in Chapter 17.) Scanned from my personal copy of Ganot [7]

Melloni demonstrated that thermal rays could be focused, reflected and refracted, just like light. (That is because it is light!) Thermal rays do not need a medium in which to propagate. The fundamental demonstration of these facts is due to Marc-Auguste Pictet (1752–1825). He was able to establish thermal contact between a piece of ice and a thermometer many meters away by using focusing mirrors. Pictet published one of the essential books on heat: *An Essay on Fire* (1791) [10].The detailed explanation of this phenomenon is attributed to Pierre Provost (1751–1839) who stated that all bodies constantly radiate thermal rays. Thermal equilibrium is always a dynamic state. Both Pictet and Provost were from Geneva. One of the most elegant demonstrations of this phenomenon was given by Humphry Davy (1778–1829) (Fig. 9.7).

The 19th century produced many highly precise instruments for the observation of heat. Regnault served as a standard for all these advances. In addition, Renault adopted an attitude towards experimental physics that remains the standard today: All mathematical theories are approximate and serve as useful guides. They all have "limits of validity." No theoretical notions should be accepted without clear demonstrations of their consilience with experimental facts.

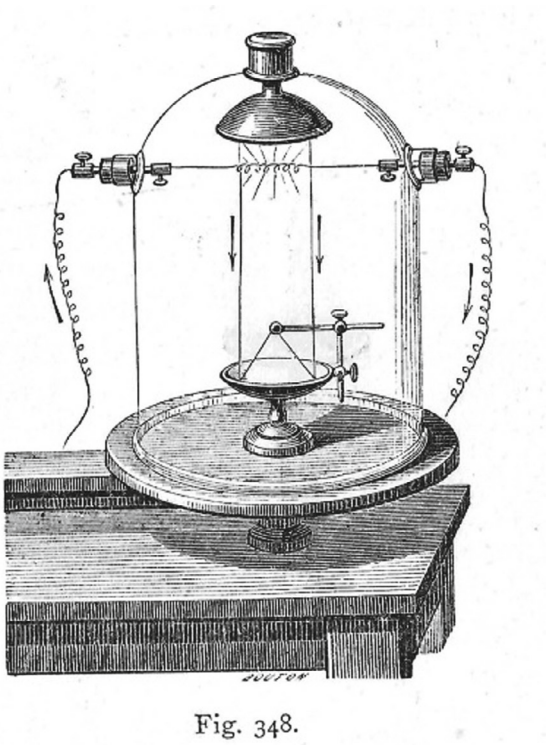


Fig. 348.

Fig. 9.7 The source of thermal radiation is a platinum wire conducting electricity. The detector is a mercury thermometer. Scanned from my personal copy of Ganot [7]

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William Rankine: The Chemical Engineering of Heat

10

Abstract

Thermodynamics is an exact, macroscopic theory. One of the clearest developments of the axioms of this science is presented by William Rankine in his magisterial *Outline of the Science of Energetics* (1855). The complete natural philosophy of engineering thermodynamics is presented in this work. The deep discussion of both work and heat as processes remains the foundation of modern engineering practice. The precise relationships between measurable thermal properties are derived by Rankine. (Modern pedagogical presentations are "kindergarten" versions!) Truesdell was proud of the work of Rankine and said so! No discussion of the history of Thermodynamics can ignore the work of Rankine.

William John Macquorn Rankine (1820–1872) FRS, FRSE was one of the central mid-19th century contributors to Thermodynamics. He was educated at the University of Edinburgh and was strongly influenced by James David Forbes (1809–1868). On the basis of his long article in the *Transactions of the Royal Society of Edinburgh* in 1850, he was elected a Fellow of the Royal Society of Edinburgh [1]. His further work earned the Society's Keith Prize for the period 1851–1853. He was appointed as Professor of Civil Engineering and Mechanics at Glasgow University in 1855. William Thomson (Lord Kelvin, Chapter 11) was also at Glasgow and these two collaborated and discussed the lively field of Thermodynamics.

It should be remembered that Sadi Carnot (Chapter 7) was an engineer. Two factors that are important for the study of heat are associated with the engineering mindset: (1) The real world should be kept in mind at all times, (2) All the power of mathematics should be brought to bear as needed. The detailed publications of Rankine are worth the effort to both decipher them and to understand them.

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In this chapter I will discuss a later synoptic paper, "Outline of the Science of Energetics," (1855) [2]. (Read to the Philosophical Society of Glasgow).

In addition to being a master of details, Rankine thought at the highest level as well. In Sect. 1 of the *Science of Energetics*, he discusses the nature of Physical Theory. This is still worth reading today. When such a theory has been perfected, it has been reduced to a set of definitions and axioms that embody all that is known about the system. Even the best examples of a Physical Theory are explicitly "tentative." (New knowledge or deeper analysis can lead to the need to revise the theory at any time.) In Sect. 2, he distinguishes between "Abstractive" methods and "Hypothetical" methods. Abstractive methods are "entirely" based on observed phenomena. (Clearly, this is a limiting position, similar to modern Empiricism. No actual observation is free of subjective elements.) Hypothetical methods employ the "method of analogy" to attempt to describe the unknown science in terms of known laws. Rankine distinguishes two forms of this approach: (1) Coherent theories for other phenomenal worlds applied to the current set of phenomena, and (2) Coherent theories for purely fictive systems that make no attempt to justify the use of "subjective" concepts. Both approaches have been found to be useful during the development of a mature "Science."

Rankine discusses 19th century Scottish Mechanics as an example of an Abstractive Science. The axiomatic system was first codified by Newton in terms of mass, force and motion. More elegant and more convenient formulations continued to be constructed during the 18th century. Because of the success of Mechanics in describing and predicting the behavior of mechanical systems, natural philosophers attempted to formulate "mechanical hypotheses" for systems outside the restricted domain of Newtonian mechanics. Three examples include light, heat, and viscoelasticity (the science of deformation of material bodies). A good mechanical theory comprehends all the known phenomena for a system and predicts effects that have not yet been observed.

As the 19th century progressed, phenomena were observed that resisted understanding in entirely mechanical terms. Eventually other basic models were constructed that produced the same coherence as mechanics using concepts such as electro-magnetic theory. Hydrodynamics (the science of fluid flow) was also a well-developed theory by the mid-19th century. Electricity and Heat were understood in terms of "fluids." Progress was made, even in the midst of error and confusion. But at some point, the discrepancies between the fictive models and the verified observations became either too large or too conspicuous to ignore. New models must be constructed that conform to the new observations.

The heat produced by friction was a fatal blow to the "caloric theory" of heat. But this theory persisted for another 75 years. Thermo-electricity violated many of the false notions of the mid-19th century. (Peletier coolers are still important today.) Rankine proposed that, in order to produce a coherent physics, a focus on the actual observations was necessary.

Section 7 contains a presentation of the "Science of Energetics." Rankine defines Energy as: "the capacity to effect changes." This understanding continues to dominate what it means to be "Physics." Energy comes in two types: (1)

actual energy, and (2) potential energy. This way of parsing energy continues to be useful today.

Physics consists of the study of "material substances." In order to be included in this scientific discipline, the objects must be observable. They must also be characterized by measurable properties. (Unobservable and unmeasurable things are the subject of metaphysics.) There must be some quantitative measure of the "amount of substance."

Substances are also characterized by "observable states," that Rankine calls "accidents." These states can be varied by a set of measurable quantities. Determining the quantitative relationships that define a particular substance is one of the goals of material physics. (Another name for material physics is chemistry!) For example, the volume, V, of a material substance can be expressed as a function of temperature, T, pressure, P, and amount of substance, m: V(*T,P,m*).

Substances can be changed by changing the quantities that define them. Rankine calls the causes of these changes "effort." (This is a historical accident.) One of the ways of changing a substance is to subject it to "processes" that either increase or decrease the energy. One of these processes is called "work." Rankine defines work as "the variation of an accident by an effort." As an example, he considers one of the forces that can change a substance, X, and x as a measure of the change of the variable upon which X depends. Work, W, is then given by:

$$W = \int_{x_0}^{x_1} X(x)dx \tag{10.1}$$

where the integral is over the range from the initial value, x_0, to the final value, x_1, This is a fully modern expression for a strictly one-dimensional case. One of the consequences of carrying out work on a substance is to increase its energy.

In Sect. 9, Rankine presents the "First Axiom" of the Science of Energetics: "*All kinds of work and energy are homogeneous.*" This means that "*any kind of energy may be made the means of performing any kind of work."* Rankine justifies this axiom as the result of the experimental work of Joule (Chapter 8). He also states another form of the axiom: "*energy is transformable and transferable.*" Rankine was in contact with all the mid-19th century workers in the science of energy,

In Sect. 10 he presents the Second Axiom: *The total energy of a substance cannot be altered by the mutual actions of its constituent parts.* Rankine attributes this to Newton: "*For every action, there is an equal and opposite reaction.*" Another way of stating this is: "*all work consists in the transfer and transformation of energy alone."*

Section 11 presents the definition of the generic force:

> *Each effort is equal to the rate of variation of the potential energy with respect to the independent accident which that effort tends to vary: or symbolically,*

$$X = \frac{dU}{dx}$$

In Sect. 13, he presents the Third Axiom: *The effort to perform work of a given kind, caused by a given quantity of actual energy, is the sum of the efforts caused by the parts of that quantity.* Rankine denotes the "actual energy" by Q. The "effort" associated with this energy can be expressed as:

$$X = Q\frac{d^2W}{dQdx} \tag{10.2}$$

Fundamental expressions of this type avoid the "ideal" cases often foisted on students.

Section 14 is the "hidden jewel" of Thermodynamics. The underlying realities of the material world are comprehended by the set of "Metamorphic Functions" developed in this discussion. There are both many forms of energy, and there are many ways of increasing or decreasing the total energy. Rankine creates arbitrary notation that could confuse later readers, but careful reading helps to stay focused.

Rankine considers the "limit" of the amount of actual energy which disappears in performing work by an indefinitely small augmentation, *dx*:

$$dH = Q\frac{dX}{dQ}dx \tag{10.3}$$

He then defines the "metamorphic function" *F*:

$$F = \frac{dW}{dQ} = \int \frac{dH}{Q} \tag{10.4}$$

This is the kind of "pure thermodynamic gold" that we will see during the discussion of the work of Walther Nernst (1864–1941) (Chapter 17). Nernst earned a Nobel Prize for his insights. Rankine earned the respect of Joule, Thomson and Clausius.

The essential third relationship is then:

$$H = \int Q\,dF \tag{10.5}$$

The literary truth revealed here is "The transformation of 'actual energy' into work by the variation of 'passive accidents' is a "reversible operation."

Rankine immediately gives the references for two examples of important metamorphic functions: (1) his own "Economy of Heat in Expansive Machines" for the metamorphic function of heat relative to "expansive power," [3] and (2) William Thomson's "Researches in Thermoelectricity" for the metamorphic function of heat relative to electricity [4].

Rankine and Thomson communicated regularly as fellow Professors at Glasgow. Their conclusions have stood the test of time and provided many of the foundations of the final theory of Thermodynamics.

In Sect. 15, Rankine seeks to generalize the transformation of energy into as many possible cases as possible within his general system. He presents a Theorem which, if translated to more modern language, would anchor the concept of "transfers of energy:"

> "If equilibrium of actual energy of a given kind takes place between a given pair of substances, possessing respectively quantities of actual energy of that kind in a given ratio, then that equilibrium will subsist for every pair of quantities of actual energy bearing the same ratio."

He then presents a mathematical proof of this theorem. The ratios are denoted: Metabatic Functions**.** In Thermodynamics the metabatic function is absolute temperature, T.

In Sect. 18, Rankine discusses "Diffusion of Actual Energy." (Heat "flows" from a hot body to a cold body.) Gradients of pressure or temperature lead to flows of mass or heat. He reminds his reader that such flows are "not directly reversible.*"* Another form of irreversible process is comprehended under the term: friction**.** He also admits that "transport processes" are not strictly the province of either his "Energetics" or our Thermodynamics. This issue will be discussed at length in later chapters.

One of the most important consequences of the work of Rankine is the rigor that should be expected when material physics is practiced. The essential quantity of physics remains as energy. In modern Thermodynamics this quantity is denoted U. Rankine envisioned an arbitrarily large collection of contributions to the total energy. His formalism allowed for this. One of the important kinds of energy that appears in modern Thermodynamics is TS, where S is the "entropy**.**" The units of entropy are J/K. Of even more interest are the relationships:

$$T = \left(\frac{\partial U}{\partial S}\right)_V \tag{10.6}$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_T \tag{10.7}$$

with P the thermodynamic pressure. All of these types of relationships are implicit in the work of Rankine. PV is a form of energy with units of Joules. Pressure has units of J/m^3. The explicit discussion of entropy needed to wait for Clausius (see Chapter 12).

Rankine also interacted with Joule on a regular basis. One good example is the pair of papers that appeared together in the *Philosophical Magazine* for January 1853 [5, 6]. Joule had sent a selection of his papers to Rankine. In addition to

reading them carefully, Rankine suggested that they jointly publish both the original paper, "On the Oeconomical Production of Mechanical Effect from Chemical Forces," and his epistolary reply together in the *Philosophical Magazine.*

One of the great strengths of Joule was his commitment to all of material physics. Every form of energy could be used to produce work. One of the persisting laws established empirically by Joule was the efficiency of a process involving changes in temperature was proportional to $(T_1\text{-}T_2)/T_1$. This arithmetic form also applies to other forms of work with different quantities than temperature in the formula. One of the important points of the formula is the use of "absolute temperature" in the denominator. Rankine wished to explore the issue of whether there was a different absolute temperature for different forms of energy. His polite letter to Joule establishes that, within experimental error in 1853, the concept of absolute temperature is universal. Rankine also acknowledges the contributions of Thomson and Clausius to the study of absolute temperature. While there remained many obscure issues in 1853, the "dream team" had converged on the validity of absolute temperature.

Truesdell gives a detailed analysis of the seminal 1850 paper by Rankine [7]: "On the Mechanical Action of Heat, especially in Gases and Vapours." [8]. The cycle considered in this work includes two isothermal changes and two isochoric changes. The key constitutive function is U(*T,V,m*). The equation of state for a real gas is then:

$$\left(\frac{\partial P}{\partial T}\right)_V = R\left(\frac{1}{V} - \left(\frac{\partial U}{\partial V}\right)_T\right) \tag{10.8}$$

Integration of this equation yields an expression for U:

$$U = \phi(T) + \int \left(\frac{1}{V} - \frac{1}{R}\left(\frac{\partial P}{\partial T}\right)_V\right) dV \tag{10.9}$$

This is already a fully modern approach. The function U is composed of a unique, temperature dependent part (later to be calculated with quantum mechanics) and an equation of state part (equivalent to a *fugacity*). Remarkably, both Rankine and Truesdell are able to infer rigorously that for an ideal gas:

$$\begin{aligned} J(K_P - K_V) &= R \\ J\Lambda_V &= P \end{aligned} \tag{10.10}$$

Now the ratio of specific heats is independent of temperature as are the individual specific heats at constant pressure and temperature.

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Lord Kelvin: Gathering the Pieces and Creating Thermodynamics

11

Abstract

William Thomson (later Lord Kelvin) was one of the central figures in the history of heat. He established both the principle of absolute temperature and a numerical value in 1848. He proved theoretically that Joule's principle of the conservation of energy was true, and that heat could not be conserved in a process that produces work. Thomson showed that it was important to consider the dynamics of heat flow in the understanding of Thermodynamics. He stated his conclusions succinctly. These statements remain true today, but are rarely included in pedagogical treatments. Thomson was also a brilliant mathematician and fully analyzed both the experimental and theoretical importance of Carnot's function.

William Thomson, 1st Baron Kelvin (1824–1907) FRS, FRSE is one of the central figures in the history of heat (Fig. 11.1).

The units of absolute temperature, T, are K for Kelvin. William Thomson contributed to the understanding of many of the key concepts of Thermodynamics.

Thomson entered Cambridge University in 1841 and graduated Second Wrangler in 1845. Of even more note, he finished First in the Smith's Prize competition in pure mathematics. He spent some time with Victor Regnault in Paris and was appointed in 1846 to the Chair of Natural Philosophy at the University of Glasgow. He served in this capacity until 1899.

This chapter will present a synoptic view of the major contributions of William Thomson to the understanding of heat. The essential biography of Thomson is the two volume *The Life of Lord Kelvin, Baron Kelvin of Largs,* published by Silvanus P. Thomson (1851–1916) FRS in 1910 [1]. Chapter VI is devoted to Thermodynamics. The complete collection of Thomson's papers is: *Mathematical and Physical Papers* (1882) by Sir William Thomson, LL.D., D.C.L., F.R.S. [2].

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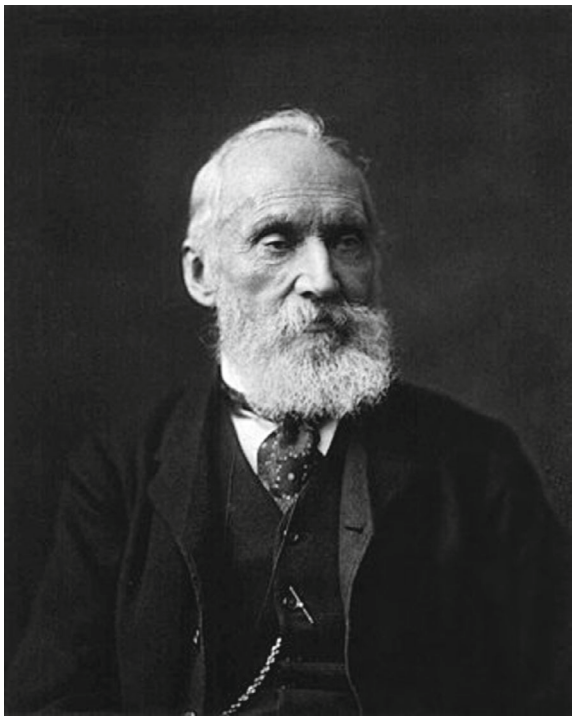


Fig. 11.1 William Thomson, 1st Baron Kelvin of Largs (1824–1907) (Public Domain)

11.1 The Concept of Absolute Temperature

Thomson's early work in Mathematics, Electricity and Magnetism secured his election as a Fellow of the Royal Society of London in 1851. He gained an interest in the subject of Thermodynamics in 1847 after listening to James Joule (Chap. 8) and discussing the topic with him. Thomson's first significant paper in the area of heat was read to the Cambridge Philosophical Society in April, 1848: "On an Absolute Thermometric Scale, founded on Carnot's Theory of the Motive Power of Heat, and calculated from the results of Regnault's Experiments on the Pressure and Latent Heat of Steam." It was printed in full in the *Philosophical Magazine* later that year [3]. Thomson states that "an absolute scale for temperature should not depend on the properties of any particular substance." The best practical thermometers in 1848 were based on the use of dry atmospheric air.

Thomson founded his absolute theory of temperature on the groundbreaking work of Sadi Carnot (Chap. 7). Carnot explained how flows of heat and changes in volume could be employed to produce mechanical work (called mechanical effect by Thomson). Thomson's proposal is that for a constant difference in temperature between the hotter source of heat and the colder sink of heat should produce a constant amount of work. In his collection of *Mathematical and Physical Papers* Thomson includes important remarks to clarify his earlier paper [3]:

> This is what we might anticipate, when we reflect that infinite cold must correspond to a finite number of degrees of the air-thermometer below zero; since, if we push the strict principle of graduation, stated above, sufficiently far, we should arrive at a point corresponding to the volume of air being reduced to nothing, which would be marked as -273° of the scale (-100/0.366, if 0.366 be the coefficient of expansion); and therefore -273° of the air-thermometer is a point which cannot be reached at any finite temperature, however low. [2]

11.2 Heat is Not Conserved

By 1849 the discussion of the nature of "Thermal agency" had reached a fever pitch [4]. In Sect. 1 of the paper, Thomson reminds his readers that "There are two distinct ways in which mechanical effect (work) can be obtained from heat: (1) alterations of volume, and (2) thermoelectric currents." Carnot focused on so-called PV work (Chap. 7). Carnot also assumed that after a complete cycle of changes that fully restored the state of the system, that "heat" was conserved. By 1849, Joule had shown that this assumption was false. Thomson chose to examine this assumption by considering an "ideal heat engine" (Fig. 11.2). Two heat baths (A and B) are needed at temperatures $T_A > T_B$. The middle stand, K, is fully adiabatic. A moveable piston can be examined before and after each step in the cycle. In the first step, the piston is placed in contact with heat bath A and allowed to rise when the vapor pressure exceeds one atmosphere until it is much larger than one atmosphere, during which the temperature is equal to T_A. It is then moved to the adiabatic stand. Since the pressure exceeds 1 atmosphere, the piston rises adiabatically until the temperature falls to T_B. The piston is then transferred to heat bath B. It is compressed mechanically until the volume reaches a unique value that will allow the fourth adiabatic compression step to return the system to its initial volume and temperature.

The understanding of the Carnot Cycle is greatly aided by a graphical representation. Thomson acknowledges the work of Émile Clapeyron (1799–1864). Clapeyron's original memoire, "Mémoire sur la Puissance Motrice de la Chaleur," was published in 1834, but I am using the more readily available English translation of 1837 [5]. The "classic" Carnot Cycle is presented in terms of a PV diagram. Thomson realized that a TV diagram would be more useful (Fig. 11.3).

The initial process is an isothermal expansion. Since the medium is an "Ideal gas," where $P = (nRT/V)$, the energy of the working medium must remain constant ($\Delta U = 0$). This means that the heat supplied by the upper heat bath, Q_A, must be numerically equal to the work: $W_I = nRT_A \ln(V_1/V_0) = Q_I$. The second step is an adiabatic expansion ($Q_{II} = 0$). The work in the adiabatic expansion is equal to: $W_{II} = C_V (T_A - T_B)$. For the isothermal compression, the work is equal to: $W_{III} = nRT_B \ln (V_3/V_2)$. As in step II, the work for the adiabatic compression depends only on the temperature difference: $W_{IV} = C_V (T_B - T_A)$. The net work due to the two adiabatic steps is 0. The net total work for the two isothermal steps is: $W_{total} = nR(T_A - T_B) \ln (V_1/V_0)$. Since the overall change in the energy is due to a cyclic process, the net work must be produced by a loss of heat

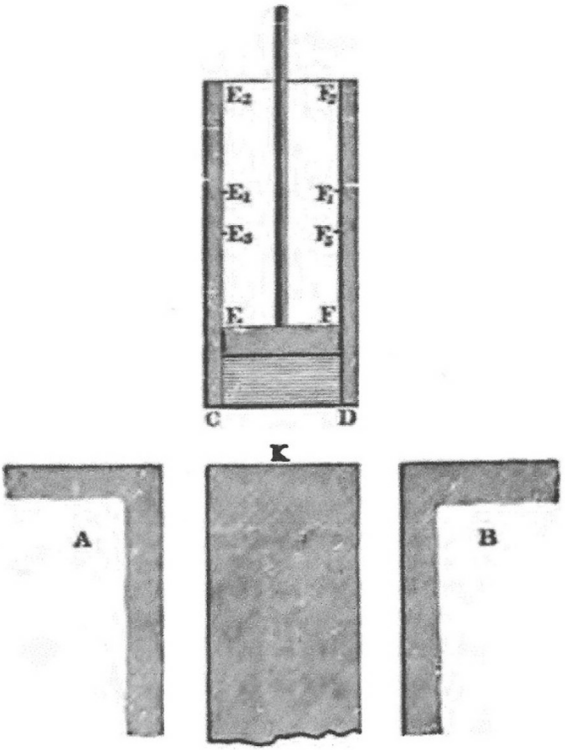


Fig. 11.2 Kelvin's ideal heat engine (scanned from my personal copy of Mathematical and Physical Papers [2].)

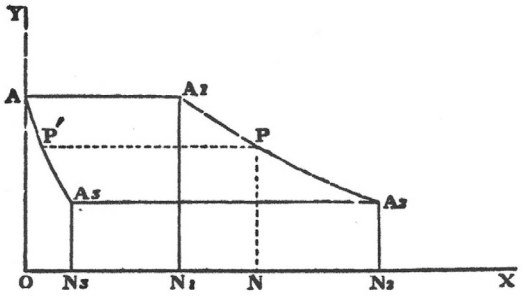


Fig. 11.3 Thomson's TV diagram for the Carnot cycle (scanned from [2])

equal to the gain in work. This vindicates Joule and contradicts the principle of the conservation of heat in cyclic processes.

11.3 Dynamic Theory of Heat

Once the principle of the conservation of energy was accepted, Thomson was able to make another major breakthrough. This is presented in his paper "On a Universal Tendency in Nature to the Dissipation of Mechanical Energy" (1852) [6]. Thomson distinguishes two kinds of mechanical energy: (1) statical and (2) dynamical. He reiterates his conclusion from his paper, "On the Dynamic Theory of Heat; with Numerical Results deduced from Mr. Joule's "Equivalent of a Thermal Unit" and M. Regnault's "Observations on Steam." [7].

> "It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest surrounding objects" [7].

He then presents four propositions regarding the dissipation of mechanical energy:

I. When heat is created by a reversible process (so that the mechanical energy thus spent may be restored to its primitive condition), there is also a transference from a cold body to a hot body of a quantity of heat bearing to the quantity created a definite proportion depending on the temperatures of the two bodies.
II. When heat is created by any unreversible process (such as friction), there is a dissipation of mechanical energy, and a full restoration of it to its primitive condition is impossible.
III. When heat is diffused by conduction, there is a dissipation of mechanical energy, and perfect restoration is impossible.
IV. When radiant heat or light is absorbed, otherwise than in vegetation, or in chemical action, there is a dissipation of mechanical energy, and perfect restoration is impossible.

He finally lists three conclusions:

1. There is at present in the material world a universal tendency to the dissipation of mechanical energy.
2. Any restoration of mechanical energy, without more than an equivalent of dissipation, is impossible in inanimate material processes, and is probably never effected by means of organized matter, either endowed with vegetable life or subjected to the will of an animated creature.
3. Within a finite period of time past, the earth must have been, and within a finite period of time to come the earth must again be, unfit for the habitation of man as at present constituted, unless operations have been, or are to be performed, which are impossible under the laws to which known operations going on at present in the material world are subject.

While William Thomson was mathematically sophisticated, he is best remembered as a scientist that thought at the highest level about physical reality.

11.4 Carnot's Function, Thomson and a Thermodynamic Definition of Temperature

Although Carnot was hampered by assuming conservation of heat, he was very insightful about many aspects of the relationship between work, heat and temperature. He constructed a function that has remained as a standard for analyzing heat engines. Thomson employed such a function in his analyses. There is a modern article that is both readable and helpful on the Carnot Function [8]. Truesdell's classic critique (see Chaps. 5 and 7) defines the measurable Carnot function in terms of two other measurable quantities: (1) the latent heat with respect to volume

$$\Lambda_V = \left(\frac{\partial H_C}{\partial V}\right)_T \tag{11.1}$$

and (2) the partial derivative of the pressure with respect to the temperature at constant volume

$$\left(\frac{\partial P}{\partial T}\right)_V \tag{11.2}$$

The relation is

$$\mu(T) = \frac{1}{\Lambda_V}\left(\frac{\partial P}{\partial T}\right)_V \tag{11.3}$$

Cropper identifies William Thomson as the one that brought all the parts together to understand Carnot's function [8]. Thomson spent six months in Paris in 1845 with Regnault (Chapter 9). He read both the original work of Carnot and the later work by Clapeyron. He stated that "Carnot's function (derivable from the properties of any substance whatever, but the same for all bodies at the same temperature), or any arbitrary function of Carnot's function, may be defined as temperature and is therefore the foundation of an absolute system of thermometry" [3].

Thomson was able to calculate numerical values for Carnot's function from Regnault's results on steam. He discovered that the Carnot function, $\mu(T)$, was numerically equal to Joule's mechanical equivalent of heat, J (see Chapter 8), divided by the absolute thermodynamic temperature, T. This is one of the central truths of Thermodynamics.

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12

Rudolph Clausius: *The Mechanical Theory of Heat* (1867, 1879) and the Formulation of the Laws of Thermodynamics

Abstract

The magisterial book, *The Mechanical Theory of Heat* (1867, 1879), by Rudolph Clausius is discussed in detail. In the Introduction (12.2) Clausius presents a clear summary of the basic concepts of classical mechanics. In Chapter 1 (12.3), The concepts of work and heat are developed in complete detail. In Chapter 2 (12.4) the differential relationships between heat, work and the variables of state (P,V,T) are developed in complete detail. In Chapters 3 and 4 (12.5), the principles of the Thermodynamics of cyclic processes are presented. In Chapter 5 (12.6), Clausius presents a "master class" in the Thermodynamics of many variables and analyzes the Clapeyron Equation and the Carnot function. In Chapter 6 (12.7), Clausius analyzes the Thermodynamics of a system composed of liquid and its vapor. In Chapter 7 (12.8), Clausius treats a solid and its corresponding liquid. In Chapter 8 (12.9) Clausius considers the Thermodynamics of Natural Rubber. In Chapter 9 (12.10) Clausius develops the key equations for the energy and the entropy. In Chapter 10 (12.11) Clausius develops the Thermodynamics of Non-equilibrium processes. In Chapter 12 (12.12) Clausius discusses the Thermodynamics of Radiant Heat. In Chapter 13 (12.13) A few concluding remarks are discussed.

In the middle of the 19th century, the leading thinker on the subject of heat was Rudolph Julius Emanuel Clausius (1822–1888) (Fig. 12.1). Clausius was born in Poland in the Province of Pomerania in Prussia. He was educated in his father's school and received a thorough classical education. He graduated from the University of Berlin in 1844 with a major in mathematics and physics. He also pursued the history of science with Leopold von Ranke (1795–1886). Clausius is known for his mathematical rigor, encyclopedic knowledge of physics and his appreciation for the actual history of physics.

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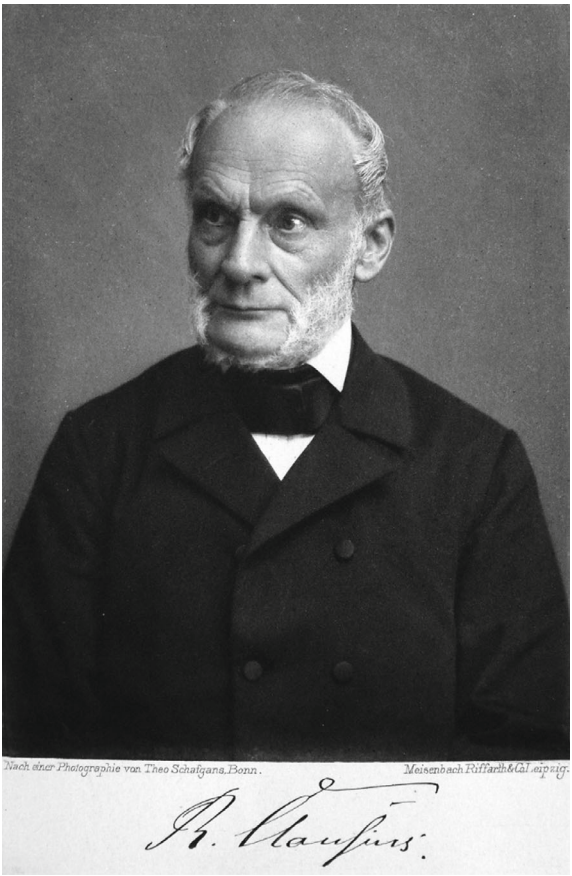


Fig. 12.1 Rudolph Clausius, the Father of 19th Century Thermodynamics (Public Domain)

Clausius was literate in many languages and used this ability wisely. He read Sadi Carnot's *Réflexions sur la Puissance Motrice du Feu et sur les Machines Propres a Développer cette Puissance* (1824) carefully. At a time when there was no formal theory of thermodynamics, Carnot had analyzed the mechanical consequences of controlled heat flow. He operated within the overall concept of heat developed by Lavoisier and Laplace, but most of his conclusions are independent of the theory of *caloric.* A detailed discussion the work of Carnot appears in Chap. 7.

12.1 *The Mechanical Theory of Heat* (1867, English Edition 1879)

The initial publication of *The Mechanical Theory of Heat* (1867) (see Chap. 1, Fig. 1.1) was enthusiastically received by scientists like Joule, Kelvin and Rankine. Eventually, there were enough revisions to require a new edition and Walter R. Browne (1842–1884), a master of Mechanics and a Fellow of Trinity College,

Cambridge, undertook to produce an English translation in 1879, with additional chapters on special topics. This work is still in print [1].

Clausius was concerned with the theory of Mechanics. (Mechanics is concerned with the time evolution of the physical system under the influence of various forces. It was brought to a high level by Newton and improved by Rankine.) He started with the notion of mechanical force [1]: "Every force tends to give motion to the body on which it acts." He then notes that forces can be balanced to produce "mechanical equilibrium." This is called the Theory of Statics. A body moving under the influence of a force produces "work." Clausius understood that force was a vector quantity: $\vec{F}(\vec{r}, t)$, where $\vec{r}(t)$ is the location of the body at time t. (The arrow above the characters means that the quantity can be expressed in terms of a mathematical vector with three components: $\vec{f}(x, y, z) = f_x \hat{x} + f_y \hat{y} + f_z \hat{z}$, where the carat above x, y and z indicates a unit vector in the x,y and z direction.) It is convenient to define a trajectory vector: $\vec{s}(t) = \vec{r}(t) - \vec{r}(0)$. The work can then be calculated as the integral of the force over the trajectory:

$$W = \int_0^{\vec{r}(t_{end})} \vec{F}(\vec{r}) \cdot d\vec{s} \tag{12.1}$$

At the start of the trajectory s = 0; at the end of the trajectory the particle is at location $\vec{r}(t_{end})$.. The bold dot indicates a scalar product of the force vector and the differential of the displacement vector. Work is a scalar entity. (Scalars are independent of the frame of reference.)

Two of the other important theoretical physicists and engineers from this time period are Sir William Rowan Hamilton (1805–1865) and William John Rankine (see Chap. 10). Clausius adopted Rankine's notion of "potential energy," and this allowed actual progress in understanding physical reality. It is total energy that is conserved, not kinetic energy alone. At the time of the writing of *The Mechanical Theory of Heat*, the concept of kinetic energy was not yet fully developed. The normal expression for the kinetic energy of "moving matter" was *vis viva.* Clausius adopted the modern form ((1/2) mv^2)). One of the triumphs of the initial chapter is the dictum [1]: "The Work done during any time by the forces acting upon a system is equal to the increase in the Vis Viva of the system during this time."

Clausius constructs a total energy function, U, a kinetic energy function, T, and a potential energy function, J (called an Ergal). The Principle of the Conservation of Energy is then expressed as: $U = T + J$. The principle of the conservation of total energy is fully embraced by Clausius, as established by James Prescott Joule (See Chap. 8).

12.2 Chapter 1: Heat and Work

Clausius adopts the notion of heat as a mode of motion whose magnitude is indicated by the *vis viva* of the constituent particles. After a thorough discussion of the meaning of words and the explanation of concepts, he summarizes his conclusions explicitly. The 1st Principle of the Mechanical Theory of Heat is [1]:

> *In all cases where work is produced by heat, a quantity of heat is consumed proportional to the work done; and inversely, by the expenditure of the same amount of work, the same amount of heat can be produced.*

The units of work are "energy units" and the units of heat are also energy units. One of the most confusing aspects of the pedagogical presentation of Thermodynamics is the tendency to hide these facts in a multiplicity of arbitrary units. For Clausius, there was an equivalence between the form of energy we call work and the form of energy we call heat. He stated this as: "Work may transform itself into heat, and heat conversely into work, the quantity of the one bearing always a fixed proportion to that of the other."

Joule carried out a magnificent number of careful experiments to establish the "facts" with regard to thermomechanical reality (See Chapter 8). One of his greatest gifts to physics was his determination of the relationship between the standard "thermal" units of energy, "calories," and the mechanical units, "kilogrammetres." The mechanical units are related to the change in altitude of a standard mass (1 kg) over a standard distance (1 m), due to the force of gravity. The calorie is the amount of heat needed to raise 1 kilogramme of water through 1 degree Centigrade. Joule's proportion was 423.55 kgm/cal. This was reported in the *Philosophical Transactions of the Royal Society* for 1850 [2]. In more modern terms, the ratio is between Joules and calories: 4.1840 J/cal.

With a solid base of experimental demonstration, and a coherent understanding of the many forms in which energy might be found, Clausius set out to construct a mathematical theory that could be applied in every engineering situation. Thermodynamics was constructed by natural philosophers, physicists, chemists and engineers. Clausius could talk to them all. Thermodynamics is grounded in "measurable properties" of actual matter. Pedagogical presentations often default to ideal situations of no practical utility. Clausius starts with the classic collection of thermodynamic variables: temperature (T) (a non-mechanical variable), mass, m, volume, V, and pressure, P. The protocol is simple:

1. Measure the initial values of the variables.
2. Add a differential quantity of heat: dQ
3. Allow the system to reach a new equilibrium.
4. Measure the new values of the variables.

Although all the energy added to the system is initially heat, at equilibrium the energy may be distributed differently. Clausius introduces the symbol dH for the

heat observed at equilibrium, and dL for the work done during the process. He then partitions the initial heat into its two final forms: $dQ = dH + dL$. He further distinguishes between work done on the internal structure of the material, dJ, and work done by external forces on the body as a whole, dW. While the resulting equation is unfamiliar today, $dQ = dH + dJ + dW$, it is well to remember that actual materials are more complicated and more interesting than the ideal systems chosen for teaching purposes.

One of the truths that appears in Clausius is that "heat is not just one thing." It is also true for work: "The internal and external work obey widely different laws." The internal state of a pure material at equilibrium is a definite function of T, V, P and m. If the system is subjected to a cyclic process, the internal state must be the same. Clausius expresses this in terms of the Ergal of the material: the potential energy that is a function of T, V, P and m. The external work is determined by the external forces and the details of the deformations. The result of this discussion is the realization that the amount of external work depends on the "path" that is followed and hence the work integral is a "path integral." Clausius distinguishes two types of paths: reversible and non-reversible. In reality, every process that is carried out in a realistically short amount of time is irreversible. Various "loss processes" convert motion into heat. Generalized frictions create such paths, since the heat produced cannot be recovered to produce work.

Deep thought and careful experimentation with regard to heat and work was also carried out by William Thomson (1824–1907) (1st Baron Kelvin) (See Chapter 11). Clausius defined the function U(T, V, m) as the Energy of the system. It is explicitly a "state function" that includes all the kinetic and potential energy (Ergal) of the body. He then formulates the fundamental equation for the differential of the heat, dQ, as: $dQ = dU + dW$. Since the calculation of the total work, W, is a path integral, he also wrote the integrated form of this equation as: $Q = U_2 - U_1 + W$. For a cyclic process $U_2 - U_1 = 0$. Hence $Q = W$! The values of Q and W depend on the path, but for a cyclic process they are equal.

Clausius discussed the case where substantial heat can flow into a sample without changing its temperature at all. Such a phenomenon requires that the sample be more complex than a single substance in a single phase. The heat capacity, $C = Q/(T_2 - T_1)$, can have many different values, depending on the path.

An especially clear discussion of this issue appears in the modern thermodynamics text by Frederick T. Wall (1912–2010) (See Fig. 12.2) [3]. Some curves are calculated for a monatomic gas for convenience and clarity. For an adiabatic path, $Q = 0$, the heat capacity is also 0. For a constant volume experiment, the classical value is $(3/2)R$. For constant pressure, $C_P = (5/2)R$. For an isothermal path, $T_2 = T_1$, and the heat capacity is infinite! For a system containing both liquid and gaseous water at constant volume, along the vapor pressure curve, the heat capacity at constant vapor pressure can be negative. The curve with larger positive heat capacity could be observed for ice and water. Raising the pressure lowers the melting point of ice!

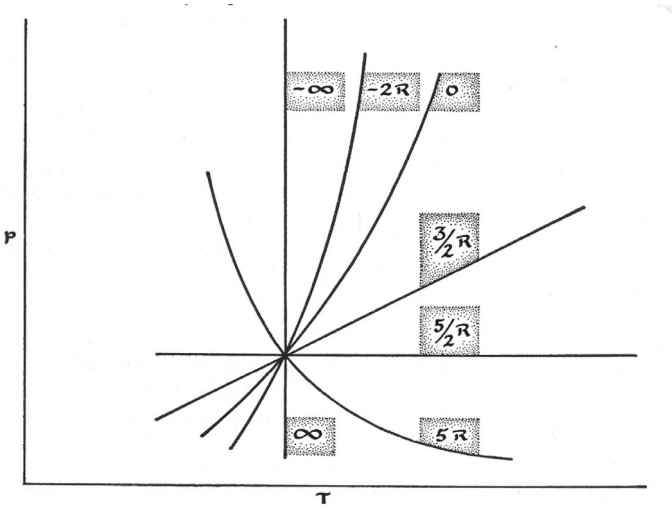


Fig. 12.2 Different heat capacities are observed along different paths in the phase space of P and T [3]

12.3 Chapter 2: Relationships Between Thermodynamic Variables

In order to illustrate the relationships between thermodynamic variables, Clausius adopts the "perfect gas" as his system. Extensive experiments on real gases by Victor Regnault established the limits of the ideal Laws of Mariotte and Gay-Lussac (See Chap. 9). Clausius adopts the defining equation for the thermal expansion coefficient for gases:

$$PV(t) = PV(t_0 = 0)(1 + \alpha t) \tag{12.2}$$

where t is the Centigrade temperature. For the class of gases denoted "permanent," this simple equation is sufficiently precise that the perfect gas model is accurate enough. The value of the thermal expansion coefficient, α, is 1/273. Clausius recognizes that this implies that the "absolute temperature," T, is then $273 + t$.

Joseph Louis Gay-Lussac carried out many experiments on gases and Clausius discusses one of Gay-Lussac's important studies of a system composed of two identical globes connected by a valve [4]. One globe was filled with dried air and the other globe was exhausted with a pump. The system was allowed to come to an initial equilibrium and the temperature was measured. When the valve was opened, gas flowed from the globe at higher pressure into the globe at lower pressure (Pressure gradients lead to mass flow). When the pressures in the two globes reached initial equilibrium, the temperatures in the two chambers were different. The initially empty globe was hotter! One of the important lessons of

this experiment is that different quantities reach equilibrium at different rates. If Gay-Lussac had waited longer, the temperature gradient would have decayed by mutual exchange of molecules. The initial "partial equilibrium" occurred because the "faster" molecules were "transported" preferentially from the full container to the empty one. This "sorting" of the gas particles occurred because there was a distribution of particle speeds in the initial gas (See Chap. 15). The lesson that Clausius took from the experiment was that the "excess" heat in the hotter globe was exactly balanced by the deficit in heat in the initial globe. There was no net change in the total heat of the system.

For a system composed of a "perfect gas" the defining equation for the differential of the heat, dQ, is: $dQ = dU + PdV$. Clausius now proceeds to expand the expression for dU in a mathematically insightful way (Clausius understands the theory of functions, even though he does not use the modern notation for a partial derivative. The modern notation is used for Eq. 12.3.)

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{12.3}$$

The partial derivative of U with respect to T at constant V, here is called the heat capacity at constant volume. The partial derivative of U with respect to V at constant T is called the partial molar energy density, π. For a perfect gas, U does not depend on the volume at all. This yields: $dU = C_V dT$. The heat equation for a perfect gas is then $dQ = C_V\, dT + PdV$. He then seeks to express dQ in terms of T and P. For a perfect gas $V(m = 1,P,T) = RT/P$, where the R employed by Clausius is for a unit weight of gas. The differential of the gas volume is then: $dV = (R/P)dT - (RT/P^2)dP$. The three equations for dQ as a function of T and V, T and P, or P and V are then:

$$\begin{aligned} dQ &= C_V dT + (RT/V)dV \\ dQ &= (C_V + R)dT + (RT/P)dP = C_P dT + (RT/P)dP \\ dQ &= (C_V/R)VdP + ((C_V + R)/R)PdV \end{aligned} \tag{12.4}$$

Virtually no modern Thermodynamics text is this thorough! For a perfect gas, the relationship between the heat capacities at constant volume and pressure appears naturally. The more general case for all pure materials will appear later (See Chapter 13).

Victor Regnault measured the two heat capacities for many gases and in Chapter II Clausius presents a table of heat capacities (see Chapter 9, Fig. 9.1) that is helpful today. In 1867 there were no laboratory samples of monatomic gases. The values are relative to dry atmospheric air. No absolute values were known at this point.

With his trinity of equations for dQ, Clausius discusses experimentally convenient calculations useful in the laboratory. The heat associated with a change of

volume at constant pressure, Q_P, is:

$$Q_P = \frac{C_P}{R} P(V_2 - V_1) \tag{12.5}$$

For a change in volume at constant temperature, the first expression yields:

$$Q_T = RT \ln (V_2/V_1) \tag{12.6}$$

For an adiabatic volume change (dQ = 0), he obtains the relationship:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{C_P - C_V}{C_V}} \tag{12.7}$$

For an adiabatic pressure change:

$$\frac{T_2}{T_1} = \left(\frac{P_1}{P_2}\right)^{\frac{C_V - C_P}{C_P}} \tag{12.8}$$

Finally, for a general adiabatic process:

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\frac{C_P}{C_V}} \tag{12.9}$$

These results are beautifully transparent in 1867. They remain as the normal paradigm for pedagogical presentations.

The external work, W, can also be calculated by definite integration of PdV. (Definite integration of a function produces the scalar area under the function on a graph. Consult an elementary calculus book for more details.) Understanding this process is facilitated by plotting the trajectory in PV space. The simplest case is for constant pressure:

$$W = \int_{V_1}^{V_2} PdV = P(V_2 - V_1) \tag{12.10}$$

Another useful trajectory keeps the temperature constant. For a perfect gas:

$$W = \int_{V_1}^{V_2} \frac{RT}{V} dV = RT \ln \frac{V_2}{V_1} = Q \tag{12.11}$$

Joule has verified this relationship with another elegant experiment (Fig. 12.3).

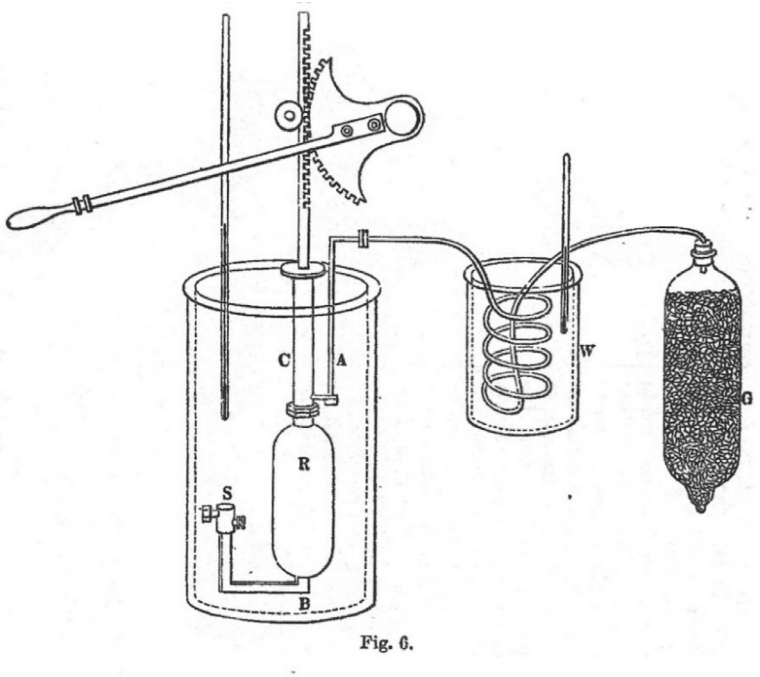


Fig. 12.3 Joule calorimeter for measuring the amount of heat associated with the isothermal compression of dry air [1]

Adiabatic compression can easily be treated with the explicit expression for pressure as a function of volume derived above.

$$W = P_1 V_1^{\frac{C_P}{C_V}} \int_{V_1}^{V_2} \frac{dV}{V^{\frac{C_P}{C_V}}} = \frac{P_1 V_1^{\frac{C_P}{C_V}}}{\frac{C_P}{C_V} - 1} \left[1 - \left(\frac{V_1}{V_2} \right)^{\left(\frac{C_P}{C_V} - 1 \right)} \right] \tag{12.12}$$

No modern textbook is likely to include (12.12)! The importance of this set of equations derived by Clausius for ideal gases is that they can often be employed both as teaching tools and as approximate expressions in the laboratory.

12.4 Chapters 3 and 4: The Thermodynamics of Cyclic Processes

In this chapter Clausius discusses the Second Main Principle of the Mechanical Theory of Heat. He immediately introduces the classic cyclic diagram in PV space (Fig. 12.4).

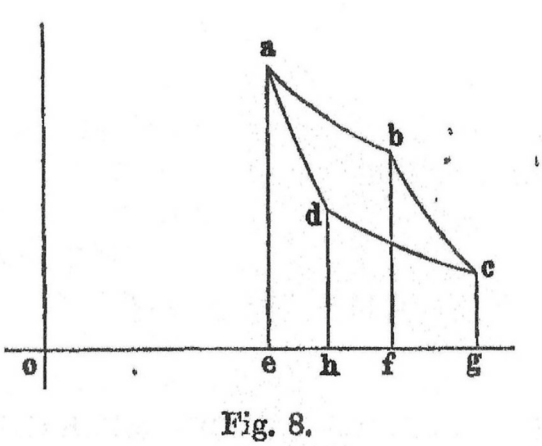


Fig. 12.4 Clausius (Clapeyron) diagram for a cyclic process in *PV* space. The y-axis is the pressure, *P*, and the x-axis is the volume, *V* [1]

Although the process is usually called the "Carnot Cycle," it was Clapeyron who drew the diagrams. The step from *a* to *b* is an isothermal expansion at temperature T_1. All steps have been treated above in Chapter II. The step from *b* to *c* is an adiabatic expansion. The temperature now falls to T_2. An isothermal compression at the new temperature produces step cd. A final adiabatic compression returns the system to the initial *P, V* and *T*! Since the overall process is both cyclic and reversible, the total energy function, U(p, v), recovers its initial value. Heat is transferred from the reservoir at T_1 to the reservoir at T_2. Work is done by the "piston" that moves during the expansions and compressions. Heat is converted into work. Carnot is vindicated and heat engines are still important to industrial practice.

Perhaps the most important new finding featured by Clausius is the discovery of a state function of the system that rationalizes Thermodynamics: the entropy, S(*T, V, m*). Since *U* is a state function, it would be useful to express it entirely in terms of other state functions. Clausius analyzes the process for the two isothermal steps and notes that two transfers of heat are observed: Q_1 and Q_2 at T_1 and T_2. He then shows analytically that Q_1/Q_2 must be a function of T_1 and T_2. The resulting equation is a true revelation:

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \tag{12.13}$$

He then proceeds to show that for a cyclic process the integral of *dQ/T* is 0.

$$\oint \frac{dQ}{T} = 0 \tag{12.14}$$

Since this is true, *Q/T* is a state function, which Clausius dubs the *entropy*: S(*T, V, m*). He explains that it is based on the Greek word τροπε, meaning transformation. The depth of Clausius' understanding of the formal structure of heat is remarkable for 1867, and it is largely lost in modern pedagogical treatments!

12.5 Chapter 5: Clapeyron's Equation and the Carnot Function

The 5th chapter is a master class in functions of multiple variables. It finishes with a thorough discussion of the "Carnot Function" and the "Clapeyron Equation." The original discussion by Clapeyron occurs in the Journal de l'École Polytechnique for 1834 [5]. Clausius reformulated the Clapeyron Equation in a more usable form that is still one of the fundamental results of Thermodynamics.

12.6 Chapter 6: Systems Composed of a Liquid And its Vapor

One of the most important physical systems for Clausius (and Carnot) was the saturated vapor. At equilibrium the system consists of both the liquid and the vapor of the substance. The "vapor pressure" is determined entirely by the temperature: $P_{\text{vap}}\ (T)$. The total mass of the system is M, with the gaseous part denoted as m. The volume is determined by the pressure and temperature of the equilibrium system. The mathematical choice of independent variables is then T and m.

Clausius analyzes this system at the full modern level. Given m and T, what is the state of the system? The answer depends on the values of a set of partial derivatives: the set of measurable properties for the system. There are the equations of state properties: thermal expansion coefficients for the liquid and gas; thermal pressure coefficients for the liquid and gas. There are the thermal properties: the heat capacity for the liquid and gas and the Joule–Thomson coefficients. There is also the heat of vaporization. The unique character of this system is the specific heat at constant vapor pressure.

Early work on this issue was carried out by James Watt (1736–1819). Careful experiments were then later made by Regnault in 1847. Clausius' analysis produces three contributions to the numerical value for the specific heat. His final equation for saturated steam is:

$$c_{cvp}(t) = 0.305 - \frac{607 - 0.708t}{273 + t} \tag{12.15}$$

As shown above in Fig. 12.2, this specific heat is negative! Clausius includes the full temperature dependence as a table (Fig. 12.5).

From this analysis, Clausius also compared the predictions of the vapor pressure of steam as a function of temperature. Steam tables are still an important part of

t	0⁰	50⁰	100⁰	150⁰	200⁰
h	−1·916	−1·465	−1·133	−0·879	−0·676

Fig. 12.5 Table of the heat capacity at constant vapor pressure as a function of Centigrade temperature for a water and vapor system [1]

Chemical Engineering. No ideal gas or liquid need be assumed. All the necessary partial derivatives are measured properties!

12.7 Chapter 7: Systems Composed of a Liquid and Its Solid Phase

Solids both melt and sublime. Clausius discusses these two processes in detail. As before, the two independent variables are T and m. M is the total mass, and m is the mass of the higher phase, liquid or gas. The heat of melting and the volume of melting are measured. The densities of the solid and the liquid must also be known. Chemists often prefer the use of pressure in atmospheres. Clausius is a master at changing the units. For the ice-water system the melting temperature falls by 0.00733 C/atm, because the density of ice is lower than the density of water at $T = 273$ K. The heat of fusion is also a function of T. The specific heat of a system containing both ice and water is also calculated. The numerical value is much higher than that for a perfect gas! Again, the importance of this chapter is that it demonstrates for a real system that the principles of Thermodynamics can be applied to real systems with a high degree of accuracy.

12.8 Chapter 8: Complete Presentation of the Thermodynamics of a Homogeneous Body.

The subject of the Thermodynamics of a "homogeneous body" is developed in complete detail. One of the technical details that had not been settled in 1865 was the notation for a "partial derivative." Clausius experimented with several forms. But there was no confusion about what was being described. For a function of two variables, $f(x, y)$, changes in the function, df, can be expressed exactly in terms of changes in the two independent variables:

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy \tag{12.16}$$

Another immediate consequence of the existence of the partial derivatives is the Euler relation:

$$\left(\frac{\partial^2 f}{\partial x \partial y}\right) = \left(\frac{\partial^2 f}{\partial y \partial x}\right) \tag{12.17}$$

(Leonhard Euler (1707–1783) was one of the greatest mathematicians of history.)

It is simple to extend this formalism to functions of many variables. Consider the variables of state: T, P, V. There are then six important measurable properties

of the system:

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \tag{12.18}$$

Clausius proceeded to derive one of the most important identities in Thermodynamics:

$$\left(\frac{\partial P}{\partial V}\right)_T x \left(\frac{\partial V}{\partial T}\right)_P x \left(\frac{\partial T}{\partial P}\right)_V = -1 \tag{12.19}$$

One of the most powerful aspects of Thermodynamics is the ability to express a quantity that we want in terms of quantities we already know, and that are readily measurable. Clausius knew that many measurements of the constant pressure heat capacity were available, but it is often the constant volume heat capacity that is needed for a particular calculation. He derived such an equation that I have rarely seen in modern textbooks.

$$C_V = C_P + T\frac{\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T} \tag{12.20}$$

Clausius discusses many other possibilities for homogeneous materials including solids and liquids. One of the most interesting phenomena analyzed by Clausius is the behavior of India rubber. If the strip of rubber is subject to no stress but atmospheric, it expands like any liquid. If the strip is stretched uniaxially, it shortens when heated! This phenomenon was discovered by John Gough (1757–1825) and extensively studied by James Joule. It was also discussed by Lord Kelvin. Clausius expresses the equation of state for an adiabatic extension as:

$$\left(\frac{\partial T}{\partial f}\right)_S = -\frac{T}{MC_P}\left(\frac{\partial l}{\partial T}\right)_f \tag{12.21}$$

where f is the force, M is the mass, and l is the length of the strip. The detailed discussion of this phenomenon is remarkable for 1865 and was only explained after the macromolecular hypothesis was proven in the 1930s.

12.9 Chapter 9: Complete Theory of the Energy and Entropy

In this chapter Clausius develops the complete theory for the energy, U, and entropy, S, in essentially its final form! He starts with a pointer to the important work done by Gustav Kirchoff (1824–1887) in this area. For the energy, only

changes can be obtained: $\Delta U = Q - W$. In 1865 it was not yet clear that an absolute entropy could be obtained, so changes were expressed as:

$$S = S_0 + \int_0^1 \frac{dQ}{T} \tag{12.22}$$

where the subscript 0 indicates the initial state of the system and the upper limit of the definite integral denotes the final state. He next considers the case for reversible changes. The level of detail of the derivations is fully modern. If the two independent variables are chosen to be T and V, the fundamental equations are:

$$\begin{aligned} dS &= \frac{\left(\frac{dQ}{dT}\right)}{T}dT + \left(\frac{dP}{dT}\right)dV \\ dU &= \left(\frac{dQ}{dT}\right)dT + \left(T\left(\frac{dP}{dT}\right) - P\right)dV \end{aligned} \tag{12.23}$$

If the independent variables are T and P, the equations are:

$$\begin{aligned} dS &= \frac{\left(\frac{dQ}{dT}\right)}{T}dT - \left(\frac{dV}{dT}\right)dP \\ dU &= \left(\left(\frac{dQ}{dT}\right) - P\left(\frac{dV}{dT}\right)\right)dT - \left(T\left(\frac{dV}{dT}\right) + P\left(\frac{dV}{dP}\right)\right)dP \end{aligned} \tag{12.24}$$

No assumptions are made about the derivatives; they are intended to be measured.

12.10 Chapter 10: The Thermodynamics of Irreversible Systems

Most physical changes are not reversible. Clausius discusses the consequences of this important reality. He proposes the following dictum: "The algebraic sum of all the transformations which occur in a cyclic process must always be positive, or in the limit equal to 0." This can also be expressed mathematically as: $dQ \leq TdS$.

Clausius considers a free expansion of a gas. The relevant equation is:

$$Q = \int_{V_1}^{V_2} \left(T\left(\frac{dP}{dT}\right) - P\right)dV \tag{12.25}$$

For a perfect gas, $PV = RT$, no heat is transferred to or from the system. The masters of experimental chemistry in the 19th century, Gay-Lussac, Joule and

Regnault, had studied real gases. Joule teamed up with Lord Kelvin to study real gases undergoing expansion through a porous plug. This is the origin of the Joule–Thomson coefficient. The relevant equation is now:

$$Q = \int_{T_1,P_1}^{T_2,P_2} \left[C_P dT - \left(T\frac{dV}{dT} - V \right) dP \right] \tag{12.26}$$

This work remains the standard for analyzing and employing the Joule–Thomson coefficient for real gases as a function of temperature. There exists a temperature at which the Joule–Thomson coefficient is equal to 0. For hydrogen, positive values have been observed at room temperature.

12.11 Chapter 12: The Thermodynamics of Radiant Heat

Clausius was fully aware that light is a form of heat. Radiant heat can be reflected and refracted. Hence it can be concentrated at a point! Two of the leading experimentalists in the late 19th century were Kirchoff and John Tyndall (1820–1893). Clausius discusses Kirchoff's work with "black bodies." These substances both absorb all radiant heat and emit the same. Clausius was also aware that radiant heat was not "homogeneous." There is a distribution of wavelengths.

For simplicity he considers two surfaces at the same temperatures. He denotes two surface elements, ds_1 and ds_2. All things being equal, the energy emitted by element 1 and received by element 2 are the same. The level of both physical and mathematical analysis is stunning.

The classic experiments by Marc-Auguste Pictet (1752–1825) employing two conical reflectors between two small volumes placed at the two foci are fully comprehended by this analysis, as is the later work by Kirchoff. If the objects at the two foci are a grain of ice and a thermometer, the temperature of the thermometer approaches the temperature of the ice! All surfaces emit radiant heat! (see Chapter 17 on Tyndall).

12.12 Chapter 13: Concluding Remarks

While the work of Clausius is now celebrated, there was considerable opposition in 1865. Preconceived notions had substantial staying power in the 19th century. Still, the ideas espoused by Clausius remain the basis for all modern Thermodynamics. For example, the principle of the equivalence of heat and work was investigated by Rumford, Davy, Carnot, Mayer, Regnault, Joule, Helmholtz, Clapeyron, Thomson (Kelvin), and Rankine, but it was Clausius that brought the discussion to its full conclusion. Furthermore, Clausius was a good mathematician, which kept him from bungling his discussions. But he was an even greater physicist. He always tried to focus on observable phenomena. His chief dictum was: "Heat flows from the hotter body to the colder body."

Many people made contributions, either theoretical or experimental, to the formal theory of Thermodynamics. Clausius acknowledged them all! Of course, in his *The Mechanical Theory of Heat,* Clausius did not specifically discuss Thermochemistry. That story required the brilliance of J. Willard Gibbs (see Chapter 13).

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Josiah Willard Gibbs: The Complete Theory of Thermodynamics

13

Abstract

J. Willard Gibbs completed the Thermodynamic analysis of systems composed of multiple components and phases. His important concept of the chemical potential is essential for understanding both complex phase diagrams and chemical reactions. This chapter presents his work in historical context and is based entirely on the original papers. I have read them in my own copy of *The Collected Works of J. Willard Gibbs* (1948). They represent the completion of the nineteenth century development of Thermodynamics.

Josiah Willard Gibbs (1839–1903) was born in New Haven, Connecticut and died in New Haven. He was Yale, through and through. But, when it came to Thermodynamics, he was a citizen of the world. He was known by all the leading theoretical physicists of the late nineteenth century. After serving as a Tutor at Yale, he traveled in Europe and attended lectures in Paris, including those by Joseph Liouville (1809–1882). He went to Berlin and attended lectures by Leopold Kronecker (1823–1891) and Gustav Magnus (1802–1870). In Heidelberg he met Gustav Kirchoff (1824–1887), Hermann von Helmholtz (1821–1894), and Robert Bunsen (1811–1899). While Gibbs carried out his work quietly in New Haven, he did send reprints to all the scientists who would be able to read them. James Clerk Maxwell was so impressed that he included a chapter on the work of Gibbs in one edition of his *Theory of Heat* (1888) [1].

Classical Thermodynamics applies to all material systems at equilibrium. Early work focused on single component systems. Gibbs completed the general development of Thermodynamics by extending it to chemical systems with many components and phases. He also created an elegant and coherent mathematical form for Thermodynamics that persists today.

Clausius had produced a coherent form of single component Thermodynamics that forms the basis for all further work (see Chap. 12). Gibbs, however, produced

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an elegant and complete theory of Thermodynamics that applies to all material systems. His first contribution to this project was his 1873 paper "Graphical Methods in the Thermodynamics of Fluids" [2]. The early efforts in this regard are due to Clapeyron and were gladly adopted by Rankine. Still, Gibbs takes the subject to completion.

Gibbs distinguished between "variables of state," (*P, V, T, U, S*) (*p, v, t, ε, η*) and "quantities of process," (*W*, *H*) (*H* is *Q*, the heat). He also is sensitive to the units chosen to express any of these quantities. When consistent units are chosen, two relationships are important:

$$\begin{aligned} d\varepsilon &= dH - dW \\ d\varepsilon &= td\eta - pdv \end{aligned} \tag{13.1}$$

Gibbs is especially careful to remind his reader that W and H depend on the "whole series of states through which the body is supposed to pass." This can be expressed mathematically as "path integrals:"

$$\begin{aligned} W &= \int pdv \\ H &= \int td\eta \end{aligned} \tag{13.2}$$

Gibbs was a master of the theory of functions of many variables. He considered systems where one of the five variables of state was held constant. He called them *isometric* (constant volume), *isopiestic* (constant pressure), *isothermal* (constant temperature), *isodynamic* (constant energy), and *isentropic* (constant entropy)(*adiabatic*). For systems of constant mass, the variables of state can be expressed as functions of two of the other variables of state.

Rankine made use of two-dimensional PV diagrams. On such a diagram, lines of constant temperature and constant entropy were drawn. The work associated with each transformation is given by the definite integral of the expression given above, as illustrated in Chap. 10. Gibbs introduces $t\eta$ (TS) diagrams as a way of representing the heat associated with a transformation. He then presents a careful argument that distinguishes work and heat: work is work, but heat flows from the hotter body to the colder body. Gibbs presents the appearance of the classic Carnot cycle in TS space (Fig. 13.1).

From the appearance of the diagram and the equations of Thermodynamics, it is easy to reach correct conclusions about cyclic processes. Gibbs selects the perfect gas for pedagogical clarity. For a fluid at constant volume, $dW = 0$. This leads to the expression for the change in energy in terms of the specific heat at constant volume:

$$c_v = \left(\frac{dH}{dt}\right)_v \tag{13.3}$$

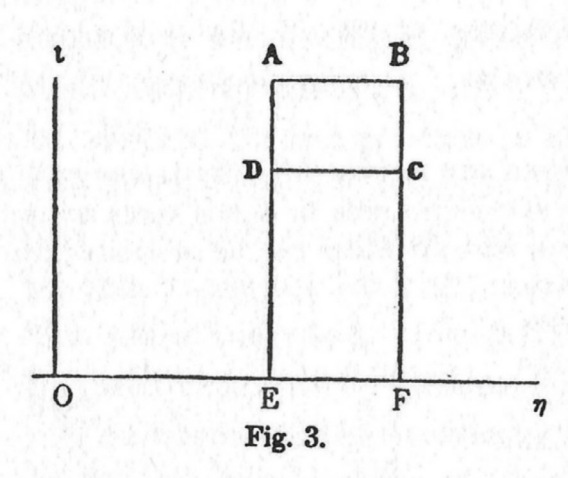


Fig. 13.1 Temperature-entropy diagram for a Carnot cycle [2]

With the form of the perfect gas law taken as: $pv = at$, and the expression for the energy of the perfect gas as: $\varepsilon = c_v t$, the entropy can be expressed as: $\eta = a \ln v + c_v \ln t + c_v \ln c_v$.. Similar relationships can be formulated for any 3 of the 5 key quantities (p, v, t, ε, η). The form of the plots might be log–log or semilog in order to produce straight lines. Gibbs selects the volume-entropy plots for extensive consideration.

Gibbs followed up this initial article with a presentation involving representation of the full function of two variables as a surface in three dimensions [3]. The trinity of the key equations are:

$$\begin{aligned} d\varepsilon &= td\eta - pdv \\ p &= -\left(\frac{d\varepsilon}{dv}\right)_\eta \\ t &= \left(\frac{d\varepsilon}{d\eta}\right)_v \end{aligned} \tag{13.4}$$

The thermodynamic "meaning" of pressure is the change in energy as a function of volume at constant entropy. The thermodynamic meaning of temperature is the change in energy with entropy at constant volume. A generic surface image for the perfect gas is (Fig. 13.2) [3]:

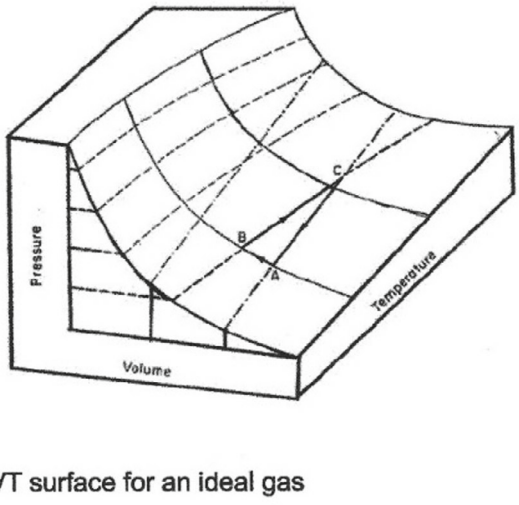


Fig. 13.2 PVT surface for an ideal gas [3]

13.1 PVT Surfaces for Real Multiphase Systems

Gibbs was also interested in the conditions of mechanical stability for a real multiphase system. The surface now becomes that shown in Fig. 13.3. Gibbs gives a detailed discussion of the lines and curves on this plot. There are also two remarkable "points." The "triple point" defines where solid, liquid and gas are all present at equilibrium. The "critical point" defines the maximum temperature and pressure at which the fluid phase is separated into liquid and gas. The system is mechanically unstable at this point with respect to small fluctuations in pressure. Many partial derivatives (the measurable properties of the system) vanish at the critical point. The curvatures also vanish there (Fig. 13.4).

The discussions in these two papers from 1873 are already at the "modern level." The phase behavior of a single component system could be understood entirely in terms of the Thermodynamics of Gibbs. The combination of graphical representation and rigorous differential relationships remains the essence of Thermodynamics.

13.2 On the Equilibrium of Heterogeneous Substances

The *magnum opus* "On the Equilibrium of Heterogeneous Substances," was published in the *Transactions of the Connecticut Academy* [5]. It starts with two dicta from Clausius: *The energy of the world is a constant. The entropy of the world trends towards a maximum.* Gibbs first considers an isolated material system. For such a system, there may be many possible microscopic states. Gibbs selects groups with the same total internal energy. Only those states for which the variation in

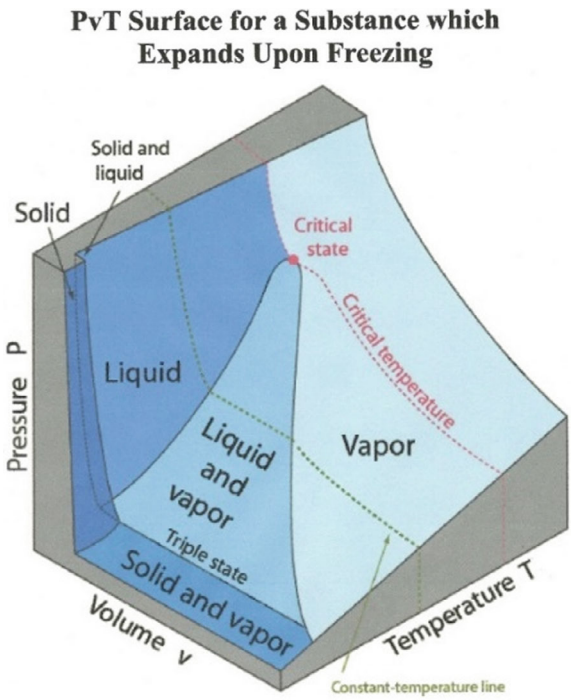


Fig. 13.3 PVT diagram for a real system like water [4]

$$\left(\frac{dp}{dv}\right)_t = 0, \quad \left(\frac{dp}{d\eta}\right)_t = 0, \quad \left(\frac{dt}{dv}\right)_p = 0, \quad \left(\frac{dt}{d\eta}\right)_p = 0,$$
$$\left(\frac{d^2p}{dv^2}\right)_t = 0, \quad \left(\frac{d^2p}{d\eta^2}\right)_t = 0, \quad \left(\frac{d^2t}{dv^2}\right)_p = 0, \quad \left(\frac{d^2t}{d\eta^2}\right)_p = 0,$$

Fig. 13.4 The partial derivatives of the thermodynamic system at a critical point [3]

the entropy is less than or equal to 0 can be in equilibrium. Conversely, for those states of equal entropy, only states for which the variation in the energy is greater than or equal to 0 can be in equilibrium. When the entropy is a maximum for a system with constant energy, it is a case of stable equilibrium.

For a heterogeneous substance, more than one type of body is present. Gibbs introduces the fundamental equation for changes in the internal energy:

$$dU = TdS - PdV + \sum_i \mu_i dm_i \tag{13.5}$$

(I have introduced modern thermodynamic symbols but retained the mass-based perspective.) Gibbs discusses the important concept that this equation must also include components that are initially absent from the mixture. This Eq. (13.5), introduces the important variable for chemical processes: the chemical potential μ. From the theory of functions of many variables, it can be seen that the chemical potential is the partial derivative of the energy with respect to the mass of component i, at constant S, V and all other components:

$$\left(\frac{\partial U}{\partial m_i}\right)_{S,V,\{m_{j\neq i}\}} \tag{13.6}$$

Gibbs considers a system with more than one phase present. The condition of equilibrium reduces to:

1. The temperature must be the same in all the phases, otherwise heat would flow and the initial system would not have been in equilibrium.
2. The pressure must be the same in all phases, otherwise mass would flow and the initial system could not have been in equilibrium.
3. The chemical potentials of each "component" must be the same in all phases, otherwise that component would flow from one phase to another and the initial system could not have been in equilibrium.

Gibbs also considers the effect of "constraints" that limit the equilibrium. One good example is the phenomenon of osmotic pressure. The membrane is selectively permeable. The common solvent may pass through, but the "solute" may not. Hence, the chemical potential of the solute on the pure side of the membrane does not appear, only the chemical potential of the solvent. This quantity is an explicit function of the pressure, which can be different on the two sides of the membrane. The chemical potential of the solvent is lowered by the presence of the solute. Solvent then flows to raise the chemical potential back towards its pure value. When the solvent flow ceases, the system is in equilibrium with regard to solvent flow.

Another interesting case would be to add ice to the pure solvent side. The temperature would then be fixed on that side. The expression for differential of the chemical potential of water on the solution side is:

$$d\,\mu_{H_2O} = -\overline{S}dT + \overline{V}dP + RT\ln a_i \tag{13.7}$$

where a_i is the "activity" of the water. In the traditional experiment, the temperature is held constant. With ice on the pure solvent side, the chemical potential of water in the ice phase and the liquid phase must be equal. The chemical potential of water on the solution side will be lowered by the activity term (which can be approximated as the mole fraction, $a_{H_2O} \approx x_{H_2O}$. It will be raised by the pressure term, as before. It can also be raised by cooling on the solution side, since entropy is positive. At equilibrium, the chemical potential of the water is uniform in all the phases.

13.3 Thermodynamics and Fundamental Functions

One of the most important concepts in the article is "Fundamental Functions." There are 7 essential thermodynamic variables: T, P, V, m, μ, U, S. They can all appear in one equation:

$$\begin{aligned} U &= TS - PV + \mu m \\ U &= \left(\frac{\partial U}{\partial S}\right)_{V,m} S + \left(\frac{\partial U}{\partial V}\right)_{S,m} V + \left(\frac{\partial U}{\partial m}\right)_{V,S} m \\ dU &= TdS - PdV + \mu dm \end{aligned} \tag{13.8}$$

For a multicomponent system, each component in each phase adds another chemical potential.

Gibbs also explained that there can be other fundamental functions. In modern dress these are the enthalpy, H, the Helmholtz energy, A, and the Gibbs energy, G:

$$\begin{aligned} H &= U + PV = TS + \mu m \\ A &= U - TS = PV + \mu m \\ G &= U - TS + PV = \mu m \\ dH &= TdS + VdP + \mu dm \\ dA &= -SdT - PdV + \mu dm \\ dG &= -SdT + VdP + \mu dm \end{aligned} \tag{13.9}$$

The significance of defining four fundamental functions is revealed by considering the details of the process of interest. The internal energy is useful when the entropy and volume are held constant. The enthalpy is chosen when entropy and pressure are held constant. The Helmholtz energy, also called the "work function," is best when temperature and volume are held constant. And the Gibbs energy is best when temperature and pressure are held constant. All of this is explicit in the treatise of Gibbs.

The concept of a "material phase" is due to Gibbs. It must be homogeneous and can consist of more than one "component." Each substance can be characterized by a chemical potential in each phase. Two or more phases can "coexist" in equilibrium when the chemical potentials of all components are "the same" in all phases in which they exist. In addition to a full set of equations, Gibbs presents geometrical illustrations of the conditions for phase equilibrium (Fig. 13.5).

Gibbs also discusses the phenomena of critical points or critical lines. At these points or along these lines, more than one phase can have not only equal chemical potentials but become identical. As the critical point approaches, fluctuations between the possible phases become macroscopic. The gas–liquid critical point produces "opalescence" as it approaches along the vapor pressure

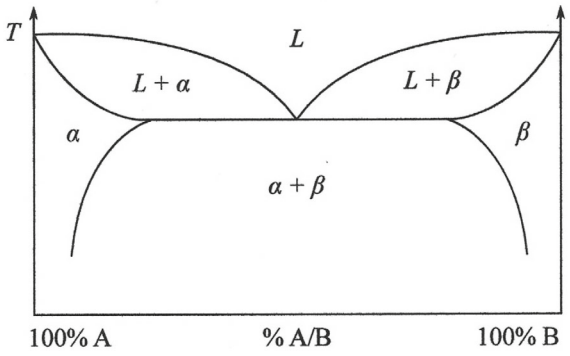


Fig. 13.5 Eutectic diagram for a two-component mixture. At high temperature, (high entropy), the system is a homogeneous liquid. Below the eutectic temperature, there exists a region of homogeneous mixed crystal. There are other possibilities: In the A rich region, pure crystalline A will precipitate from the homogeneous liquid mixture upon cooling until it reaches the eutectic temperature, and conversely for the B-rich region. For very A-rich mixtures, component B and component A will separate into regions of pure crystalline A and pure crystalline B, and conversely for very B-rich mixtures. This phase diagram is fully comprehended by the work of Gibbs, as well as much more complicated systems

line. Two-component liquid mixtures can also exhibit critical points and become opalescent.

When one of the components of a two-component mixture is very small with respect to the other component, approximations can be made which simplify the calculations. The chemical potential of component 2 can be expressed as:

$$\mu_2(T, P, m_2) = A(T, P) + B \log\left(\frac{m_2}{V}\right) \tag{13.10}$$

This form is especially useful for dilute gas phase and solution chemical reactions. Gibbs applies it to a derivation of Henry's Law for the solubility of gases in liquids.

While elementary textbooks pretend that Chemistry does not depend on gravity, Gibbs includes a thorough discussion of equilibrium when it is present. The energy is elevated by "mgh", where g is the gravitation constant and h is the height above the surface of the Earth. For a stable equilibrium in a "tall tube," the chemical potential must decrease as the quantity gh increases. The barometric distribution in an isothermal column is:

$$\wp(h) = \left(\frac{mg}{k_B T}\right) \exp\left(-\frac{mgh}{k_B T}\right) \tag{13.11}$$

Gibbs already anticipated this result.

One of the most important concepts for mixtures is the entropy of mixing. For two ideal gases contained in identical volumes, V/2, the mixed gas in volume V

will have an increased entropy given by $\Delta S = (PV/T) \ln 2$. Gibbs generalizes this to real gases and arbitrary volumes.

This complete theory allows a discussion of chemical reactions in real gases. It must be remembered that Gibbs published these papers in the 1870s. Very little experimental work had been published at this point. The classic work of van't Hoff on Chemical Dynamics was only published in the 1880s and only translated into English in the 1890s.

Gibbs introduces this subject with a simple gas phase chemical reaction from a mass-based perspective:

$$\begin{aligned} \aleph_3 &= \lambda_1 \aleph_1 + \lambda_2 \aleph_2 \\ \lambda_1 + \lambda_2 &= 1 \end{aligned} \tag{13.12}$$

He then presents the condition of chemical equilibrium:

$$\lambda_1 \mu_1 + \lambda_2 \mu_2 = \mu_3 \tag{13.13}$$

This clear and simple relation is easily generalized to any gas phase reaction. It is also easily generalized to any chemical reaction. Once the concept of a chemical potential and the "arithmetic of stoichiometry" had been invented, Chemical Thermodynamics came into being. Gibbs applied the formalism to the discussion of the dimerization reaction of nitrogen dioxide as a function of temperature and pressure. The level of understanding and the consilience between the theory and the experiments of Playfair and Wanklyn was encouraging [6].

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James Clerk Maxwell: Towards a Microscopic Theory of Heat

14

Abstract

One of the most essential books for the understanding of heat in the nineteenth century is *Theory of Heat* (1872,1888) by James Clerk Maxwell. Maxwell knew the works reviewed in Chaps. 1–13, and presented the results in the language of 1888. He was still confused about many things, but he promoted the microscopic perspective for the understanding of material bodies. There are also rare insights in this book that do not appear anywhere else. This chapter surveys the entire book, and gives detailed discussions of areas where necessary. It is, in effect, the record of the last gasp of nineteenth century understanding and the first movement towards the twentieth century perspective.

England and Scotland were blessed with many great physicists in the nineteenth century. James Clerk Maxwell (1831–1879) (Fig. 14.1) summarized his contributions to the understanding of heat in his monograph *Theory of Heat* (1871, revised 1888) [1]. Maxwell was a product of the great Scottish educational system. He entered the Edinburgh Academy in 1841 at the age of 10. He both tended to his official studies and carried out professional level work in mathematics. His first published paper was written when he was 14. He entered the University of Edinburgh in 1847. He was mentored by people like James D. Forbes and William Hamilton (1805–1865). He was encouraged to follow his intellectual star and publish scientific and mathematical papers. Finally, at the age of 19 he left Scotland for Cambridge University. He graduated Second Wrangler and First in Smith's Prize. He was made a Fellow of Trinity College and stayed until he was called back to Scotland at Marischal College, Aberdeen. He later taught at King's College, London from 1860–1865.

During these years he was elected as a Fellow of the Royal Society and mastered electricity and magnetism. He was often at the Royal Institution. In 1871

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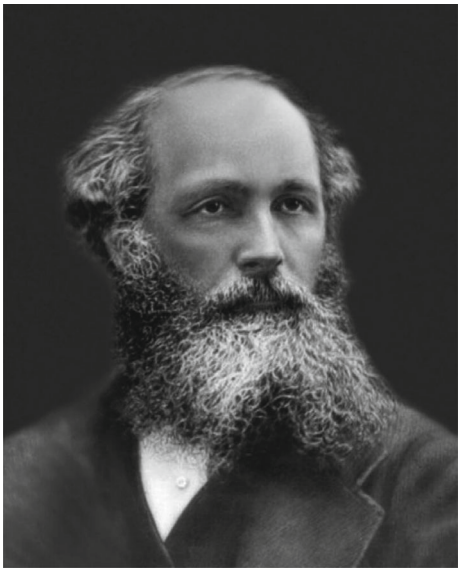


Fig. 14.1 James Clerk Maxwell. One of the deepest thinkers about heat (Public Domain)

he was called to be the new Cavendish Professor of Physics at Cambridge University. His classic book on heat was first published in 1871 as well. Although he is remembered as a great theorist, Maxwell was always well-connected to the experimental side of material physics. The classic biography of Maxwell is *The Life of James Clerk Maxwell* (1884) by Lewis Campbell and William Garnett [2].

14.1 Detailed Discussion of *Theory of Heat*: Chapter 1 Introduction

Chapter 1 of *Theory of Heat* focuses on the measurement of quantities that matter for the Theory of Heat. He employed the best thermometers in the world at Cambridge University and thoroughly understood the concept of temperature, T. He insisted that heat itself was a "measurable quantity." The instrument used to measure heat is called a "calorimeter," even though the theory of "caloric" is now abandoned. Another important observation is that heat diffuses from regions that are hotter (greater T) to regions that are cooler (regions of lower T).

Maxwell distinguished three "processes" for diffusion of heat:

1. Conduction: flow from a hotter region to a cooler region
2. Convection: mass flow of the hot body itself
3. Radiation: energy transfer by processes that involve propagating waves, such as light and sound.

Metals are good conductors of heat and Maxwell used the behavior of a silver teaspoon to illustrate the process. He reminds his reader that on the coldest day we still feel the "heat of the sun." Radiant heat is absorbed by our skin. He introduces the term for matter that transmits radiant heat: "diathermous**."** Radiant heat obeys "ray optics." It can be focused. There are also different "colors" of radiant heat.

Maxwell discussed radiant heat (light) and its interactions with matter. Radiant heat can propagate in a vacuum or in a diathermous medium. No actual material medium is completely transparent. Maxwell chose to restrict the name "heat" for some property of a material medium. (I have chosen to consider light as a form of heat that allows energy to be transferred from one body to another.)

Maxwell defined a material body as a substance that responds to "forces." He distinguished solids as bodies that can support longitudinal pressure. He could have just as easily chosen to focus on being able to support a transverse force. Fluids flow under such stress. (The study of stress–strain relationships is called "viscoelasticity.") Maxwell distinguished two kinds of fluids: liquids which can partially fill a closed container, and gases which entirely fill the container. He is even aware that liquids can sustain negative hydrostatic pressure.

Maxwell presents an introduction to the effect of heat on a solid body. Consider a solid body currently at temperature T_0. Add a quantity of heat (designated as Q). Wait for equilibrium. He asserts that under all circumstances far from a phase boundary, the system will achieve an increase in temperature, T_1. (This means that the normal heat capacity, $C = Q/\Delta T$, of a solid body is uniformly positive.) The dimensions of the body can also change. (There is a persistent notion that heat is a kind of hylomorphic substance that confers expansion.) Maxwell notes that some crystalline substances, like silver iodide, actually contract when heat is added! He was also aware that the change in the geometric dimensions could be nonuniform for particular crystalline materials. Solids are also characterized by mechanical moduli. There is, again, a notion that heat "softens" a solid. Maxwell asserts, correctly, that it need not be so. He cites steel wire as an example of a material that is "stiffer" at 100 °C than at 0 °C. He also cites my favorite solid: caoutchouc. When a strip of natural rubber is held under tension, adding heat produces an increased tensile modulus. This phenomenon had been extensively studied by Joule. (It was only explained in the twentieth century by Kuhn, Mark and Flory.)

Maxwell was aware that solids have a sublimation pressure. Well below the ultimate "melting point," solids can exist in equilibrium with their vapor. Adding heat increases the sublimation pressure. Solids sublime "at the surface." (This suggests that there is something special about many solid surfaces, and that the energy of particles in the surface layer fluctuates, just as in liquid surfaces.)

Solids can also "melt." One of the signature characteristics of this event is that the temperature remains the same as long as there is both solid and liquid present. The total heat necessary to fully melt a sample of solid is called the "latent heat of fusion." (Joseph Black is generally credited with creating this discussion (see Chap. 4). Maxwell wisely restricts his discussion to the observed facts. He chooses

to consider the solid state in its complexity and the liquid state as well. The location of the melting point will be determined by concepts yet to be presented. The specific volume (volume/gram) of the solid may differ from that of its corresponding liquid. Naïve notions tempt one to infer that the liquid volume is always larger, but actual observations contradict this assertion. The actual volume of a particular substance in its crystalline state is determined by the microscopic crystal structure. The local structure of a liquid is constantly changing, but there exists a "pair-correlation function" for each pure liquid. Highly structured liquids, such as water, contain strong interparticle interactions ("bonds"). Maxwell knew that, for solid–liquid pairs where the volume of the solid exceeded that of the liquid, increased pressure would lower the melting point. William Thomson (Lord Kelvin) inferred that the deep interior of the earth must be solid, since tidal forces from the moon and sun would deform the earth drastically if it were not. This means that the substances that make up the crust must have a solid form with a volume lower than the corresponding molten form.

Maxwell now addresses the general properties of liquids. The observed heat capacity of most liquids is higher than their corresponding solids. The heat capacity is also an explicit function of temperature and pressure: $C(P,T)$. Liquids cannot support a static transverse shear. One manifestation of this is the existence of the shear viscosity, discussed by Newton. Generally, the viscosity is an explicit function of temperature and pressure, η(T,P), and it decreases with temperature and increases with pressure. Maxwell was aware of the properties of liquid sulfur. Soon after melting sulfur undergoes a drastic increase in its viscosity. This reaches an equilibrium value. Further heating changes both the local structure of the liquid and the local friction between sulfur "chains." Chemical reality is more complicated and more interesting than naïve physics.

Like solids, liquids can exist in equilibrium with their corresponding vapor phase. There is also a corresponding heat of vaporization. John Dalton explored this phenomenon in detail. The vapor pressure is a function of the temperature, $P_{\mathrm{vap}}(T)$.

When a liquid is heated in an open vessel, the external atmospheric pressure acts on the surface of the liquid. When the vapor pressure of the liquid exceeds the atmospheric pressure, bubbles of gas can form anywhere in the liquid and this phenomenon is called "boiling." (Boiling can also be observed at constant temperature by evacuating the head space until the vapor pressure exceeds the new imposed low pressure.) Maxwell also discussed the important fact that liquids in contact with the atmosphere contain dissolved gases. Heating the liquid (now solution) will drive off the dissolved gases first. He also notes that water boils at a lower temperature on high mountains, since the atmospheric pressure is lower. Maxwell also notes that salt solutions boil at a higher temperature than pure water. (van't Hoff and Raoult would eventually explain this phenomenon).

Finally, Maxwell discusses the properties of gases. Careful measurements by Boyle and Hooke, and by Mariotte in France, revealed that, at constant temperature, the pressure times the volume is reasonably constant. Maxwell was a great

admirer of the Scottish engineer, William Rankine (1820–1872). At constant volume, the pressure of the gas increases approximately linearly with the temperature. (Although it is often called "Charles Law," Maxwell notes that Dalton published it first. Gay-Lussac and Regnault also made many measurements of the equation of state for a gas.) Maxwell notes that gases are "ideally" suited for the study of universal laws because they exhibit fewer special cases. The science of Thermodynamics was developed using both the actual data obtained on real gases and the idealized properties of the "perfect gas."

14.2 Detailed Discussion of Chapter 2: Thermometry

Maxwell states his own definition of temperature: "The temperature of a body is its thermal state considered with reference to its power of communicating heat to other bodies." This is both a Newtonian and a Fourierian perspective that assumes nothing other than the phenomenological behavior of a body at temperature T. Two bodies are at the same temperature when "no heat flows between them when placed in contact." He also states the Zeroth Law of Thermodynamics: 'Two bodies that display the same temperature with a third body, are themselves at the same temperature." Maxwell identifies the "third body" as the ideal thermometer.

There are several different approaches to standardization in science. One protocol is to create a unique "standard" and then compare every other instrument to it directly. For example, there is a standard meter bar in Paris. Another approach is to determine the standard value for readily available circumstances that can be realized anywhere. Isaac Newton employed the freezing and boiling points of water as his standards in 1701. This allowed any two thermometers to be calibrated in the same way. The next issue is the size of the "scale" between the two fixed points. Maxwell discusses the history of the temperature scale, but this is well-trod ground.

The important new subject associated with the measurement of temperature is the use of electrical resistance, R. (My own most accurate and precise measurements of temperature were carried out with a "platinum resistance thermometer.") Maxwell cites the work of Werner von Siemens (1816–1892). The measured resistance of metals could be represented by the equation:

$$R = \alpha\sqrt{T} + \beta T + \gamma \tag{14.1}$$

14.3 Detailed Discussion of Chapter 2: Calorimetry

Maxwell references the foundational work of Lavoisier and Laplace. One type of calorimeter is the isothermal system, such as the ice/water mixture. Another common type is the adiabatic, constant volume calorimeter. He makes reference to some of the leading thermal experimentalists of the nineteenth century, such as Robert Bunsen (1811–1899) and Victor Regnault.

The most important assertion in the chapter is: "all heat is of the same kind." By this he means that it can produce the same temperature change. He also considers the differential changes along a particular path. For example, energy can be transferred to a sample by placing it in contact with a heat bath at a higher temperature, or it can be heated by a wire conducting electricity, or it can be heated by exposing the sample to sound, or it can be heated by exposing the system to infrared (thermal) radiation. If the energy transferred in each case is the same, and if no other sinks are present, then the thermal effect must be the same.

There are many possible thermal effects. The simplest effect is a rise in temperature. The heat capacity is then $C = Q/\Delta T$. Another simple effect is a change in volume. The thermal expansion coefficient is then $\alpha = \Delta V/\Delta T$. Maxwell is quite aware that this coefficient can be either positive or negative. Adding heat may lead to a phase change. Maxwell discusses the Thermodynamics of phase changes. He notes the foundational work on the heat associated with a phase change by Joseph Black. In a two-component liquid mixture, adding heat may lead to demixing. Merely stating the "bare" definitions and equations of Thermodynamics obscures the rich and interesting world of thermal phenomena!

14.4 Detailed Discussion of Chapter 4: Elementary Dynamical Principles

Maxwell was part of the great English tradition in Mechanics. He cites Thomas Young (1773–1829) as his early muse**:** *A Course of Lectures on Natural Philosophy and the Mechanical Arts* (1807) [3]. Two other foundational sources were Rankine (see Chap. 10) and Thomson and Tait: *Elements of Natural Philosophy,"* (1872) [4].

Maxwell expresses the General Statement of the Conservation of Energy as [1]:

> *The total energy of a body or system of bodies is a quantity which can neither be increased nor diminished by any mutual action of these bodies, though it may be transformed into any of the forms of which energy is susceptible.*

He gives a clear statement about heat [1]:

> *The reason for believing heat not to be a substance is that it can be generated, so that the quantity of it may be increased to any extent, and it can also be destroyed, though this operation requires certain conditions to be fulfilled. The reason for believing heat to be a form of energy is that heat may be generated by the application of work, and that for every unit of heat which is generated, a certain quantity of mechanical energy disappears*

14.5 Detailed Discussion of Chapter 5: Measurement of Internal Forces and Their Effects

This chapter is one of the fundamental documents of materials science. It starts with a few remarks about the generalized solid. Not all solids are at equilibrium. There are many ways to discuss the structural state of a solid. Crystalline solids are characterized by a definite external and internal symmetry. Non-crystalline solids lack long-range order, but can exhibit short-range order. Maxwell defines a solid as a material that will support longitudinal and transverse shear forces. As long as the forces are small enough, the solid will transform into a unique state of strain. The strain can have three components, which quantify the deformation of the sample. Stresses are also characterized by three components. The mathematical relation between stress and strain involves a second-rank tensor, usually called the "pressure tensor." The ordinary thermodynamic pressure is the sum of the diagonal elements divided by three. Thomas Young constructed a coherent theory of elasticity of solid bodies.

While we now acknowledge a very large number of possible condensed phases of matter, Maxwell focuses on fluids and hence wishes to carefully define them. In reality, the local structure of a liquid varies over a very wide range at any particular time. This reality is emphasized by the phenomenon of "Brownian Motion." The Thermodynamic (hydrostatic) pressure, P, is an average over the local structure, either in space or in time. One clear mathematical definition of the fluid pressure is that all three diagonal elements must be equal. Another characteristic is that when a fluid is subjected to shear forces, the fluid "flows." The rate of flow depends on the strength of the shear force and the fluid "viscosity."

When a fluid is subjected to a spherical (hydrostatic) pressure its volume decreases. The thermodynamic volume can be expressed as a function of temperature and pressure: V(T,P). Changes in volume can then be written as:

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \tag{14.2}$$

Maxwell defines the "elasticity" of a fluid as the reciprocal of the pressure derivative. (The negative of the direct derivative is often normalized by the volume and called the compressibility: κ) The elasticity of a fluid is a positive quantity. Pressing on the fluid reduces the volume, as long as no phase transition occurs. (In spite of continuing notions that increasing the temperature always increases the volume of fluids, the thermal expansion coefficient can be negative.)

14.6 Detailed Discussion of Chapter 6: Lines of Equal Temperature on an Indicator Diagram

In addition to being a master of equations, Maxwell employed diagrams to good effect. He presents the classic PV diagram with its isothermals as hyperbolae. He discusses the gas–liquid isothermals for steam and water. He is fully aware of both

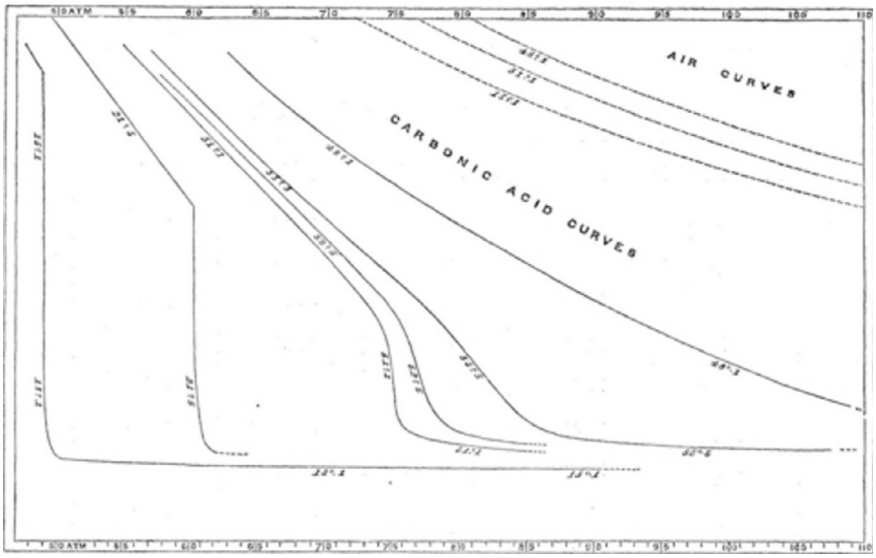


Fig. 14.2 Original VP diagram from Andrews' 1869 Bakerian lecture. The lines are isotherms and show the critical isotherm at 30.92 °C. (V on y-axis, P on x-axis) [5]

the critical point and the "continuity of the liquid and gaseous state." Maxwell references the careful work of Thomas Andrews (1813–1885) FRS, FRSE. His Bakerian lecture for 1869, "On the Continuity of the Gaseous and Liquid States" [5], remains the standard reference for the clear presentation of the critical point and the full gas–liquid phase diagram (Fig. 14.2).

Another important but often overlooked contributor to the science of heat was James Thomson (1822–1892) FRS, FRSE. He was the Regius Professor of Civil Engineering and Mechanics at the University of Glasgow, following Rankine. He was William Thomson's older brother. He speculated that below the critical point, the shape of the *PV* curve was continuous and appeared as shown in Fig. 16 in *Theory of Heat* (Fig. 14.3) [1].

This shape inspired the famous van der Waals equation of 1873 [6]. But Maxwell reminds his readers that in order to be mechanically stable, the following must be true:

$$\left(\frac{\partial P}{\partial V}\right)_T \leq 0 \tag{14.3}$$

In the two-phase region, the value is 0!

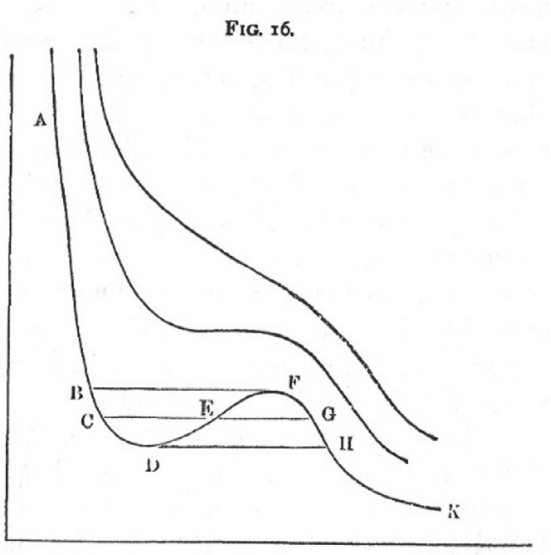


Fig. 14.3 Speculative PV curve for the liquid gas behavior near the critical point. (scanned from my personal copy of *Theory of Heat*)

14.7 Detailed Discussion of Chapter 7: Adiabatic Lines

This chapter discusses adiabatic processes. Maxwell references the foundational work of Rankine (see Chap. 10) and Clausius (see Chap. 12). He finally produces a sort of phase diagram for water (Fig. 14.4).

14.8 Chapter 8 Heat Engines and the Carnot Cycle

In this chapter Maxwell discusses heat engines and the Carnot Cycle. It is a nice summary of the work of others.

14.9 Detailed Discussion of Chapter 9: Thermodynamic Relations Between Variables

Once again, the master of mathematics demonstrates that analytical geometry is twice as effective in helping us to understand Thermodynamics. An initially confusing diagram eventually opens the door to understanding (Fig. 14.5).

Maxwell also provides a masterclass in the difference between specific heats at constant volume and constant pressure, and between compressibility (elasticity) at constant temperature and constant entropy.

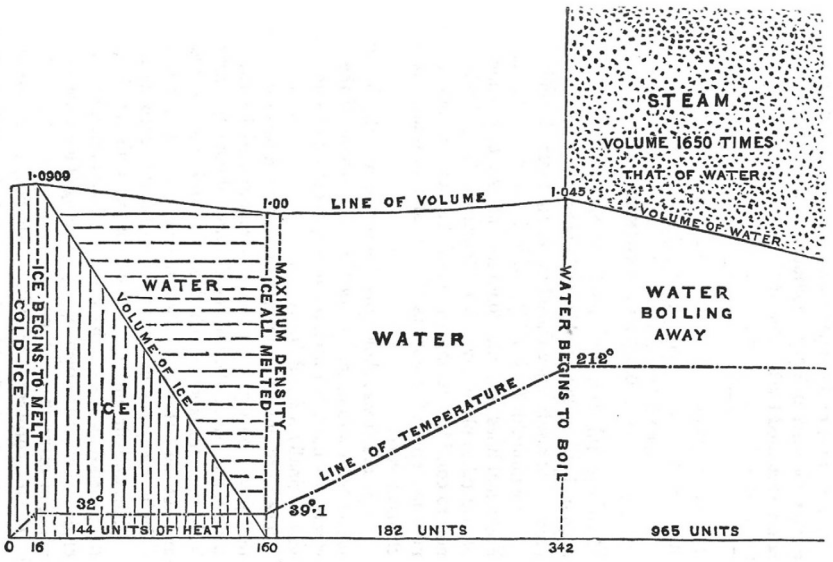


Fig. 14.4 Phase diagram for ice, water and steam [1]

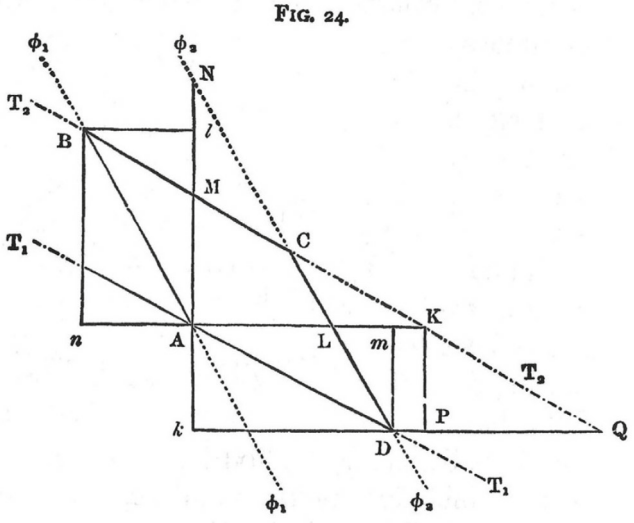


Fig. 14.5 Maxwell created a diagram that relates temperature, pressure, entropy and volume (entropy is ϕ). Lines of constant T,V,P and ϕ are indicated. Areas on the diagram allow work and heat to be calculated. Figure 24 in *Theory of Heat* [1]

14.10 Detailed Discussion of Chapter 10: Latent Heat

While Joseph Black introduced the concept of "latent heat," Maxwell helped to clarify the real thermodynamic issues involved. Gibbs provided the rigorous thermodynamic equations for multi-phase systems. Energy alone is not enough to understand phase transitions. If it were, there would be no liquids because the internal energy of the crystalline solid state remains below the energy of the liquid at all temperatures!

Both James Thomson and William Thomson contributed both experiments and concepts about phase transitions. Why is the melting temperature of ice so high?! And why does the melting temperature fall with an increase in pressure? How is it possible for a substance to exist in three phases in equilibrium at the same temperature and pressure? The answers were often published in the Proceedings and Transactions of the Royal Society of Edinburgh. The simple story is told in the language of the Gibbs energy:

$$\begin{aligned} dG &= -SdT + VdP \\ d\,\Delta G &= -\Delta SdT + \Delta VdP \end{aligned} \tag{14.4}$$

If there are two phases, denoted by α and β, the condition of phase equilibrium is $\Delta G_{\alpha\beta} = 0$. The key result was already known by Clapeyron!

$$\frac{dT_{\alpha\beta}}{dP} = \frac{\Delta V_{\alpha\beta}}{\Delta S_{\alpha\beta}} \tag{14.5}$$

(One of the most remarkable phenomena of the ice-water system is the behavior of the system below the density maximum of the water at 277 K. Water can be supercooled well below the "normal freezing point" at 273.15 K. As the molar volume of the water increases as the system is cooled in this range, it approaches the molar volume of the ice at around 233 K. Both the volume change on freezing and entropy change on freezing approach 0!).

At the normal freezing point, the volume change on freezing is large and positive. The entropy change on freezing is large and negative. Increasing the pressure leads to a decrease in the freezing temperature. The triple point is slightly below the normal freezing point and is at a lower pressure! It can be visualized clearly as the intersection of the sublimation line and the vapor pressure line. (Naïve descriptions of the "melting process" as a "shaking apart" ignore the realities of Thermodynamics. Solids become more stable thermodynamically as they access more and more vibrational states, both acoustic and optical. Melting occurs at the surface of the solid as particles occasionally have enough energy to leave the surface. The mobility and much higher entropy of the liquid state finally create a phase with lower chemical potential when TS is large enough. Even below the melting temperature, particles can leave the surface with enough energy to populate the gaseous phase. Sublimation is a well-known process! The local energy necessary to either sublimate or melt is usually provided by acoustic waves (sound) in crystalline solids.)

14.11 Chapter 11: Gases

Thermodynamics marches to the tune of actual data. No formalism is of any use without accurate measurements of the mechanical and thermal properties of real materials. Maxwell cites the precise measurements of Regnault and the cogent application of Thermodynamics by Rankine to the properties of real gases.

14.12 Detailed Discussion of Chapter 12: On the Intrinsic Energy of a System of Bodies

In this chapter Maxwell discusses energy at many levels. It is impossible to determine the total energy of a gas. But it is possible to measure the "available energy," ΔU. This is accomplished by considering the work and heat associated with changes in the "state" of the system. He also discusses changes in the entropy of the system in detail. He creates diagrams that drive home the experimental and thermodynamic facts.

One of the key concepts introduced in this chapter is the "dissipation" of energy associated with actual changes. Dynamic processes are subject to the loss of the availability of energy. A presentation of the work of J. Willard Gibbs is given. Maxwell focuses on the surface diagrams associated with changes of state, as shown in Fig. 14.6, with a detailed explanation of this figure given as Fig. 14.7.

14.13 Discussion of Chapter 13: On Free Expansion: Theory of a Fluid in Which no External Work is Done During a Change of Pressure

This chapter is a discussion of the Joule–Thomson effect (Chap. 8). The system is composed of two regions at different pressures, separated by a "porous plug" that allows gas to flow from one chamber to the other. In addition to the pressure difference, a temperature difference is created. Although it would be many years before the name was coined by Heike Kamerlingh Onnes (1853–1926) Nobel 1913, in 1909, Maxwell clearly identifies the function $U + PV$ as important. Onnes called it the "enthalpy, H." The key to understanding the Joule–Thomson effect is the constancy of the enthalpy in the system. To illustrate the Joule–Thomson effect, Maxwell constructed the diagram given in Fig. 14.8.

The Joule–Thomson coefficient is given by:

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H \tag{14.6}$$

Maxwell shows that it is also equal to:

$$\mu_{JT} = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} \tag{14.7}$$

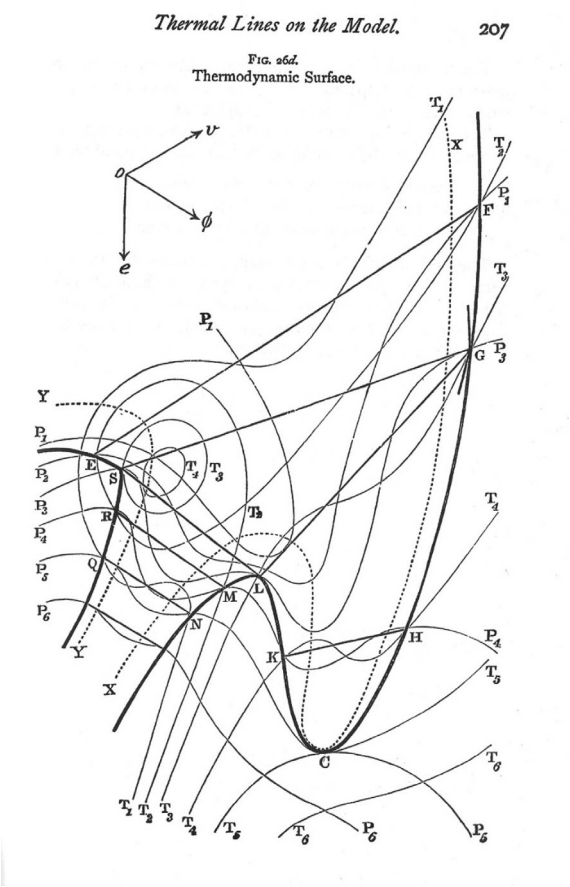


Fig. 14.6 Gibbs diagram for the phases of a single component system composed of solid, liquid and gas [1]

The combination of Joule, Thomson, Clausius, Gibbs, and Maxwell arrived at the modern form of Thermodynamics.

14.14 Chapter 15 on the Propagation of Waves of Longitudinal Disturbance

At last Maxwell starts to flow towards an understanding of heat as energy that moves. He references the work of Rankine on longitudinal waves: "On the Thermodynamic Theory of Waves of Finite Longitudinal Disturbance,"(1869) [7]. The speed of sound is fast enough that there is no time for heat to flow during individual cycles. This means that the compressibility that determines the speed of sound is adiabatic. (Although this chapter does not focus on the dissipative issues in longitudinal sound waves, the Longitudinal modulus, $M = K + (4/3)G$, is frequency dependent. Both K, the modulus of compression, and G, the shear modulus, are

Fig. 14.7 This dense representation of the realities of phase equilibrium in a single component system is a masterpiece of Maxwellian understanding

THERMAL LINES ON THE THERMODYNAMIC SURFACE.

(FIG. 26*d*.)

O Origin.
O V Axis of volume.
O ϕ Axis of entropy.
O e Axis of energy.
$P_1 \ldots P_6$ Isopiestics or lines of equal pressure.

Of these P_1 represents a negative pressure, or, in other words, a tension, such as may exist in solids and in some liquids.

$T_1 \ldots T_6$ Isothermals, or lines of equal temperature.

The curves T_3 and T_4 have branches in the form of closed loops.

FGHC. To the right of this line the substance is gaseous and absolutely stable. To the left of FG it may condense into the solid state, and to the left of GHC it may condense into the liquid state.

CKLMN. Below this line the substance is liquid and absolutely stable. To the right of LKC it may evaporate, to the left of LMN it may solidify.

QRSE. To the left of this line the substance is solid and absolutely stable. To the right of SRQ it may melt, and above SE it may evaporate.

C is the critical point of the liquid and gaseous states.

Below this point there is no discontinuity of states.

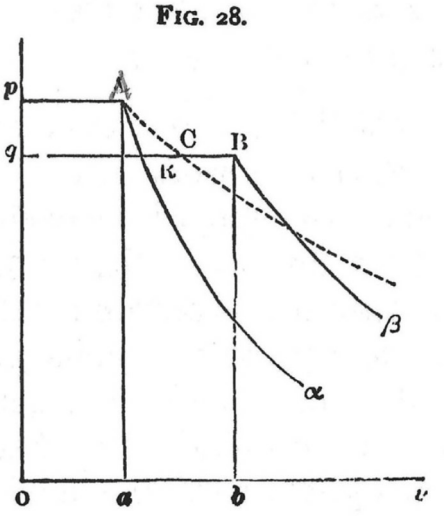
C is called in geometry the tacnodal point.

The curves FG, GHCKL, LMN, QRS, and SE are branches of what is called in geometry the node-couple curve.

The curves XCX and YY are branches of the spinode curve.

Above this curve the substance is absolutely unstable. Between it and the node-couple curve the substance is stable, but only if homogeneous.

Fig. 14.8 Maxwell's PV diagram for the Joule–Thomson effect. The change is between the point A(P_1,V_1,T_1) to B(P_2,V_2,T_2). The line Aα is an adiabatic process. The dotted line between A and C is an isothermal process



complex. The complex parts depend on the "volume viscosity" and the "shear viscosity." All sound waves are subject to loss.) Sound waves are characterized by both energy and momentum. They are a form of heat!

14.15 Chapter 16 Infrared Radiation and Heat

Electromagnetic waves do not require a medium in order to propagate, but they do propagate in dense media. Maxwell chooses to distinguish these moving bundles of energy from heat, but I will make the other choice, as did John Tyndall. Maxwell ignores loss in propagating electromagnetic waves, but all propagating waves are subject to loss in a dense medium. He also adopts a macroscopic perspective where both sound waves and electro-magnetic waves originate "outside" the sample in question. He has not yet "seen" that all bodies "at finite temperature" emit both sound and light continuously. This appears to Maxwell as a violation of the fundamental dictum of heat: Heat flows from a hot body to a cold body. Perhaps that is why he raised the issue of the "Demon."

Maxwell does acknowledge the phenomenon of "black-body radiation." But he is uncertain about the "form" of this radiation. He does know that black-body radiation raises the "temperature of a thermometer." (The Pictet effect.) Maxwell justifies his stance because the caloric theory of heat has been shown to be false.

He considers thermal radiation to be a wave-phenomenon traveling in the ether. Thus, it is not a particle with energy and momentum! His thoughts are consistent with the age in which he lived and worked.

Another important phenomenon ignored by Maxwell is Raleigh scattering. All "transparent" material substances scatter light and can be seen clearly as a line of light propagating through the sample. The invention of lasers made this phenomenon easier to see, but highly collimated sunlight is sufficient! Since light is scattered in directions different than the initial light wave, momentum must be transferred. The energy of the scattered wave is distributed over a spectrum of energies. Much more will be discussed about this "window" into the realities of material substances.

Since we now know that "radiant heat" is actually infrared electro-magnetic radiation, it is no surprise to us that it can undergo all the optical phenomena associated with visible light, including interference. Radiant heat can be polarized. And, hence, crossed polars will block the radiation. Maxwell assumes that the "intensity" of radiant heat is a continuous function. More modern experiments detect "photons" one at a time. It is no fault of Maxwell that he lived in the pre-quantum age. But his aversion to infrared radiation as heat was not helpful!

14.16 Chapter 17 Convection

In Chap. 1 three modes of heat transfer were listed. Chap. 17 briefly discusses "convection." Convection involves active mass transfer. The force that drives the motion can vary. Gravity is a constant source of force. Bouyancy can oppose gravity. The significance of convection is that it promotes much more rapid heat exchange than diffusion or conduction. It can also be employed to produce thermal effects that would not happen otherwise.

One of the most dramatic thermal convection phenomena is called the Rayleigh–Benard instability.

14.17 Chapter 18 On the Diffusion of Heat by Conduction

Heat can "diffuse" by thermal conduction. Maxwell gives his thoughts on this phenomenon in this chapter. He considers a metal slab of thickness c. Heat is provided from below at temperature T, and the slab is in contact with a sink above at temperature S. The slab is characterized by a thermal conductivity, k. Maxwell introduces a key protocol that remains a useful approach to the study of transport processes. He divides the overall slab into thin layers: the method of finite element analysis. Heat can diffuse between the thin layers according to the theory of Fourier (see Chap. 6).

Maxwell also employs the consideration of the "dimensions" of thermal conductivity. The dimensions of k are:

$$\frac{\text{heat}}{\text{thickness} \times \text{time} \times \text{temperature}} \tag{14.8}$$

The "state" of the slab can be followed from its initial temperature profile, for example uniform at temperature equal to the average of T and S, until "steady flow" is produced.

The exact solution of this problem was given by Fourier in his *Theorie de la Chaleur.* Fourier divides the sample into small volumes and assigns an initial temperature to each location. Heat will flow from one of these volumes to all the rest and heat will flow from all the rest to this volume according to the temperature difference and the time and distance factor:

$$\exp\left(-\frac{r_{ij}^2}{4kt}\right) \tag{14.9}$$

The evolution of the temperature profile, $T(\vec{r}_i, t)$, can then be calculated using the method of Fourier series. Maxwell includes this Fig. 14.9 of the temperature profile of a slab created by introducing a source of heat in the middle at $t = 0$.

The thermal conductivity of many metals had been determined by 1872. What was not known was the mechanism for heat conduction in these substances. This subject will be considered in Chap. 21.

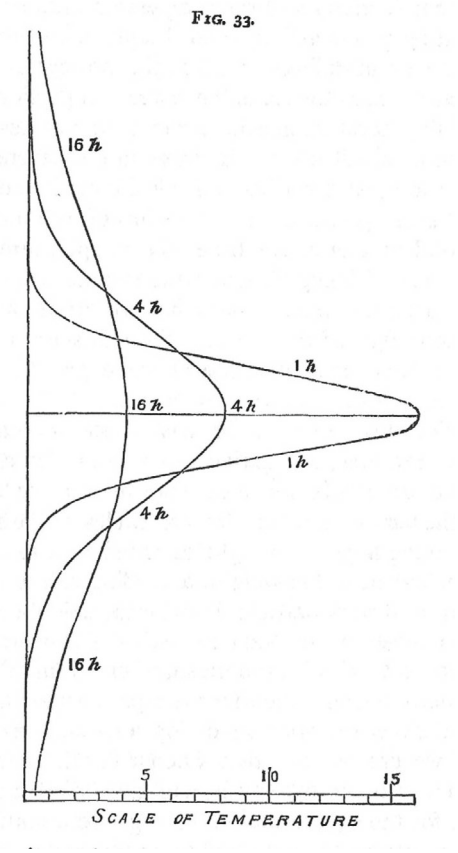


Fig. 14.9 Temperature profile in a slab after an initial introduction of heat at the midpoint plane. Figure 33 in *Theory of Heat* [1]

14.18 Chapter 19 Molecular Theory of the Constitution of Bodies

In the last chapter Maxwell addresses the microscopic nature of bodies and calculates some transport coefficients. He starts with a reminder that material bodies at equilibrium are characterized by a Thermodynamic average kinetic energy and potential energy.

One of the conundrums still raging in 1872 was how the energy of a body could radiate into free space with no reference to any other body. The false notion that light required a medium in order to exist produced strange arguments that led nowhere. When Pictet demonstrated that ice communicates with a thermometer through the mirror arrangement, eager speculators invoked "frigorific radiation." The idea that all material surfaces at finite temperature constantly emit infrared radiation seemed to violate the fundamental dictum of heat flow. But matter obeys its own laws, not those of physicists! "Precious" concepts like "calorique" and

the "ether" needed to be abandoned for Natural Philosophy to benefit from actual observations, uninfected with false dicta.

Maxwell chooses to join the future by asserting "a body consists of a great many small parts, each of which is in motion." He designates these parts as "molecules." (The dissonance between chemists and physicists in the late nineteenth century is easy to detect. Nature is unaware of both chemists and physicists.) Maxwell is sensitive to the issue of the scale of order in a material body. René-Just Haüy postulated that crystalline solids were characterized by a unique symmetry that was repeated at smaller scales until the primitive "unit cell" was reached. Further decreases in size revealed new geometries. The full theory of the solid state needed to wait for the twentieth century.

Tremendous progress was made in the theory of the gaseous state in the late nineteenth century. Maxwell cites Clausius as the scientist that brought the "kinetic theory of gases" to a point where it was both useful and precise. Maxwell's version of this theory was still cluttered with assertions that have not persisted. One of them is the claim that all the "molecules" in a pure sample of a gas are identical. (Even the simplest molecule, H_2, exists in many different states. There are two forms of hydrogen based on the magnetic moments of the two nuclei. There is a multiplicity of states associated with rotation of the molecules. Natural samples of hydrogen gas often contain other forms of hydrogen (deuterium or tritium).)

One of the characteristic properties of a fluid in this description is that each molecule can occupy any location in the volume eventually. This Brownian diffusion is one of the strongest pieces of evidence for the molecular description of fluids. Maxwell presents a heuristic discussion of the kinetic theory of gases. Each molecule executes a trajectory characterized by long stretches of free motion terminated by "collisions." (The average free trajectory is called the "mean free path, l.) Maxwell prefers to refer to the interactions between two molecules as an "Encounter." (He also delimits the liquid state as consisting entirely of encounters with no free paths.) During an encounter in the gaseous state, both energy and momentum are conserved. (Alas, actual chemical "encounters" can be inelastic and some of the original energy can be transformed into rotational and vibrational energies. Maxwell was aware of this!).

Maxwell is sensitive to the difference between the highly averaged properties of fluids and the trajectory of any particular molecule. The use of statistical methods allows the theorist to obtain meaningful information without needing to know everything!

Velocity is a vector quantity. If the gas as a whole is "at rest," the average over all velocities must be 0. The average speed, however, must be positive and finite. Maxwell uses this fact to calculate the average pressure of a gas at rest. For a gas of N molecules of mass M, the average momentum flux is $(N/V)M < v^2 >$. The pressure at any plane in the system is (1/3) of this: $P = (1/3)(N/V)M < v^2 >$.

The work of Maxwell was a monumental contribution to the evolving understanding of the nature of heat, but it left more questions unanswered than answered. Fortunately, another scientist, Ludwig Boltzmann, was also thinking along these lines and will be considered in Chap. 15.

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Ludwig Boltzmann: The Creation of the Full Theory of Statistical Thermodynamics and Kinetics

15

Abstract

Ludwig Boltzmann was one of the greatest classical physicists, along with James Clerk Maxwell (Chap. 14) and Lord Rayleigh. He adopted the full dynamic perspective with regard to the material world, and developed, along with J. Willard Gibbs (Chap. 13), the full theory of Statistical Thermodynamics. The statistical perspective allowed Boltzmann to see that it was the distributions of energy that allowed an understanding of entropy. The *Lectures on Gas Theory* and *Lectures on Natural Philosophy* complete the classical development of the structure and dynamics of material media.

Ludwig Boltzmann (1844–1906) is one of the Olympians of Heat (Fig. 15.1). Although he lived before the construction of Quantum Mechanics, he was able to bring Classical Mechanics to its highest level. He received his Ph.D. from the University of Vienna in 1869 with Joseph Stefan (1835–1893). During his habilitation period he studied with Bunsen in Heidelberg and with Kirchoff and von Helmholtz in Berlin. He had a brilliant career at the University of Graz from 1876–1890. Two of his most famous students were Svante Arrhenius (1859–1927) and Walther Nernst (1864–1941). Eventually he returned to the University of Vienna in 1894. Two of his leading students from this period were Paul Ehrenfest (1880–1933) and Lise Meitner (1878–1968).

Boltzmann's contributions to the subject of heat are well summarized in his magisterial *Lectures on Gas Theory* (1896, 1898) [1]. The following essay follows this book in detail.

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G. D. Patterson, *From Heat to Thermal Science*, Perspectives on the History of Chemistry, https://doi.org/10.1007/978-3-031-99676-4_15



Fig. 15.1 Ludwig Boltzmann, The Master of Classical Statistical Thermodynamics (public domain)

15.1 Introduction to the Theory of Heat

Boltzmann openly acknowledges the fundamental contributions of Clausius and Maxwell to the Theory of Heat. He also relates his own work to that of essentially all the other physicists of his era. He saw the process as a team effort, although some of the episodes were more like wars. Unlike many of the German physicists of the late nineteenth century, Boltzmann was pragmatic about the ability of physicists to completely comprehend physical reality. While a phenomenological theory had its uses, the microscopic perspective was essential for deeper understanding. Boltzmann was also a consummate mathematician. This allowed him to interact at the deepest level with all of nineteenth century physics.

Boltzmann distinguished between the "General Theory of Heat," by which he meant pure Thermodynamics and Hydrodynamics, and the "Special Theory of Heat," by which he meant a systematic development of the macroscopic consequences of a microscopic model of matter. The utility of the model was judged by its ability both to "save the phenomena" and to point to key new experiments to test matter at the microscopic scale. Boltzmann was the enemy of obdurate dogmatism.

Boltzmann anticipated the importance of the role of "waves" in the understanding of the dynamics of condensed media. While a wholly Newtonian perspective focuses on the actual "particles" of which the matter is composed, Boltzmann envisioned matter as an ensemble of collective excitations involving many particles.

Boltzmann also viewed himself as a "Natural Philosopher." His magisterial *Lectures on Natural Philosophy* (1903–1906) are the "last word" on the classical view

of Nature [2]. He knew that Chemistry and Crystallography were only a coherent science on the assumption of microscopic units. René-Just Haüy (1743–1822) constructed the correct theory of crystalline solids by examining the faces of the crystals, both before and after "cleavage." He rationalized this theory by proposing that there were "unit cells" in the crystal that fully reflected the geometry of the full crystal. Long before the discovery of X-ray diffraction, Haüy envisioned the geometry of the unit cells. John Dalton (1760–1844) rationalized the known chemical reactions by positing a set of "Chemical atoms" that fully contained the essential physics that distinguished each known element. The "dawn of modern Chemistry" was a long way from the present, and the concept was violently resisted by physicists for another century. But every scientist that adopted this perspective made progress in their understanding of Chemistry. The results of the Positivists were mostly "negative." Remarkably, Haüy's theory of crystals was immediately adopted and refined.

Boltzmann viewed his work as that of a "conductor." He needed to know all the possible models for physical reality and how they might be combined to produce the observed macroscopic effects. If his model was incoherent, it would not be of use to anyone. He was "willing to be wrong," but not to be confused!

Boltzmann realized that the "simplest" type of solid matter would be a lattice of particles. He reasoned that each particle was characterized by a potential energy that depended on its location relative to its neighbors. He also intuited that, at finite temperature, each particle would have a fluctuating amount of kinetic energy. Good ideas often come to prepared minds.

15.2 Calculation of the Gas Pressure

Boltzmann starts with a simple model of a gas: N spherical particles of mass, m, contained in a vessel of volume, V, and characterized by a total kinetic energy, E. He understood very well that the thermodynamic pressure, P, was the long-time average of the force per unit area on the wall. (Pressure is also defined locally as proportional to the long-time average kinetic energy per unit volume.) The derivation is clear and careful. The final result is the familiar:

$$P = (1/3)(N/V)m\langle c^2\rangle \tag{15.1}$$

where $\langle c^2\rangle$ is the mean-squared particle speed. Given the extensive experimental demonstrations of this result, and the rigorous theoretical derivation, it required strong "ideology" to reject this explanation of the gas pressure. Starting from this fictive theory, improvements were easy to include to achieve better and better "equations of state:" $P(N, V, T)$.

15.3 Boltzmann's Proof of the Distribution of Particle Velocities

Boltzmann always thought more deeply about real situations than was required for pedagogical purposes. He discussed the consequences of collisions among the particles of finite diameter, d. Even if the system started off with all particles having the same velocity, after a while there would be a distribution of velocities:

$$f\left(v_x, v_y, v_z, t\right) \tag{15.2}$$

Boltzmann was an expert in functions of many variables. For the equilibrium distribution, no particular direction can be preferred. This means that the distribution can be factored into three parts:

$$f(\vec{v}, t) = F(v_x, t)F\left(v_y, t\right)F(v_z, t) \tag{15.3}$$

Boltzmann included an explicit time in these functions. He "knew" that, in addition to the long-time average, there would be continuous "fluctuations" in the instantaneous assembly of particle velocities. He strongly "suspected" that the understanding of the entropy depended on the existence of both distributions and fluctuations.

There are many forms of the "Boltzmann Equation" in current literature. In this book only the effect of collisions is considered. The mathematical form in modern dress is:

$$\left(\frac{\partial f(\vec{v}_1, t)}{\partial t}\right) = \pi N d^2 \int\limits_{\text{all } \vec{v}} \|\vec{v}_2 - \vec{v}_1\| \left[f\left(\vec{v}_1', t\right) f\left(\vec{v}_2', t\right) - f(\vec{v}_1, t) f(\vec{v}_2)\right] d\vec{v}_2 \tag{15.4}$$

where the primed velocities are "after the collision." One of the consequences of the existence of the distribution function is the so-called Boltzmann H Theorem:

$$H(f(\vec{v}, t)) = \int f(\vec{v}, t) \ln f(\vec{v}, t) d\vec{v} \tag{15.5}$$

The function, H, eventually approaches "stationarity." When it does, the only mathematically possible form is then:

$$f(v) = A 4\pi v^2 \exp\left(-Bv^2\right) \tag{15.6}$$

where the Maxwell form for the speed distribution is obtained. For the uninitiated modern reader, Boltzmann takes the reader on a long journey through obscure mathematical territory in order to reach a well-known result. But, the use of the H Theorem was well worth the effort. Heat is as much about the distribution of energies as it is about the average values. Boltzmann notes that the average value of v^2 is: $< v^2 > = (3k_{\mathrm{B}}T/m)$, which means that $B = (m/2k_{\mathrm{B}}T)$.

15.4 Specific Heat of Real Gases and the Meaning of Entropy

Boltzmann was well aware that there are two forms of energy: kinetic and potential. He adds the potential energy contribution to the obvious kinetic energy part and obtains both constant volume and constant pressure specific heats:

$$c_V = \left(\frac{3R}{2M}\right)(1 + \beta(T))$$
$$c_P = \left(\frac{R}{2M}\right)[3(1 + \beta(T)) + 2] \tag{15.7}$$

where M is the atomic or molecular weight of the gas and $\beta(T)$ can be obtained from the actual equation of state for the gas.

As part of the derivation of the specific heat Boltzmann constructs an equation for the differential of the heat, dQ. This is not an exact differential, but dQ/T is exact. He then integrates the result to yield:

$$\int \frac{dQ}{T} = Nk_B \ln\left[\frac{T^{(3/2)(1+\beta)}}{\rho}\right] + \text{const.} \tag{15.8}$$

Boltzmann immediately recognizes this as the entropy, $S(T, \rho, N)$, of the gas!

He then evaluates the function H for a perfect gas that is characterized by the Maxwell–Boltzmann distribution:

$$f(v) = A \exp\left(-\frac{mv^2}{2k_B T}\right) \tag{15.9}$$

The result is:

$$H = N \ln A - (3N/2) \tag{15.10}$$

Evaluation of A yields, apart from a temperature and density independent constant:

$$H(T, \rho) = -N \ln\left(\frac{T^{3/2}}{\rho}\right). \tag{15.11}$$

Boltzmann notes the clear relationship between H and S! This very detailed analysis of the thermodynamics and transport of real gases produces a compelling argument. Boltzmann summarizes: “The second law is thus found to be a probability law. We have generalized the conception of the entropy to include non-stationary gases.”

15.5 Advances in Kinetic Theory

While most chemists remember Boltzmann for his theories of equilibrium, most of his major work was concerned with the transport properties of gases. Thermal conductivity is indeed a transport property and must be considered in tandem with the other simple measurable quantities: the viscosity and the diffusion coefficient. The key issues in kinetic theory are the "collision frequency," the "mean free path, λ" and the "velocity distribution." Boltzmann presents a mathematically precise discussion of the role of each of these quantities in the description of transport.

With the general concepts in hand, specific transport coefficients can be discussed in terms of "what is being transported." The approach is still the classic version taught in all advanced undergraduate courses in Chemical Engineering. A group of thin layers is considered. In order to have transport, there must be a gradient in the property of the particles. For example, the shear viscosity is discussed in a system with an average velocity gradient in the direction perpendicular to the layer: $v_z(z)$. The quantity being transported is momentum: mv_x. The total flux at some value of z is approximated by the downward flux of momentum from one mean free path above the test layer plus the upward flux from one mean free path below. Boltzmann presents a general equation for the flux of some quantity, G, due to a gradient in G:

$$\Gamma = \left(\frac{n}{3}\right) c\lambda \left(\frac{\partial G}{\partial z}\right) \tag{15.12}$$

where n is the number density and c is the "average" speed. Applying this to the shear viscosity yields:

$$\eta = m\left(\frac{k_B T}{\pi m}\right)^{1/2} \left(\frac{1}{\pi d^2}\right) \tag{15.13}$$

where d is the collision diameter. Boltzmann also presents a more sophisticated calculation that yields an initial multiplier of $(5\pi/16)$ instead of 1. The relevant flux for thermal conductivity is the energy flux, and the relevant gradient is the temperature gradient. All the "energy" in this system is translational kinetic energy: $(1/2)mv^2$. The thermal conductivity is then:

$$\lambda = 2\left(\frac{3k_B}{2}\right)\left(\frac{k_B T}{\pi m}\right)^{1/2} \left(\frac{1}{\pi d^2}\right) \tag{15.14}$$

While Boltzmann was satisfied with this result, more precise treatments yield $(25\pi/32)$ rather than 2 as the initial factor. This formula helps to explain the lack of a density dependence in the thermal conductivity; the higher density is counteracted by a lower mean free path. It also explains the temperature dependence. But, when molecules are measured, the thermal conductivity is much higher. Each particle now also transports rotational energy.

Boltzmann was especially sensitive to the influence of dissipative processes on the production of entropy in transport processes. He was joined in this line of reasoning by Lord Rayleigh. The demarcation between "equilibrium properties" and "transport properties" is not a helpful restriction.

In spite of the rigor and coherence of Boltzmann's work, the dogmatic culture of European science in the late nineteenth century was opposed to "approximate" theories of matter. Only macroscopic, measurable properties could be discussed and related to one another through exact thermodynamic identities. There was also a cult of "energy." One of Boltzmann's greatest contributions to science was his exploration of the role of distributions of energy in the properties of matter. Boltzmann's name will be remembered long after most scientists have forgotten the Nobel Prize winner, Wilhelm Ostwald.

One Nobel Prize winner that appreciated Boltzmann's work was Johannes van der Waals (1837–1923). He presented his thesis, "On the Continuity of the Gaseous and Liquid States," in 1873. Maxwell hailed it as a triumph (see Chap. 14). The van der Waals equation is explicitly "empirical," but it explains qualitatively the complex phase diagram for a liquid and its corresponding gaseous state [3]. Only by adopting both the notion of interparticle repulsion and attraction could such a phenomenon be modeled. Modern liquid theory employs a Boscovicean interparticle potential. Van der Waals employed an averaged approach including an "occupied volume," (v_0), and an average attractive potential energy, ε, that changed the pressure. The form is the familiar:

$$P(N, V, T) = \left(\frac{Nk_BT}{V - Nv_0}\right) - \frac{N\varepsilon}{V^2}. \tag{15.15}$$

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John Tyndall: Infrared Radiation as Heat

16

Abstract

John Tyndall was a major transitional figure in the History of Heat. One of his areas of expertise was Radiant Heat (Infrared Radiation). He carried out thousands of experiments on all forms of matter subjected to infrared radiation. Selections from two of his monographs are discussed in detail: *Contributions to Molecular Physics in the Domain of Radiant Heat* (1873) and *Heat: A Mode of Motion* (1900). Much of his apparatus constructed at the Royal Institution in London is still intact. He was a worthy successor to Michael Faraday.

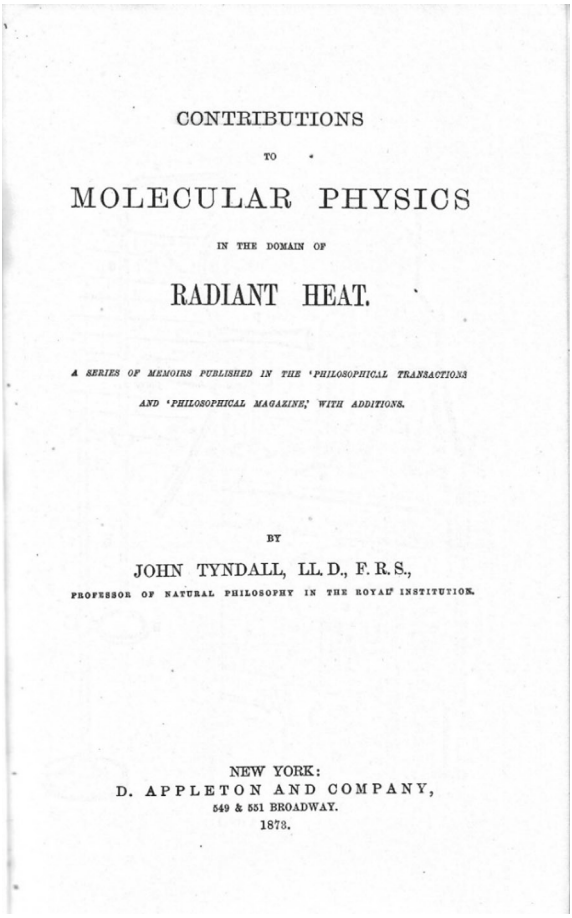
The Royal Institution was the site of many seminal investigations of heat. John Tyndall (1820–1893) was the Professor of Natural Philosophy from 1854–1887. Some of his research in this area is published in his collection: *Contributions to Molecular Physics in the Domain of Radiant Heat* (1873) (Fig. 16.1) [1].

Tyndall was a consummate experimentalist. He attended the University of Marburg and worked with Robert Bunsen and Hermann Knoblauch. He received his Ph.D. in 1850. He also worked with Heinrich Gustav Magnus at Berlin. He returned to England and conducted independent research on magnetism. He was elected a Fellow of the Royal Society in 1852. He became a Professor at the Royal Institution in 1854. He and Michael Faraday were staunch colleagues, and Tyndall wrote a sweet biography of Faraday [2]

While Tyndall carried out many "fundamental" studies of heat, he was always thinking about the material world in which he lived. He was able to explain why the Earth is warm enough at the surface to support life. Light from the sun warms the surface of the Earth, which then emits "radiant heat." This form of light is absorbed by water vapor and carbon dioxide in the atmosphere and is hence not lost to space. (The greenhouse effect.)

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CONTRIBUTIONS

TO

MOLECULAR PHYSICS

IN THE DOMAIN OF

RADIANT HEAT.

A SERIES OF MEMOIRS PUBLISHED IN THE 'PHILOSOPHICAL TRANSACTIONS AND 'PHILOSOPHICAL MAGAZINE,' WITH ADDITIONS.

BY

JOHN TYNDALL, LL.D., F.R.S.,

PROFESSOR OF NATURAL PHILOSOPHY IN THE ROYAL INSTITUTION.

NEW YORK:
D. APPLETON AND COMPANY,
549 & 551 BROADWAY.
1873.

Fig. 16.1 Title page of Tyndall's *Contributions* (1873) [1] (Scanned from my personal copy)

16.1 Memoir I: On the Absorption and Radiation of Heat by Gases and Vapours, and on the Physical Connexion of Radiation, Absorption, and Conduction

Tyndall used this thinking to study the absorption of radiant heat (infrared light) by many gases. His source of radiant heat was a blackbody (a copper vessel with lampblack on the surface) warmed by boiling water within. In addition, he used two such sources and detected them with a thermopile. He adjusted the intensity of one of the sources to balance the output of the thermopile to create a differential detector. Absorption by simple gases like nitrogen and hydrogen was barely detectable. Devices like the thermopile (a collection of thermocouples in series) allow heat to be converted to electrical potential energy. The Royal Institution had the best galvanometers in the world and when the two leads of the thermopile were

connected across the galvanometer it could be nulled by adjusting the temperature of the two sides of the thermopile. This was a masterpiece of classical physics.

Tyndall also verified and discussed one of the most important "facts" of molecular optics: systems that are good absorbers of radiant heat are also good emitters. He lived during the era when light required a "medium" (the aether) in order to facilitate transmission. He also lived too soon to realize that there were intramolecular processes that could interact with electromagnetic waves. He also was confused about the compound nature of elementary gases such as oxygen and nitrogen. He envisioned them as monatomic. But he observed directly that heteronuclear molecules often absorbed heat strongly.

From a more modern perspective, what kind of infrared radiation was being emitted from a blackbody at 373 K? The peak wavelength would be near 3.86×10^{-5} m. This corresponds to vibrational frequencies of molecules. Tyndall chose molecules that were transparent to visible light. These molecules do absorb ultraviolet light. Ozone is formed when diatomic oxygen molecules are dissociated by ultraviolet radiation and the atoms combine with diatomic molecules. Molecular optics had a long way to go in 1873.

16.2 Memoir II: Further Researches on the Absorption and Radiation of Heat by Gaseous Matter

Tyndall decided to use a radiant source at a higher temperature: A copper plate coated with lampblack was the emitter. A special heater based on a Bunsen burner produced the constant heat source at 270 °C. His first gas was chlorine. It absorbed in the visible range and in the infrared. Tyndall was able to produce and purify ozone, O_3. Unlike diatomic oxygen, ozone is a strong absorber in the infrared. It is not clear from the memoir that Tyndall knew that ozone was triatomic. It is also clear that Tyndall did not know why chlorine absorbed in the visible range when other elementary gases did not.

Tyndall compared pure diatomic chlorine to hydrochloric acid gas. The acid is transparent in the visible range and absorbs more infrared radiation than chlorine. He also examined pure bromine vapor, Br_2, and hydrobromic acid gas. Bromine is highly colored in the visible and in the infrared region. Hydrobromic acid is transparent in the visible range and highly absorbing in the infrared range. Tyndall established the "facts" but had no coherent explanations.

Tyndall did understand that electromagnetic radiation had a characteristic frequency. In order for another physical system to absorb this specific radiation, there needed to be a corresponding process in the system with the same or similar frequency. The physical principle of "resonance" was firmly established in pure mechanics. And there was every reason to believe that the principle would apply to light. But without a clear spatio-mechanical model of a molecule, there was no way to calculate the intramolecular dynamics. This issue was solved by Jacobus van't Hoff (1852–1911).

Tyndall also compared nitrogen (N_2), nitric oxide (NO) and nitrous oxide (N_2O). Nitrogen absorbs very little infrared radiation. Nitric oxide absorbs substantial amounts and nitrous oxide even more. Ammonia (NH_3) absorbed much more. Tyndall could have made a career carrying out more experiments using this apparatus, but until a better understanding of the structure and dynamics of a molecule was obtained, no cogent theory would be possible.

16.3 Memoirs V and VI: Contributions to Molecular Physics

Liquids and solids also absorb radiant heat. Tyndall studied many substances in both the gaseous and liquid states. He concluded that infrared absorption was dominated by intramolecular processes.

Memoir VI is a reprint of the Bakerian Lecture for 1864. This represents the pinnacle of work in this time frame. Tyndall now uses a spiral of platinum as his optical source. He also invented a liquid cell with rock salt plates as the windows (Fig. 16.2).

Tyndall examined 11 different liquids. Bisulphide of carbon (CS_2) absorbed the least and water absorbed the most. He then examined the same substances, except water, as gaseous vapors. The order of absorption changed for some of the gases, indicating that the condensed state did influence the overall absorption. Tyndall understood that equal volumes of gases at the same temperature would have the

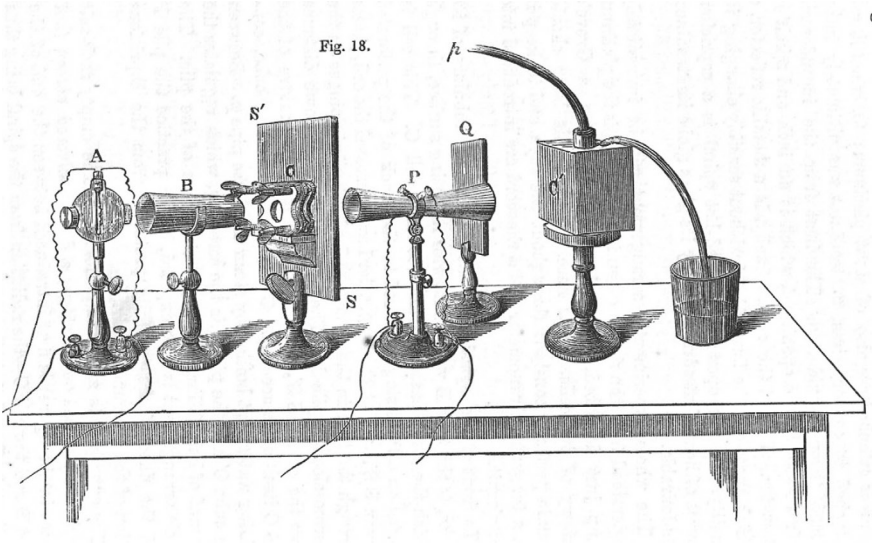


Fig. 16.2 Infrared absorption apparatus: A, platinum source; B, infrared waveguide; C, rock salt plate liquid cell; S, insulating screen with circular hole; P, thermopile; Q, compensating screen; C', hot water infrared source

same number density of molecules. In the liquid state, this need not be so, since the molar volumes of these liquids differ. When the substances were compared at constant number density, the order in both liquid and gas was retained.

Tyndall was at the forefront of thinking about molecules. He reported correct atomic formulas for all his substances. One empirical correlation might be that the absorption is proportional to the absolute number of atoms in the molecule. This turns out not to be true. The presence of oxygen elevates the absorption. These are early days in the rapid progress in chemical understanding of the late nineteenth century.

One optical property that did correlate well with the atomic direct contributions was refractive index, n. But, even here, different atoms made different contributions. The classic formulas for the molar polarizability and the dependence on the refractive index are:

$$\alpha_{\text{mol}} = \sum_i n_i \alpha_i$$
$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi \rho N_A \alpha_{\text{mol}}}{3M} \tag{16.1}$$

where the n_i are the number of atoms of type i in the molecule, the atomic polarizabilities α_i become constitutive contributions to the molecular polarizability, ρ is the mass density, M is the molar mass and N_A is Avogadro's number. The second equation is called the Lorentz-Lorenz equation.

16.4 Memoir VII: On Luminous and Obscure Radiation

Tyndall discovered that bisulphide of carbon was almost transparent to infrared radiation. Solid iodine dissolves well in CS_2. The iodine absorbs all the visible light, but does not absorb infrared light. As a result, a prism could be filled with a solution of iodine in carbon disulfide and only infrared light would be dispersed in the transmitted light. He did not know exactly why, but this "fact" remains true today. With a spectrum of infrared light now available, Tyndall could progress to true spectroscopy.

While the earliest studies of the infrared spectrum depended on sunlight, Tyndall could use platinum wire as his "glower." He started at the lowest current that could be detected with the thermopile. He placed the thermopile in the infrared region, which then corresponded to a "slice" of the emission spectrum. As he heated the platinum, the intensity of the slice continuously increased (Fig. 16.3).

We now know what the full "black-body spectrum" looks like as a function of temperature (see Fig. 16.4), but in 1864 Tyndall was already on the correct track. Even from a classical perspective, the Boltzmann factor (16.2) rises with temperature for all values of the energy, ε:

$$\exp\left(-\frac{\varepsilon}{k_B T}\right) \tag{16.2}$$

TABLE I.

Appearance of Spiral	Deflection by obscure rays °	Appearance of Spiral	Deflection by obscure rays °
Dark	1	Full red	27
Dark	6	Bright red	44·4
Faint red	10·4	Nearly white	54·3
Dull red	12·5	Full white	60
Red	18		

Fig. 16.3 Relative deflection of the thermopile as a function of the visible color of the platinum wire

The Wien displacement law locates the peak in the blackbody spectrum wavelength at a value inversely proportional to the absolute temperature.

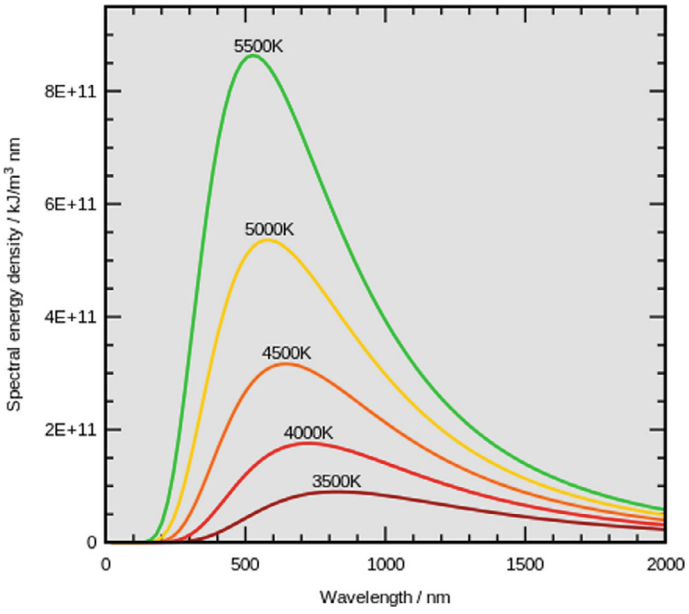


Fig. 16.4 Blackbody spectrum as a function of temperature (CC BY-SA 3.0, https://en.wikipedia.org/wiki/Wien%27s_displacement_law). The peak of the spectrum at approximately 4000 K is the longest wavelength visible to humans

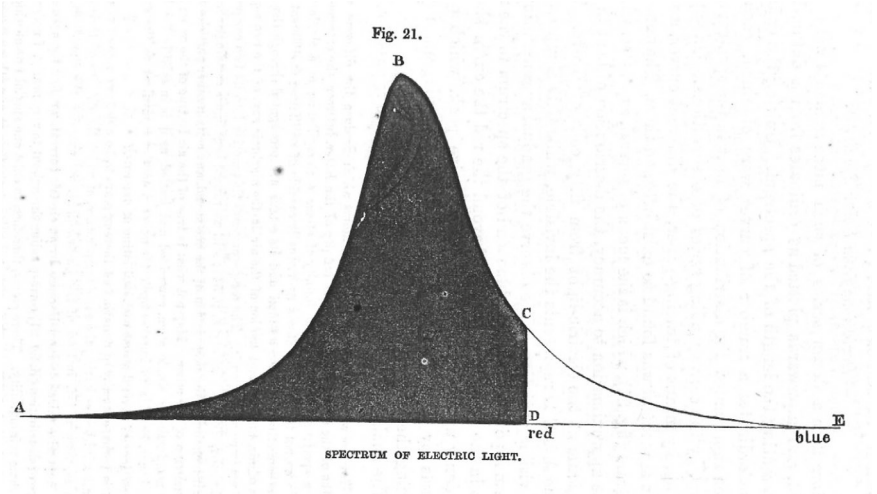


Fig. 16.5 Visible and IR spectrum of a carbon-arc electric light (scanned from my copy of "Contributions." Most of the light is not visible by humans!

16.5 Memoir VIII: On Calorescence, or the Transmutation of Heat Rays

Tyndall knew that the infrared rays were a form of energy. He could focus them and produce combustion in any inflammable substance. He explored what would happen if his platinum was placed at the focus of his IR beam. Once the energy was absorbed by the platinum, the overall temperature of the sheet of platinum could be raised. When it did, the sheet became a glower of blackbody radiation of much shorter wavelength than the exciting IR radiation (radiant heat). While total energy is conserved, the distribution of radiated energy adopts the blackbody spectrum. Tyndall called this "calorescence." In a solid, the local energy fluctuates until the distribution reaches the "most probable state." Boltzmann would have been proud.

Another source of both visible and infrared light is the carbon arc electric-light. Tyndall measured the emission spectrum of this source (Fig. 16.5).

16.6 Lord Rayleigh and the Scattering of Light

John Tyndall carried out thousands of experiments on the interaction of infrared light with matter. When it is absorbed, the material is strongly heated and becomes an emitter of blackbody radiation. Further experiments in his era would not have advanced our understanding very much, since the model of reality was limited by the influence of the "aether." Nevertheless, there was still much to be done to complete the classical model of reality.

Lord Rayleigh took Maxwell's Equations and derived an explicit formula for the scattering of light by atoms and molecules. Atomic matter is "polarizable." This means that when atomic matter is subjected to an electric field, a dipole moment is induced. The simple equation is: $\vec{p} = \underset{\sim}{\alpha}\vec{E}$, where the full tensor character of the polarizability is acknowledged. Since the electric field of light is oscillating, the dipole also oscillates at the same frequency. An oscillating dipole is an emitter of electromagnetic radiation. The Rayleigh formula for the normalized intensity of light scattered by a gaseous collection of atoms, R, is:

$$R = \left(\frac{16\pi^4}{\lambda^4}\right)\left(\frac{N}{V}\right)\alpha^2 \tag{16.3}$$

where λ is the wavelength of the light and N/V is the number density of atoms. This predicts that light scattered in the atmosphere will be predominantly blue. Tyndall observed the blue tint in the laboratory by creating strongly scattering systems and strong collimated sunlight. He also observed that pristine glaciers appear blue due to light scattering. C.V. Raman (1888–1970, Nobel 1930) observed the blue of the clearest ocean water as well.

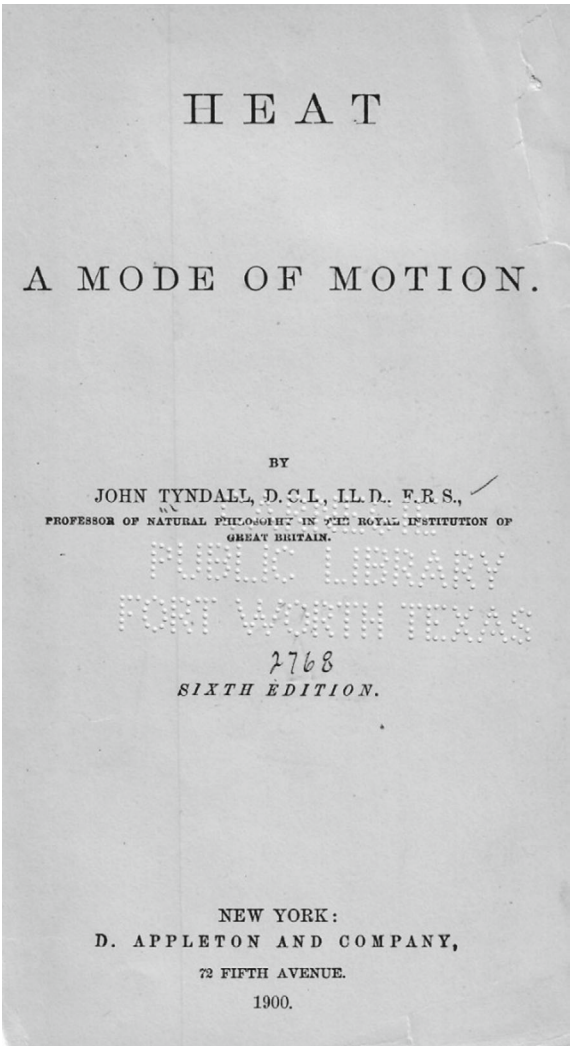
16.7 Heat: A Mode of Motion (1900)

In 1880 Tyndall published the first edition of his classic "Heat: A Mode of Motion." It was updated until after his death and finally issued as a Sixth Edition in 1900 (Fig. 16.6) [3]. The book is organized as a series of "Lectures." It is the last word from the Classical Era.

Observable natural phenomena can be characterized by a set of defining experiments that expose the full range of facts associated with them. Tyndall always tried to push as far as he could to collect these facts. He then presented them to the scientific public in London at the Royal Institution, just like Faraday. The book is organized around 17 such lectures. Any "theory" of heat must be able to explain all the facts demonstrated by Tyndall! But any fact actually comes with its own set of circumstances and experimental details. Tyndall was sensitive to the realities of real science.

16.8 Lecture I: Introduction and Experimental Descriptions

Tyndall was an expert in the use of the "thermopile." It is a very sensitive detector of heat. One of the realities of motion in a real physical world is friction. When a solid object interacts with its environment during motion relative to the environment, kinetic energy is lost due to the creation of heat energy. Tyndall demonstrated this with the thermopile after subjecting cold knives to motion on a sharpening stone. They became warmer. When viscous liquids are subjected to


HEAT

A MODE OF MOTION.

BY

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2768

SIXTH EDITION.

NEW YORK:
D. APPLETON AND COMPANY,
72 FIFTH AVENUE.
1900.

Fig. 16.6 Title page of the Sixth Edition of *Heat: A Mode of Motion* (1900) [2] (scanned from my personal copy)

flow within a bounding surface they transfer kinetic energy to heat energy. Even pouring a liquid between two glasses raises the temperature of the liquid. When a solid is forcibly deformed, the energy of deformation eventually produces heat.

Tyndall also discusses the transport of kinetic energy by matter such as raindrops or meteorites. When raindrops are captured by a pond, the temperature of the pond is raised. The kinetic energy of the falling matter is stored by the pond as heat. In the context of our discussion of heat, it is coherent to treat moving matter (convection) as a form of heat: energy that moves.

Tyndall employed the Peltier effect in his studies of heat. Jean Charles Athanase Peltier (1785–1845) was a French physicist that explored electromagnetic effects.

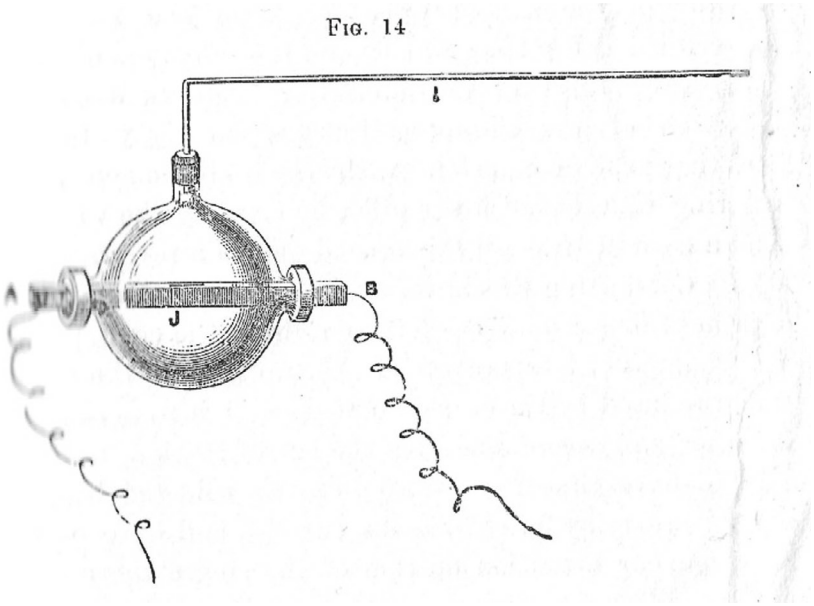


Fig. 16.7 Peltier junction differential thermometer (scanned from Heat [3])

One of his sets of experiments involved a junction between two different metals, such as bismuth and antimony. When current flows in one direction through this junction heat is produced. When the direction of the current is reversed the junction becomes colder. Tyndall created his own precise apparatus to study this phenomenon (Fig. 16.7).

A small liquid drop in the horizontal tube serves as the indicator. *J* is the intermetallic junction, and an external source of voltage can be attached at electrodes A and B. When the current flows one way the bead moves to the right, indicating an increase in the temperature of the gas in the large bulb. When the current is reversed, the bead moves to the left. This classic experiment never failed to excite the audience, but is usually forgotten today. This effect is still employed in many ways industrially. Tyndall pictured the system as like a waterfall. If the electrons had to overcome the increase in potential, they would lose energy and the metal would be cooled. If they gained energy by moving from the higher to the lower potential, they could heat the metal on that side of the junction.

Tyndall was a great believer in the universal truths of physical reality, especially the conservation of energy. Many "particles" can carry energy, including electrons. The twentieth century would make explicit that energy could be transported by coherent excitations in both material media (phonons) and in the electromagnetic field (photons).

Tyndall was also a keen observer of Nature. He was a noted Alpinist and wrote a book on glaciers. He thought about the coupling between the energy of the

atmospheric particles and the gravitational field of the earth. The average velocity of atmospheric particles must decrease as they ascend, due to the pull of the Earth. And by 1900, the correlation between temperature and the average speed of gas particles had been calculated by Maxwell and Boltzmann (see Chap. 15).

16.9 Lecture II: Historical Discussion of the Nature of Heat

In addition to being a great lecturer and a writer of worthy prose, Tyndall was a keen student of the history of science. He noted that Plato considered heat to be a kind of motion. This perspective was expressed by Francis Bacon as well. Descartes believed that heat was a kind of motion.

Isaac Newton had particular ideas about both light and heat. He believed that light was a form of matter. Euler, on the other hand, considered heat to be a form of matter. Robert Boyle understood that mechanical deformation, a process that required the expenditure of energy, transferred energy to the solid in the form of heat. But the greatest philosopher of heat in the Early Royal Society was Robert Hooke. Although Hooke was a great mathematician, he was an even better geometer, and could visualize many phenomena, including particle motion. Hooke discussed the phenomenon of "shaken sand." It behaves like a liquid and can dissipate disturbances rapidly. Hooke claimed that all known matter was in constant motion at the smallest scale.

Tyndall was a great admirer of the founder of the Royal Institution, Count Rumford. Benjamin Thompson proved that heat was imponderable. There is a difference between the carrier of the heat and the heat itself.

16.10 Lecture III: The Notion of Chemical Heat

Humans have been "burning" matter for millenia. Where does the "heat" come from? Tyndall envisioned matter as having chemical potential, which is analogous to electrical or gravitational potential. When the chemical potential of the products of a chemical reaction is lower than the reactants, heat can be produced. Humans often focus on the light associated with combustion, but Tyndall knew that most of the energy was associated with infrared radiation. The oxy-hydrogen torch has one of the hottest flames, but is almost invisible in the laboratory. This is dangerous! The product, water vapor, does not produce much visible light.

When the oxy-hydrogen flame is directed on a lime sample, the phenomenon of "calorescence" occurs: the energy is processed into very bright white light. (Yes, solids can take infrared light and convert it to visible light. YAG lasers produce infrared light which can be doubled or tripled in appropriate crystals.)

16.11 Lecture IV: The Notion of Dilatation

While the volume of a gaseous sample can be linearly proportional to the absolute temperature at constant pressure, the volume of a solid can be insensitive to temperature. Liquids can even display a decrease in volume upon heating. The natural philosophy of pure substances has now been studied in great detail. Tyndall knew that the "equation of state" for each phase was a complicated function of temperature and pressure: $V(P, T)$. His own specialty was precise measurement of small deviations.

The "facts" he documented implied that the structure of dense gases, liquids and solids was more complicated than the isotropic dilute gas phase. While for Tyndall, heat was a "mode of motion," he knew there was more to the story.

One of the most dramatic effects in materials science is the retraction of stretched natural rubber when it is heated. This effect was discovered by John Gough, the blind genius. James Joule carried out exhaustive measurements of this effect as a function of temperature and extension (see Chap. 8). In addition to the increase in the force function $f(T, L)$ with temperature, rubber can crystallize and release heat! This is the "latent heat of crystallization" observed for any liquid to crystal phase transition. The increase in the length produces both a decrease in diameter and optical birefringence in the sample. This oriented liquid now has a higher melting point and can undergo crystallization. Relaxed rubber will also crystallize when cooled.

It would be almost a century after Joule before the microscopic theory of rubber elasticity was constructed by Mark, Kuhn and Flory, but Joule already knew that energy alone was not sufficient to explain the phenomenon. It takes entropy**.** An "Energeticist" theory of matter must fail.

16.12 Lecture V: The Phases of Matter

Even so, following the energy is highly informative. The heat capacity of a material body is determined by the change in energy of the sample divided by the change in temperature. While there can be many types of heat capacities, two forms dominate thermodynamic discussions. When the sample is kept at constant volume, the heat capacity is denoted $C_V(m, V, T)$, where m is the mass. For liquids and solids, the more common form is measured at constant pressure: $C_P(m, P, T)$. In the full Thermodynamic theory of matter, these quantities are expressed as partial derivatives. The partial derivatives of Thermodynamics are the measurable properties of matter.

Both Michael Faraday and John Tyndall often studied systems that were not at equilibrium. Heat flow is explicitly a non-equilibrium phenomenon. Left to itself, such a system will evolve until the temperature is uniform, the pressure is uniform, and the chemical potential is uniform. Tyndall cautioned his listeners to remain patient until the full story was known. He did not live long enough to see that day, but he eagerly hoped for it.

During the late nineteenth century, the technology of refrigeration made rapid progress. One triumph was the liquefaction of atmospheric nitrogen. Pure nitrogen gas was compressed isothermally at the temperature of "dry ice" (CO_2(s)) 195 K. When the pressure was released, the nitrogen expanded, and the work done against the intermolecular attractions of the nitrogen molecules produced rapid cooling. The boiling point of liquid nitrogen is 77 K. Tyndall was highly interested in the value of the absolute zero of temperature. (Even to this day, docents at Science museums claim that there is no motion at $T = 0$ K.) In his own time, Tyndall cited the work of Raoul Pictet (1846–1929) in 1877 announcing the liquification of oxygen. He could estimate the absolute zero of temperature from the equation of state of a dilute gas. He obtained -273 °C. It would be the twentieth century before anyone produced a temperature in this range.

16.13 Lecture VI: The Influence of Pressure on Material Phenomena

Tyndall understood that pressure could influence the phase behavior of matter. One of the most important phenomena for our Earthly system is the pressure dependence of the melting point of water. Ice has a greater molar volume than water. By increasing the pressure, the melting temperature can be lowered below 273 K.

The behavior of a slab of ice when subjected to a beam of infrared light is dramatic. Local melting produces regions of vacuum since the water occupies less volume than the ice from which it was melted. The nonequilibrium history of this system produces the remarkable figure drawn by Tyndall (Fig. 16.8).

John Tyndall was an inveterate traveler and Naturalist. He loved to observe geysers. He liked even more to explain them in detail (Fig. 16.9).

Tyndall knew by experience that the boiling point of water was a function of the geographical elevation of the system. A geyser contains a more or less vertical tube containing water. It is also connected to a geothermal source of steam. The steam heats the water. The column of water also exerts a pressure on the system and raises the boiling point. When the column becomes hot enough, the water superheats until gas pressure from the steam drives the column up. When the local boiling temperature falls below the ambient temperature of the column, violent boiling instigates an explosion as heated steam forces the water upwards and produces more steam which vaporizes more water which produces more steam! Eventually all the water is blown upwards until it is exhausted. It then falls back to earth and trickles back into the subterranean column as cool water. Then the nonequilibrium process starts again.

With Nature as his guide, Tyndall produced a tabletop geyser that he demonstrated to his adoring audience at the Royal Institution.

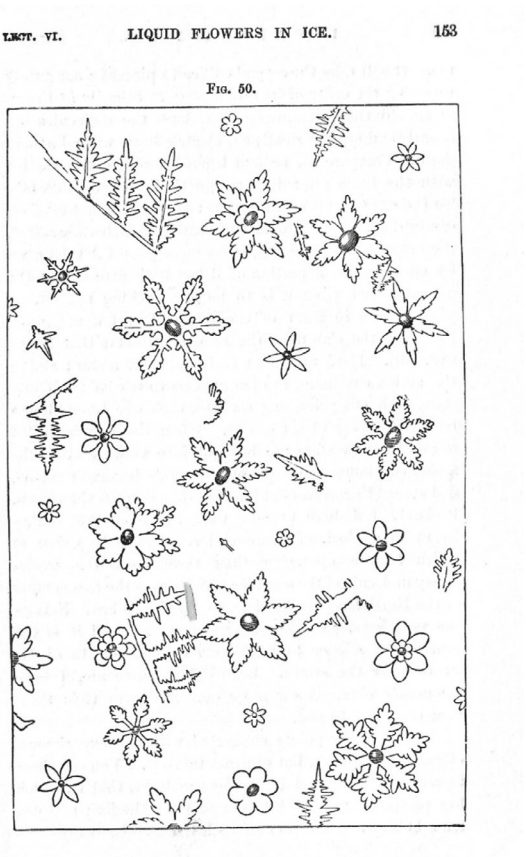


Fig. 16.8 Appearance of a slab of ice after being subjected to a beam of infrared light. Recrystallization of the water produces many different forms. The vacuum regions also remain! (scanned from my copy of *Heat.*)

16.14 Lecture VII: Detailed Discussion of the Complexity of Material Systems

Tyndall was a master of both macroscopic physics and microscopic physics. One of the key concepts of the particle model of matter is that collisions could be elastic (ideal) or inelastic (real). In an elastic collision, kinetic energy is conserved, as is momentum. The kinematics of two body collisions was well-known to him. But he knew that not all collisions were elastic; where did the lost energy go? In addition to kinetic energy (proportional to *vis viva)* the system could contain potential energy stored in either internal modes of the particles or in the interparticle potential field. In this era of physics, there was still terminological confusion about energy and "force." The modern view is that force is the spatial derivative of the potential energy:

$$\vec{F} = \vec{\nabla}\phi(\vec{r}). \tag{16.4}$$

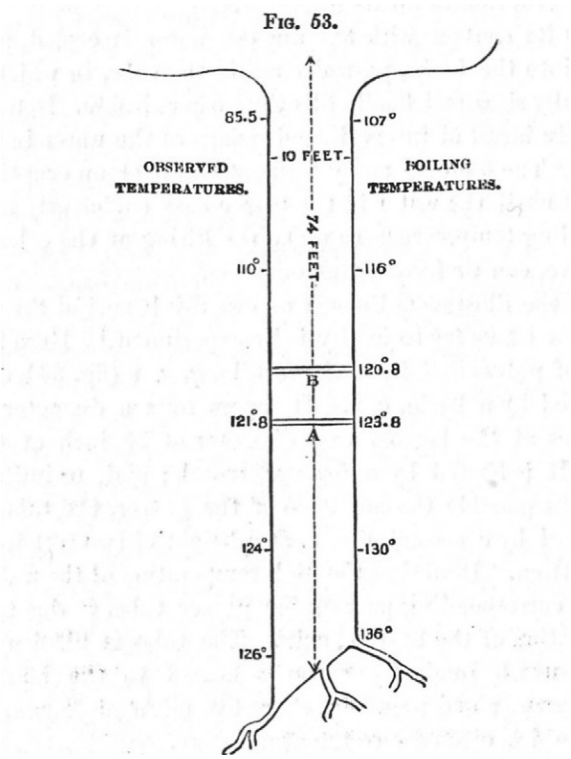


Fig. 16.9 Drawing of the essential structure of a geyser. (from *Heat*)

Tyndall was a master collector of remarkable observations. Lead is certainly known as a solid at ambient temperature and pressure. Water is a liquid under the right conditions of temperature and pressure. Water can be confined in the inside of a hollow globe of lead. When sufficient external pressure is applied to the globe of lead, water exudes from the surface. Yes, water can be "forced" through the metal by sufficient force. (Mercury is often cleaned by forcing it through leather.) (Helium cannot be stably contained in certain metal containers, such as nickel and copper.)

Tyndall's microscopic picture of a sample of lead included the crystalline structure of the metal characterized by its volume, $V(T, P)$, and the vibrations of the atoms in the lattice. He did not know that the unit cell was face-centered cubic, but he did know that, even though the atomic weight of lead is the highest of the stable elements(206), its density is only about ½ that of osmium(190). This open structure allows small particles to diffuse through the lattice. Lead also has a very high thermal expansion coefficient for a metal (or any solid). This produces a molar heat capacity (26.650 J/K mol) far in excess of the Dulong-Petit limit ($3R =$ 24.9 J/K mol). It is quite easy to heat lead by beating it! The thermal conductivity of lead (35 W/m K) is low for a metal (silver is 406 W/m K).

Matter can exist in many different phases. A phase is a homogeneous system with its own unique chemical potential, $\mu(T, P)$. Each phase is also characterized by a unique molar enthalpy, $\overline{H}(T, P)$, and molar entropy, $\overline{S}(T, P)$. The absolute condition of phase equilibrium is that the chemical potentials of the two phases must be the same: $\mu_i(T, P) = \mu_j(T, P)$. But the molar enthalpies of the two phases almost always differ. The "latent heat" of a phase transition is the difference in the enthalpies of the two phases:

$$\Delta H_{\text{trans}}(T, P) = \overline{H}_i(T, P) - \overline{H}_j(T, P) \tag{16.5}$$

The enthalpy of the liquid phase is higher than the enthalpy of the solid phase, and heat must be added at constant pressure at the phase transition. The entropy of the liquid phase is also higher than the solid phase. The Gibbs Energy of Transition is:

$$\Delta G_{\text{trans}}(T, P) = \Delta H_{\text{trans}}(T, P) - T\Delta S_{\text{trans}}(T, P) \tag{16.6}$$

Since the Gibbs energy of transition is 0 at the phase transition, there is a unique relationship between the enthalpy and entropy of transition.

Tyndall was aware of the Thermodynamic theory of phase transitions. He was also aware of the Thermodynamic theory of chemical reactions. But he liked to present highly visible demonstrations of these principles. One of his favorite devices was the "Cryophorus" of William Hyde Wollaston (1766–1828). It consists of two glass globes connected by a glass tube. During its construction water is placed in one of the two globes and heated to boiling. A small orifice in the other bulb allows steam to escape until no ordinary air remains. The second bulb is then sealed as well. All the water is now condensed and transferred to one bulb. The rest of the system contains only the vapor pressure of water. The empty bulb is then placed in a vessel with a freezing mixture (below the normal melting point of ice). Water vapor is condensed in this bulb. In order for the water vapor to be produced, it must evaporate from the other bulb, lowering its temperature. Eventually the temperature in the first bulb becomes low enough to crystallize the water! Heat is transferred by the water vapor from one bulb to the other. The heat is then transferred to the freezing mixture.

16.15 Lecture IX: Conduction of Heat

Tyndall gets down to business in this lecture with a deep consideration of the phenomenon of conduction of heat. His initial focus is on thermal conductivity in metals. He first established an ordering of different metals. Silver is the best and bismuth is the worst. Tyndall also noted that the thermal conductivity of metals is proportional to the electrical conductivity. Bismuth has a very low electrical conductivity and hence a very high electrical resistivity.

One of the most important observations of the electrical resistivity is that it increases with temperature. Tyndall could not have known why this was true, but

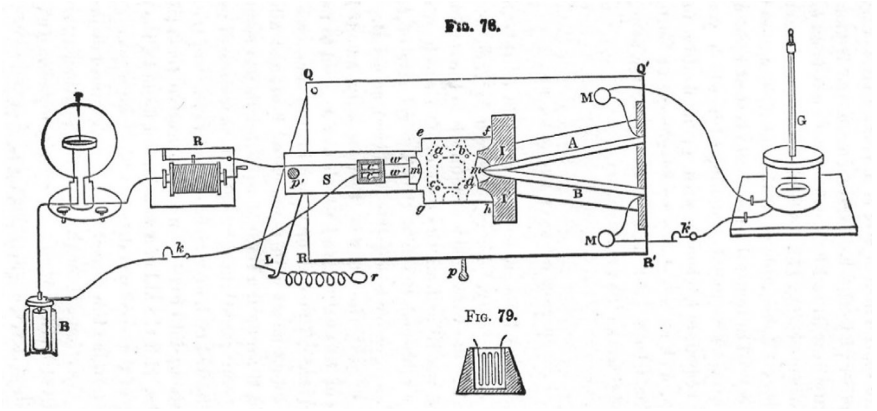


Fig. 16.10 Instrument to measure thermal conductivity. The addition of heat can be carefully controlled. The temperature changes are measured with the bimetallic junction and galvanometer. Precision mechanical adjustments allow precise alignment of all parts of the apparatus

he was sure that it was. He also knew that passing current through a wire led to heating of the metal. Part of the energy of the current was lost due to the production of heat. (All active transport processes in finite density materials produce heat!) John Tyndall was a master experimentalist. His thermal conductivity apparatus is still admirable today (Fig. 16.10).

16.16 Lecture X: Sound and Radiant Heat

In this lecture Tyndall discourses on his favorite subject: Radiant Heat. He also discusses another important thermal phenomenon: Sound. The two types of heat have many of the same properties, but sound requires a material medium and radiant heat is a form of light (infrared). They both are "energy in motion." Sound moves much slower than light, but for materials like diamond, it provides the bulk of the thermal conductivity. For solid materials that can be prepared as "black bodies," heat is communicated to the environment as infrared radiation.

Tyndall died in 1893, just as the issue of the luminiferous ether was being settled. In this volume (written in 1880) Tyndall still needed to work within the dominant paradigm for light. The nineteenth century form of the theory of light was developed by Thomas Young, the Professor of Natural Philosophy at the Royal Institution, just like Tyndall.

A thorough discussion of infrared radiation and its interaction with matter was presented above. Tyndall included some new observations and experiments here. He especially explored the transmission of "radiant heat" and included reflection, refraction and interference. He employed the same type of conical mirrors used by Pictet to focus infrared light, but used his thermopile to detect it. Ever the showman, Tyndall used two very large conical mirrors to transmit the infrared



Fig. 16.11 Tyndall sending "heat" aloft to ignite a balloon filled with hydrogen and oxygen [3]

light from a red-hot blackened copper ball device to ignite a sample 25 feet above him Fig. 16.11).

John Tyndall was one of the best natural philosophers of the nineteenth century. His breadth of both knowledge and interest was stunning. But molecular physics only makes sense when the quantum perspective is adopted. The energy landscape of a molecule is not a continuous function of time and space. All his careful experiments were not enough to allow him to explain his results.

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17 Walther Nernst: *Experimental and Theoretical Applications of Thermodynamics to Chemistry* (1907) and *The New Heat Theorem* (1917)

Abstract

Walther Nernst is perhaps the most important contributor to the understanding of heat in the period surrounding 1900. He was both a great theorist and a consummate experimentalist. He made contributions both at very low and very high temperatures. This chapter is one of the essential parts of the entire book.

Walther Nernst (1864–1941) (Fig. 17.1) was fully aware of the work of Maxwell and Ludwig Boltzmann (1844–1906). He understood that, even in the face of strong resistance to a microscopic (fictive) description of matter, it was the only viable way forward. Nernst was a student of Wilhelm Ostwald (1853–1932) and carried on a long and profitable correspondence, even though Ostwald was a Positivist and did not believe in atoms. Nernst also corresponded with Max Planck (1858–1947) (see Chap. 20) and received his own Nobel Prize in 1920, two years after Planck in 1918. Nernst was both the most knowledgeable physical chemist in this era and the best experimentalist. He was uniquely equipped to attack the hardest problems associated with heat. A good biography of Walther Nernst is *Walther Nernst and the Transition to Modern Physical Science* (1999) by Diana Barkan [1].

17.1 *Experimental and Theoretical Applications of Thermodynamics to Chemistry* (1907) [2]

Building on the work of Joule, Nernst addressed the question of the thermodynamic energy of a physical system [2]. Energy comes in two flavors: kinetic and potential. Kinetic energy can be translational, rotational or vibrational. Potential energy requires that the system be out of equilibrium with respect to the stable state. A simple example is the length of a "spring." The potential energy of the spring at its rest length, l_0, is 0. Hooke's Law expresses the potential energy of

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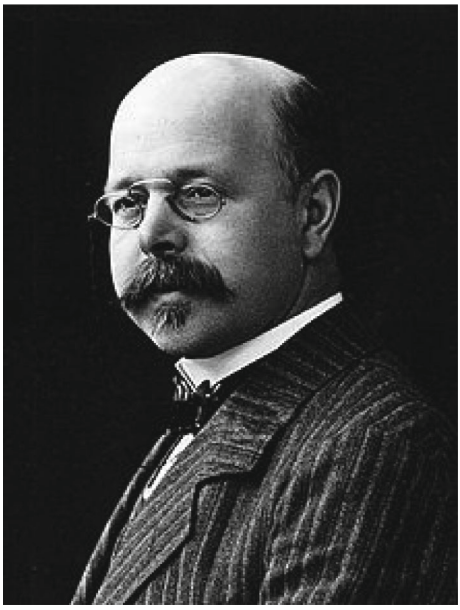


Fig. 17.1 Walther Nernst, the 3rd Prince of Thermodynamics (Public Domain)

the spring as a function of deformation: $u(l) = k_{\mathrm{H}}(l-l_0)^2$, where k_{H} is the linear spring constant. Another common form of potential energy is the gravitational potential energy: $u_{\mathrm{G}}(h) = mgh$, where g is the gravitation constant. If a mass, m, is released from a height, h, it will accelerate towards the surface of the earth. The potential energy will be converted to kinetic energy. A weight driven clock converts gravitational potential energy into mechanical motion. A spring driven clock converts the spring's potential deformation energy into kinetic energy.

One of the forms of energy that Nernst is best known for is electrical potential energy. The potential energy associated with the interaction of two point-charges is:

$$u_E(r_{12}) = k\frac{q_1 q_2}{r_{12}} \tag{17.1}$$

where $k = 9.0 \times 10^9$ N is the Coulomb constant. This electrical potential energy can be converted into other forms of energy, including kinetic energy, heat, or chemical potential energy.

One way of converting electric potential to heat is to induce electric current, I, in a conductor of resistance, R. Ohm's Law states that the current induced is equal to the potential, V, divided by the resistance: $I = V/R$. All "currents" are subject to "loss." The loss energy per unit time associated with electrical conduction, P, is given by Joule's Law: $P = I^2R$. This energy appears as heat.

Joule used electrical conduction in a wire immersed in a known amount of water to measure the heat energy transferred from the metal conductor. (This amounts to the electrical equivalent of heat!) Electrolyte solutions are also conductors of

known resistance. Subjecting salt solutions to an electric potential difference leads to heating of the solution. (It can also produce chemical effects at the electrodes.) The resistance depends on the charge and size of the ions and the viscosity of the solution. Viscosity is a measure of the loss that occurs when an object is moved through a fluid. The momentum of the object is transferred to the solution. In the case of a metal, the current carrier is an electron. The momentum of the electron is transferred to the "body" of the wire. Heat is energy that has been transferred from a carrier of momentum to the body of the environment.

While a diamond at room temperature appears to be quite quiescent, it is actually a region of highly active motion. A perfect diamond (not actually possible) is composed of a fully three-dimensional covalent network of carbon–carbon bonds. The speed of sound in diamond is very high: 12,000 m/s. At room temperature, there are thermal sound waves (phonons) that are created and annihilated constantly. These coherent excitations can be "seen" with Brillouin scattering. (Light is scattered by phonons and the frequency of the light is shifted, based on either the creation or annihilation of the phonon.) When a diamond at very low temperatures is heated, the energy appears as phonons in the body of the sample. Sound is one form of heat: energy that moves! Sound is vibrational energy in a viscoelastic medium.

The speed of sound in a liquid is much lower, since the moduli of compression and shear are much lower than in diamond. Phonons in liquids suffer much more loss than in a solid like diamond. Ultrasonic waves are a good way to heat liquids! Brillouin scattering in liquids probes the distribution of motion in the gigahertz region and when local dynamics are comparable to the frequency of the hypersonic waves, maximum loss is observed. Liquids are anything but quiescent.

Walther Nernst was always curious about physical and chemical reality. If the actual phenomena are not well-characterized, no theoretical clarity will be obtained. Both thermodynamic issues and kinetic issues needed to be settled in order to achieve a coherent picture of heat. Nernst became the leading experimental physicist of his age at both high and ultralow temperatures.

One of the greatest surprises of the late nineteenth centuries was the rapid decrease in the heat capacity of solids at genuinely low temperatures: below 77 K. One of the most illuminating papers on the heat capacities of diamond was published by Sir C.V. Raman in 1957 (Fig. 17.2) [3].

The "theoretical curve" is the famous T^3 Law of Peter Debye (1884–1966). The energy (heat) added to the diamond excites acoustic phonons at low temperature. At sufficiently high temperature, the heat capacity must approach the Dulong and Petit limit:$3R = 5.96$ cal/mol K. The value for diamond at 1000 K is still only 5. At the lowest measured temperature, the value is less than 0.0001 cal/mol K. Above 60 K, a new feature becomes apparent in the vibrational spectrum of diamond: discrete frequencies determined by the actual atomic structure of diamond. Detailed analysis of the symmetries of these local vibrations yields 9 unique frequencies distributed over the 45 possible vibrational degrees of freedom for the diamond unit cell. They are visible in the Raman spectrum of diamond. The discrete vibrations contribute to the heat capacity, since they represent actual

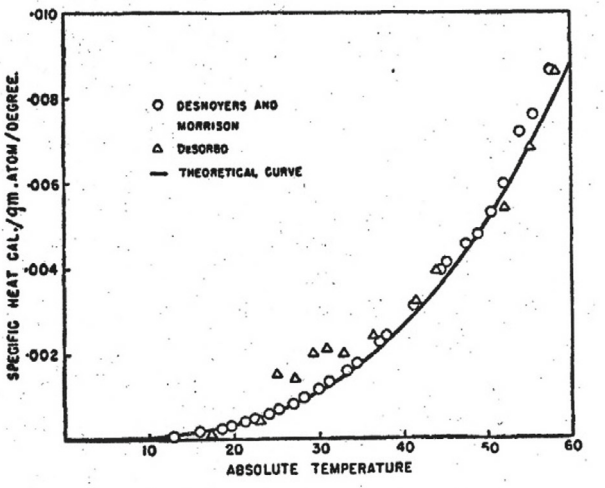


Figure 4. Specific heat of diamond from 0° to 60°.

Fig. 17.2 Specific heat of diamond as a function of temperature [3]

kinetic and potential energy within the diamond sample. But they do not transport energy to other parts of the sample. Hence, they do not contribute to the thermal conductivity.

Liquids retain some of the features of the solid state and some of the features of the gaseous state. Individual particles (molecules or atoms) are free to move throughout the sample, and hence can transport energy as they go. The diffusion of molecules in liquids is a slow process and contributes very little to the thermal conductivity. The velocity of sound is much lower than for diamond, but the phonon contribution to the thermal conductivity of liquids is usually the dominant contribution. Molecules do have internal vibrational modes, which contribute to the heat capacity as the temperature rises, but vaporization may limit the extent to which these modes contribute while the substance is still a liquid.

One way to probe the nature of the molecular vibrational modes and their coupling to the local liquid dynamics is with Brillouin scattering. Longitudinal waves are adiabatic in the hypersonic range. In the "compressed" part of the wave, the temperature is elevated. This means that, if there is a possible coupling between the local temperature and the molecular vibrations, energy can flow between them. This phenomenon is visible as a broadening of the Brillouin spectrum in addition to that due to ordinary viscous effects. (The effect is often called "volume viscosity" since it leads to a loss.) Heat flows between regions of either elevated or depressed local temperature within the acoustic phonon. This heat can either lead to ordinary local heating or cooling (translational or rotational motion) or to the excitation of vibrational modes of the molecules. The macroscopic thermal conductivity of

liquids is easy to measure, and usually contributes a very small broadening to the Brillouin lines. The viscosity is also easy to measure. The excess broadening for many liquids is significant and represents the coupling between the molecular vibrational modes and the translational and rotational motions of the molecules.

17.2 *The New Heat Theorem* (1917)

Nernst received the 1920 Nobel Prize in Chemistry for his formulation of the Third Law of Thermodynamics (The Nernst Heat Theorem). He focused on the thermodynamic Helmholtz free energy, $A(T, V, n)$. Using the relations given above:

$$A - U = -TS = T\left(\frac{\partial A}{\partial T}\right)_{V,n} \tag{17.2}$$

The Helmholtz energy is often called the "work function." Nernst realized that as T approached 0, A-U must also approach 0 (Fig. 17.3). He also realized that it did so asymptotically.

Since $(A\text{-}U)/T$ also approaches 0 as T approaches 0, the entropy itself must approach 0 as T approaches 0. While this may seem merely an arcane mathematical conclusion, it was the magic bullet for chemical thermodynamics. Since an absolute value can be defined for the entropy (S cannot be negative and is 0 for $T = 0$) chemical equilibria can be calculated from measurements of the heat capacity as a function of temperature. At high temperature, the entropy increases

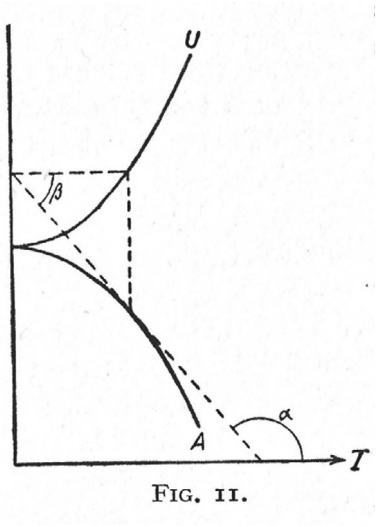


FIG. 11.

Fig. 17.3 Temperature dependence of U and A at low temperatures [4]

logarithmically with temperature:

$$S(T, V, n)_{V,n} = \int_0^T \frac{C_V(T, V, n)}{T} dT \tag{17.3}$$

since heat capacities approach a constant.

Nernst was also quite interested in chemical reactions at high temperatures. All diatomic molecules tend to dissociate at sufficiently high temperature. The thermodynamics of multicomponent systems was developed by J.Willard Gibbs (1839–1903) (see Chap. 13). For a system at a temperature T and a constant volume, V, the Helmholtz energy for a multicomponent system is:

$$A(T, V, \{n_i\}) = \sum_i n_i \mu_i(T, V, \{n_i\}) \tag{17.4}$$

For each component, the number of moles of substance changes as the reaction proceeds.

$$\begin{aligned} n_i(\xi) &= n_i(0) + \nu_i \xi \\ \nu_i &= dn_i/d\xi \end{aligned} \tag{17.5}$$

The derivative of the number of moles of component i with respect to the advancement of the reaction, ξ, is called the stoichiometric coefficient.

The condition for chemical equilibrium in this gaseous system is:

$$\Delta A_{r\times n}(T, V, \{n_i\}) = \frac{dA}{d\xi} = 0 \tag{17.6}$$

In order for the system to be at chemical equilibrium, the Helmholtz energy of reaction, $\Delta A_{r\times n}$, must be 0. This can be expressed as:

$$\Delta A_{r\times n} = \sum_i \nu_i \mu_i = 0 \tag{17.7}$$

For a substance in the ideal gas phase, the chemical potential can be expressed in the form:

$$\mu_i(T, V, \{n_i\}) = \mu_i^0(T, P = 1) + RT \ln\left(\frac{n_i RT}{V}\right) \tag{17.8}$$

The standard state pressure is 1 atm. The standard state chemical potential is an explicit function of temperature:

$$\mu_i^0(T, V, \{n_i\}) = \mu_i^0\left(T^0, P^0\right) - \int_{T^0}^T \overline{S}_i(T) dT \tag{17.9}$$

TABLE I.—FORMATION OF NITRIC OXIDE

T	x (obs.)	x (calc.)	OBSERVER
1811	0.37	0.35	Nernst (l. c.).
1877	0.42	0.43	Nernst and Jellinek (l. c.).
2023	$0.52 < \ldots < 0.80$	0.64	" " " "
2033	0.64	0.67	Nernst (l. c.).
2195	0.97	0.98	" "
2580	2.05	2.02	Nernst and Finkh.*
2675	2.23	2.35	" " "

Fig. 17.4 Calculated and observed amounts of nitric oxide for the system of nitrogen and oxygen at high temperatures [2]

One of Nernst's greatest insights was that at high temperatures the entropic contribution to the chemical potential would dominate the energetic part. In order to prove this in the laboratory he invented special high temperature reaction vessels of iridium. He chose either simple diatomic molecules or triatomic molecules like water. For a reaction involving nitrogen, oxygen and nitric oxide, the high temperature limit should be determined primarily by the simple statistics (Fig. 17.4). (There will also be a small concentration of nitrogen and oxygen atoms.)

The formation of nitric oxide from nitrogen and oxygen is a highly endothermic process ($\Delta H_{\text{rxn}} = 180.5$ kJ). Nevertheless, at very high temperatures, there are as many nitric oxide molecules (approximately) as there are nitrogen and oxygen molecules at equilibrium. Nernst won the Nobel Prize in Chemistry, and he is extremely important for the history of chemistry. He realized just how important entropy was for chemistry.

Heat flows "where it can go!" In this respect it is like water. But, in addition to slowly diffusing heat (more like calorique), there is heat that moves at the speed of sound (phonons). This rapidly moving heat can couple to vibrational and rotational modes in molecular condensed phases.

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Max Planck: Towards a Quantum Understanding of Heat

18

Abstract

Max Planck was one of the greatest scientists of all time. He both made major contributions to the understanding of heat and fully understood all the work of his contemporaries and prior workers. This chapter considers both his work on Thermodynamics and his derivation of the spectrum of Blackbody radiation. He lived at a time when the understanding of the particle of electric charge, the electron, was rapidly evolving. He received the Nobel Prize in 1918 for his contributions to the concept of physical quanta of energy.

Many natural philosophers have contributed to our current understanding of the phenomenon of heat. Some of them have fully understood the previous history of this area of investigation in their own time and pointed clearly to the future. Max Planck (1858–1947, Nobel 1918) was an outstanding example of such a person (Fig. 18.1).

After a good local education Planck came to the University of Berlin and studied under Hermann von Helmholtz (1821–1894) and Gustav Kirchoff (1824–1887). Planck devoured the monograph by Clausius and learned Thermodynamics at that level. The best discussion of the Carnot cycle appears in Planck's *Treatise on Thermodynamics* (1926) [1]. Planck's own Ph.D. thesis was on the theory of entropy. Rather than merely focusing on the equations, he thought deeply about the meaning of the Second Law. Again, the best discussion of the meaning of entropy is found in the *Treatise.* And he thoroughly discussed the meaning of chemical equilibrium. He derived independently all the relations published by Josiah Willard Gibbs (1839–1903) (see Chap. 13). While the credit of priority is given to Gibbs, Planck continued to probe this field in complete depth. Planck became a Professor of Theoretical Physics at the University of Berlin in 1889.

Planck was able to adopt any frame of reference that helped to both describe and explain an established physical phenomenon. He understood that heat is energy

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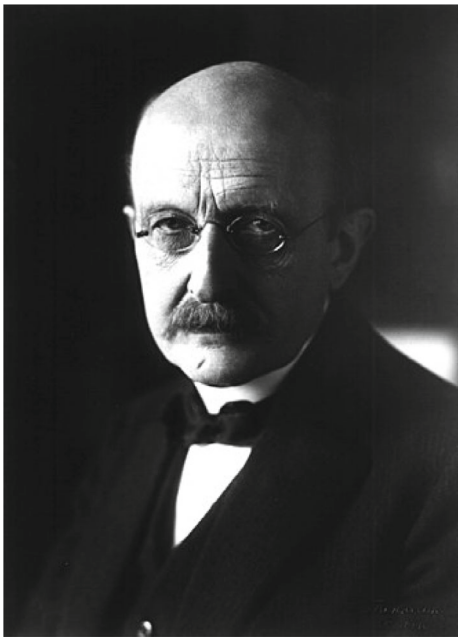


Fig. 18.1 Max Planck, University of Berlin (Public Domain)

that flows. This had immediate consequences: all physical energy flows are subject to loss (they are "irreversible). Fluid viscosity and electrical resistivity are classical necessities. The kinetic theory of fluids invokes the mean free path between collisions between the moving particles. Any particular particle undergoes a complicated trajectory and interacts with the other particles in many ways. Heat that is transmitted by particle motion will be "scattered" into the "medium." Electrons in metals are carriers of energy in an electric field. They are scattered by phonons and undergo a complicated trajectory.

Planck was also open to the discovery of new phenomena. Physicists were quite reticent to believe in Brownian motion. Planck saw it as evidence that fluids were dynamic systems. In a dynamic system, fluctuations are possible. Planck also understood that fluctuations can be of two sorts: coherent and diffuse. The dynamic realities of liquids can be "visualized" using Brillouin scattering. The spectrum reveals a "central peak" (at frequencies centered at the excitation frequency of the light) and two "shifted peaks" determined by the speed of sound and the angle of scattering. The width of the central peak is determined by the thermal conductivity of the liquid and the scattering angle. Diffuse temperature fluctuations produce regions of different refractive index than the macroscopic average, unless the thermal expansion coefficient of the liquid is 0. (There is no central peak for water at its density maximum at 4 °C.) The width of the Brillouin (shifted) peaks is more complicated. Since the longitudinal waves are adiabatic, heat conduction makes a small contribution. The adiabatic longitudinal modulus of the liquid depends on both the modulus of compression and the shear modulus: $M = \gamma K + (4/3)G$. Heat

can flow from the phonon to any sink in the medium. This includes the number of molecular vibrational modes. The medium is also subjected to compressions and rarefactions as the phonon propagates. This can couple to the local molecular structure of the liquid. The dynamics of this interaction depends on the volume viscosity of the liquid. And finally, the medium is subjected to shear forces. These couple to the transverse motions of the molecules and depend on the shear viscosity of the liquid. Liquids are much more interesting than was suspected by Boyle and Newton (and many nineteenth and twentieth century physicists). Planck was delighted that real liquids were so interesting.

Planck also understood that solids were dynamic systems. The speed of sound in solids is much greater than in liquids or gases. One way to visualize the dynamics of transparent solids is through Brillouin scattering. The Brillouin splitting is now much greater for the same angle. Phonons are mechanical energy in motion. This requires that there be a mechanism for loss. The central peak is again broadened by thermal conduction. There can be two types of Brillouin peaks, since shear waves are now allowed. One way of discussing the width of the Brillouin peaks is in terms of the "phonon mean-free path." Sound waves in solids are both created and annihilated by mechanical disturbances in the medium. Physicists like to picture this in terms of phonon–phonon scattering. Planck was the inspiration for the later work by Peter Debye on the phonon theory of solid heat capacity.

Although he received the Nobel Prize in 1918 "in recognition of the services he rendered to the advancement of Physics by his discovery of energy quanta," Planck was one of the greatest classical physicists, comparable to Rayleigh, Kelvin and Maxwell. He had one of the deepest understandings of Thermodynamics. He knew the full history of this subject. He appreciated the contribution of Carnot to the elucidation of entropy. In his lucid book, *A Survey of Physics* (1925) [2], Planck clearly followed the argument developed by Carnot. Consider a system composed of two heat baths at temperatures $T_1 > T_2$. Heat, Q, will flow from the hotter bath to the colder bath. The Carnot Law is then:

$$\frac{Q_2}{T_2} - \frac{Q_1}{T_1} > 0 \tag{18.1}$$

Planck immediately recognized this as the signature of an irreversible process. Heat does not flow macroscopically from a colder body to a hotter body without work being done. Heat will continue to flow until $T_1 = T_2$.

Of all the philosophical issues addressed in the *Survey,* the most important one would today be called the question of Critical Realism. Actual scientists are humans who need a reason to undergo the rigors of scientific work. (Science is hard and usually results in failure!) If the scientist does not believe that there is actually a real physical world to be studied and understood, she will not succeed. This is the realism part of the stance. But, at any point in time, scientists have only partially succeeded in describing and explaining the observable world. Nevertheless, if the current theory is both coherent and conforms to all known observations,

it forms a sound base for further investigations. The inherent provisionality of science is the "critical" part. Many current treatises on this scientific stance have been written, but the essential aspects are all present in Planck.

Matter looks continuous, but only because we do not have X-ray vision. When John Dalton inferred that the world of Chemistry only made sense if there were very small atoms that differed for each element, some natural philosophers, like Thomas Thomson (1773–1852) and William Henry (1774–1836) rejoiced. Max Planck was willing to join the chorus and even write a new tune. At the atomic level, energy can occur as coherent excitations of discrete magnitude: quanta. Newton had been right about light! But, the wave theory of Huygens (1629–1695) and Young (1773–1829) was empirically fruitful and predicted remarkable phenomena that were true. Perhaps particles were not just little hard balls! Planck was open to physical reality in a way that has persisted to the present.

Since heat "flows" like water, it was tempting to envisage it as a continuous material. But at the atomic level, nothing is continuous except space and time. Remarkably, classical mechanics still suffices to carry out calculations of the structure and dynamics of monatomic fluids. What is missed by this approach is the coherent excitations of the fluid: sound waves (phonons). Max Planck had read Lord Rayleigh's monumental book: *The Theory of Sound* (1894) [3]. Heat "diffuses" slowly by the complicated trajectories of discrete particles and rapidly by the coherent propagation of sound waves. Diffuse heat is more like water, while phonons inspire thoughts that lead to the quantum world. Even the phonon picture includes many steps, of creation and annihilation, as the energy diffuses on a macroscopic scale. Fourier's Law of heat conduction is a macroscopic description, not a detailed microscopic theory.

18.1 The Role of Electrons in Generating Light

Lurking in plain sight, one key to the understanding of physical reality was lightning. It involves electricity, light and sound. When the electric potential energy between the cloud and the ground exceeds a certain level, current flows through the air to achieve neutralization. Charge flows from a high potential to a low potential. Electric charge was visualized in the eighteenth century as a fluid. Benjamin Franklin (1706–1790) and Joseph Priestley (1733–1804) made great progress in understanding electricity using such a model. Matter could have more or less electrical fluid. But, where did the light come from?! Planck was quite aware of the work of William Crookes (1832–1919). When a large electric potential is applied to a dilute gas contained in a glass tube, current flows and light is given off (Fig. 18.2).

What is carrying the current and why does it produce light? J.J. Thomson (1856–1940) received the Nobel Prize in Physics in 1906 "in recognition of the great merits of his theoretical and experimental investigations on the conduction of electricity by gases." He called the particulate carrier of electricity the *electron***.** But, if the electron is moving, it is a form of heat! The electron interacts



Fig. 18.2 Crookes tube showing the electric current and the emission of light [4]



Fig. 18.3 Lightning (Public Domain)

with the gaseous atoms and excites them to higher energy states. These states fluoresce and reflect the complicated internal structure of the atom. The visible spectra of monatomic gases had been thoroughly investigated. The intensity of a "thunderclap" is unforgettable. But what is producing the sound? The energy transferred from the moving electrons produces a rapid rise in temperature. This "shock wave" eventually propagates as sound as it organizes along its way. (The detailed explanation of an actual lightning event is as complicated as real lightning (Fig. 18.3).)

Metals are composed of atoms and arranged in regular lattices. The medium undergoes vibrational motions from long wavelength sound to local harmonic atomic motion. The current model of a metal includes a "sea of electrons." This means that the overall lattice is composed of positively charged ions. Fluctuations of the lattice produces fluctuating electric fields. Fluctuating electric fields produce electromagnetic waves: photons. Each photon is characterized by a discrete energy: $E = hv$, where $h = 6.626 \times 10^{-34}$ Js is Planck's constant and v is the frequency of the propagating photon.

Any modern discussion of the thermal properties of matter includes quantities that depend on Boltzmann's constant: $k_B = 1.38 \times 10^{-23}$ JK^{-1}. The average thermal energy per particle is proportional to $k_B T$. Visible light (500 nm) has a wavelength much larger than the lattice spacing (of order pm). In order for the Blackbody radiation to be dominated by thermal energy, the temperature needs to be thousands of degrees Kelvin. This is exactly what is observed (Fig. 18.4).

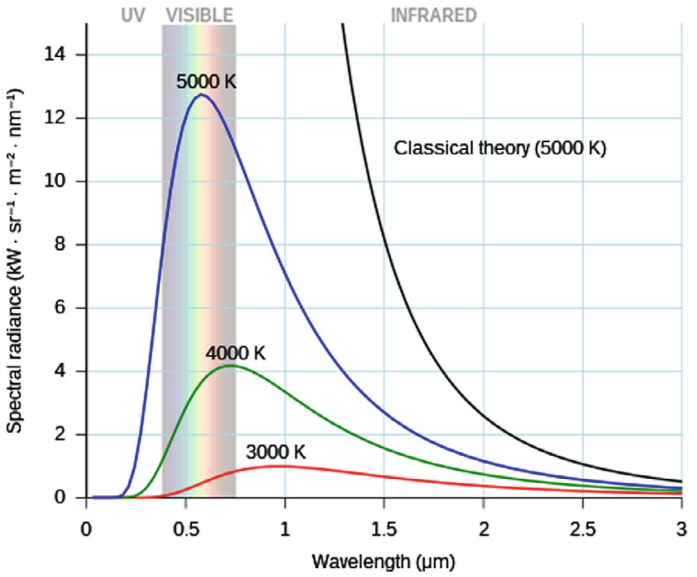


Fig. 18.4 The spectrum of Blackbody radiation as a function of temperature, compared with the classical prediction of Lord Rayleigh [5]

The understanding of electromagnetic radiation starts with Maxwell. One of the solutions of Maxwell's Equations in a vacuum is transverse waves with a velocity of 3×10^8 m/s. This work was published in the *Philosophical Transactions of the Royal Society of London* in 1865 [6]. Experimental realization of this phenomenon is attributed to Heinrich Hertz (1857–1894). Over the period from 1886–1889 he carried out seminal experiments culminating in both creating and detecting electromagnetic waves in the MHz range. Max Planck was a great believer in the unification of physics, and soon promoted the notion that such phenomena could have frequencies over a very wide range, including infrared, visible and ultraviolet light.

Hertz also investigated the interaction of ultraviolet light and charged metal spheres. The charge could be discharged by shining UV light on the metal. Hertz died young (age 36), but his student, Philipp Lenard (1862–1947), explored the photoelectric effect in great detail. He showed that only light of sufficient frequency produced the effect. Intense light of lower frequency just warmed the metal, while the faintest light of sufficient frequency produced photoelectrons in the Crookes tube. This set the stage for Albert Einstein to think about how this could be so (see Chap. 20). He proposed that light particles had specific total energies corresponding to their frequencies, and that there was a specific amount of energy needed to liberate the electron from the metal. More energetic light produced photoelectrons of higher kinetic energy. Lenard and Einstein received the Nobel Prize in 1905 for their work on the photoelectric effect. Photons were quantum particles with energies $E = hv$.

18.2 Planck's Theory of Blackbody Radiation

The classical theory of electromagnetic radiation in a thermal cavity was constructed by Lord Rayleigh. It disagreed with the careful observations of blackbody radiation shown above. The result was predicated on the assumption that all "vibrators" contribute to the radiance equally. Under these conditions the distribution of wavelengths is proportional to: $T\lambda^{-4}\,d\lambda$. The essence of the researches of Boltzmann established that the relative probability of two energy states was given by:

$$\exp\left(-\frac{E_2 - E_1}{k_B T}\right) \tag{18.2}$$

When this criterion is added to the basic calculation of the wavelength distribution, the distribution derived by Wilhelm Wien (1864–1928) is obtained (Fig. 18.5).

Max Planck was the Professor of Theoretical Physics. One approach to the description of experimental reality is to produce an equation that reproduces the observations: the empirical approach. Planck was able to do this with the equation:

$$B(\nu, T) = \left(\frac{2h\nu^3}{c^2}\right)\left[\frac{1}{\exp\left(\frac{h\nu}{k_B T}\right) - 1}\right] \tag{18.3}$$

where h is the Planck constant, k_B is the Boltzmann constant, ν is the frequency, and c is the speed of light. At low frequencies, expanding the exponential leads to

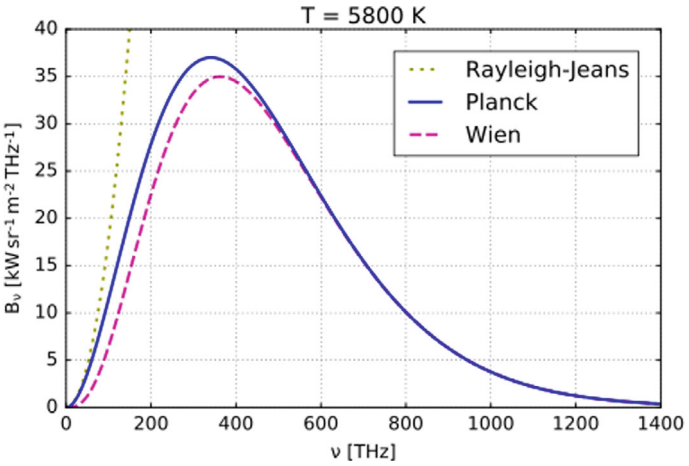


Fig. 18.5 Theoretical predictions of the spectrum of the Blackbody radiation at $T = 5800$ K [7]

a v^2 dependence, the classical result. At high frequency, the distribution falls off as an exponential, just as the experimental result.

The "ultraviolet catastrophe" is avoided, but the long wavelength modes are underestimated relative to the higher frequency ones. The table was now set for Max Planck. Wilhelm Wien did receive the Nobel Prize in 1911 for his extensive research into thermal radiation.

Planck could have been satisfied with this adequate phenomenological result (many nineteenth century physicists were quite satisfied with merely empirical formulae), but he wished to understand it at a deeper level and derive the equation from a model. Planck had already considered a gas composed of particles with mass. He now considered a gas composed of electromagnetic waves at temperature T. The EM waves must terminate at the boundaries of the cubic box of side length L. Thus, not all frequencies are possible. The formula for the energies is:

$$E(n_1, n_2, n_3, r) = (r + (1/2))\left(\frac{hc}{2L}\right)\sqrt{n_1^2 + n_2^2 + n_3^2} = (r + (1/2))\varepsilon \tag{18.4}$$

where the n_s and r are integers and $r = 0$ is a possibility. The probability of such a state at temperature T depends on the Boltzmann factor and the number of states with this energy:

$$g(\varepsilon)d\beta\varepsilon = \left(\frac{8\pi L^3}{h^3c^3}\right)\varepsilon^2 d\varepsilon \tag{18.5}$$

The energy distribution is then:

$$\varepsilon\wp(\varepsilon) = \frac{\varepsilon}{\left(\exp\left(\frac{\varepsilon}{k_B T}\right) - 1\right)} g(\varepsilon) \tag{18.6}$$

Converting to units of frequency and per unit solid angle yields the Planck formula given above. It is a marriage of the ideas of both Planck and Boltzmann. The key step is the understanding of the physics of "standing electromagnetic waves" in a box. They are naturally "quantized." The statistical mechanics aspects are those of Boltzmann, without which the temperature dependence of the spectrum would not appear. While the two giants were not on good terms most of their professional lives, their ideas mated and produced great offspring.

Planck had a positive relationship with Walther Nernst. He read Nernst's "New Heat Theorem" with delight. Until Nernst, the entropy was considered to be like the energy: only determined up to an additive constant. When Nernst showed that the minimum value for the entropy was 0, and that this could only be obtained at the absolute zero of the temperature scale, Planck rejoiced. Thermodynamics was now "complete."

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Albert Einstein: The Invention of the Full Theory of Nonequilibrium Thermodynamics

19

Abstract

Albert Einstein could have received the Nobel Prize many, many times. In this chapter his contributions to the theory of fluctuations, the theory of Brownian motion and the theory of the heat capacity of monatomic solids are discussed.

Albert Einstein (1879–1955) made major contributions to many areas of physics. In this chapter I will focus on his treatment of thermal physics. He derived his own version of Statistical Physics [1]. While pedagogical treatments stress the long-time averages of thermodynamic variables like temperature, Einstein considered other measures of the system. The local temperature, $T(\vec{r}, t)$, fluctuates in both time and space. Statistical Mechanics allows the mean-squared fluctuations of the temperature to be calculated:

$$\left\langle \Delta T^2 \right\rangle = \left(\frac{1}{V^*} \right) \frac{k_B T^2}{C_P} \tag{19.1}$$

where V^* is the fluctuation volume. In a liquid, the local density also fluctuates. Einstein derived that the mean-squared density fluctuations are:

$$\left\langle \Delta \rho^2 \right\rangle = \left\langle \rho^2 \right\rangle \frac{k_B T \kappa}{V^*} \tag{19.2}$$

where κ is the isothermal compressibility [2]. Einstein and Marian Smoluchowski (1872–1917) put this result to immediate use and calculated the intensity of light scattering due to density fluctuations:

$$\frac{I}{I_0} = \left(\frac{\pi^2 V}{2\lambda^4 L^2} \right) \left(\rho \left(\frac{\partial \varepsilon}{\partial \rho} \right)_T^2 \right) k_B T \kappa \left(1 + \cos^2 \theta \right) \tag{19.3}$$

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where I_0 is the incident intensity, V is the "scattering volume," ε is the optical dielectric constant for the liquid at density ρ, L is the distance to the detector, and θ is the scattering angle. As the liquid approaches the critical point, the isothermal compressibility diverges, since the density fluctuations increase dramatically [3].

Einstein also understood that, while liquids are macroscopically isotropic, both mechanically and optically, they are not isotropic on small scales. The local anisotropy can be due to an anisotropic distribution of particles (molecules), or it can be due to the local orientations of the molecules. (I studied liquid anisotropy in monatomic liquids and isotropic molecular liquids. The dynamics were characteristic of the local motions of the liquid cage. I also studied the rotational motion of anisotropic molecules. Non-random local orientation leads to local optical anisotropy and the phenomenon of depolarized light scattering.) All these motions contribute to the heat capacity of liquids. But they do not contribute to rapid conduction of heat by sound waves. A discussion of heat conduction by hypersonic sound waves will be deferred to the chapter on Brillouin and Heat (see Chapt. 20).

Jean Perrin (1870–1942) received the Nobel Prize in Physics in 1926 for his experimental studies of Brownian motion and his demonstration of the physical reality of atoms and molecules. He measured the "trajectory" of colloid particles and verified the Brownian diffusion law calculated by Einstein [4].

Einstein considered a liquid as a "continuous" field of force: $\vec{F}(\vec{r}, t)$. This "random force" was constantly changing, and at any location averaged to null. The mean-squared random force did NOT vanish. This led to an equation of motion for any object in a liquid:

$$m\frac{d\vec{v}}{dt} = -\varsigma\vec{v} + \vec{F}(\vec{r}, t) \tag{19.4}$$

where $\varsigma = 6\pi\eta R_h$ is the "friction coefficient," η is the viscosity of the medium, and R_h is the "hydrodynamic radius." The self-diffusion coefficient of a particle in a fluid medium is then:

$$D = \frac{k_B T}{\varsigma}. \tag{19.5}$$

The particle explores the volume of the medium, but no work is done. Energy is exchanged along the way, but the total energy remains constant. One of the meanings of temperature is the facilitator of energy exchanges in physical systems. The catalytic process is the existence of the local fluctuations of the structure of the medium.

The quintessential biography of Einstein is by Abraham Pais: *Subtle is the Lord: The science and life of Albert Einstein* (1982) [5]. Pais stresses the importance of "statistical thinking" in the work of Einstein. While Einstein labored mightily to establish the microscopic perspective, it was his use of the appropriate statistical approach that allowed him to calculate observable phenomena. When Planck

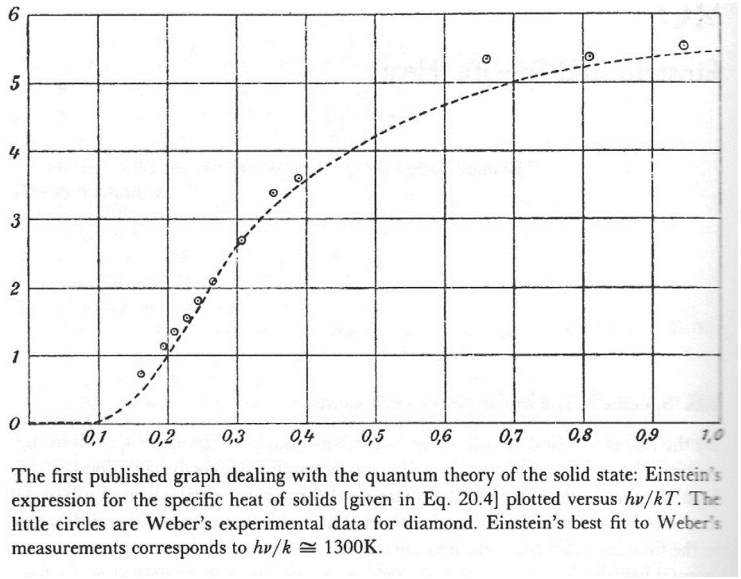


Fig. 19.1 Heat capacity of diamond as a function of $h\nu/k_BT$ [5]

opened the door to a truly revolutionary fact of reality, the "quantum hypothesis," Einstein immediately added this to his theoretical tool-bag.

One of the central facts of thermal physics in the nineteenth century was the measurement of the heat capacity of monatomic solids. This produced the Law of Petit and DuLong. In a fully microscopic frame of reference, the heat capacity per atom is: $C_{\text{atom}} = 3k_B$. When there is a mole of atoms ($N = N_{\text{A}}$), the molar heat capacity is $3R$. This allowed chemists to infer accurate atomic weights for many metals.

Later in the nineteenth century, physicists were able to achieve lower and lower absolute temperatures in the laboratory. One of the leading scientists in the study of cryogenic liquids was Sir James Dewar (1842–1923) at the Royal Institution. He invented the Dewar flask. The first Nobel Prize, 1913, in this area was received by Heike Kamerlingh Onnes (1853–1926) of the University of Leiden. He liquified helium in 1908.

The heat capacity of diamond is well below the Petit-Dulong limit at room temperature and increases steadily throughout the normal temperature range, 0–200 °C. Accurate measurements of the heat capacity were carried out by Heinrich Weber (1843–1912) in 1872 (Fig. 19.1).

The explanation of this phenomenon started with Maxwell and Boltzmann. The probability of a particular state of energy ε is proportional to:

$$\exp\left(-\frac{\varepsilon}{k_BT}\right) \tag{19.6}$$

It continued with Planck and his distribution law for black-body radiation:

$$\rho(\nu, T) = \frac{8\pi h\nu^3}{c^3}\left(\frac{1}{e^{\frac{h\nu}{k_B T}} - 1}\right) \tag{19.7}$$

The energy function for a photon of frequency ν in an ensemble at temperature T is then:

$$U(\nu, T) = \frac{h\nu}{e^{\frac{h\nu}{k_B T}} - 1} \tag{19.8}$$

Einstein modeled the crystal as 3N one-dimensional harmonic oscillators [6]. The new wrinkle is the assumption that there was only one possible frequency for the system. The molar heat capacity is then:

$$\overline{C}_V = 3N_A k_B \frac{\left(\frac{h\nu}{k_B T}\right)^2 e^{\frac{h\nu}{k_B T}}}{\left(e^{\frac{h\nu}{k_B T}} - 1\right)^2}. \tag{19.9}$$

Einstein always knew that there would need to be a distribution of vibrational frequencies, but his simple model already pointed the way to deeper understanding. His expression for the energy function was:

$$U(\nu, T) = \frac{\int E(\nu)\exp\left(-\frac{E}{k_B T}\right)\omega(E, \nu)dE}{\int \exp\left(-\frac{E}{k_B T}\right)\omega(E, \nu)dE}. \tag{19.10}$$

When the right time came, Peter Debye (1884–1966) was ready to propose a better distribution function for the vibrations. While, again, it was not realistic for an actual crystal, it did include a high frequency cutoff and a good approximate frequency dependence for the vibrations. The "modern" theory for the heat capacity of crystalline solids will be deferred to the chapter on Leon Brillouin (see Chapt. 20).

The major contribution of Albert Einstein to the theory of heat is his insight that fluctuations and statistical mechanics were important for our understanding. Matter is inherently dynamic at finite temperature; and it is impossible to achieve absolute zero.

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Leon Brillouin: Solid State Physics and the Importance of Phonons

20

Abstract

Leon Brillouin brought the full power of Solid State Physics to the discussion of heat. Phonons propagate in dense media and transport energy. Photons interact with phonons and are scattered. Deeper thoughts about entropy revealed the importance of "information." This insight defeated Maxwell's Demon!

One of the greatest physicists not to have received the Nobel Prize was Léon Brillouin (1889–1969) (Fig. 20.1). He attended the École Normale Supérieure and studied under Jean Perrin (1870–1942). He studied with Arnold Sommerfeld (1868–1951) and Max von Laue (1879–1960, Nobel 1914) at Munich. And, after the War, he received his doctorate from the University of Paris with Paul Langevin (1872–1946). His thesis topic was the quantum theory of solids. He discussed the phonons that propagate in solids. This led him to consider the interactions of light (photons) with these phonons and the discovery of Brillouin Scattering in 1922. (I used Brillouin scattering to probe the properties of polymeric solids.)

Brillouin held many prestigious posts in France, including the Professorship of Theoretical Physics at the Institut Henri Poincaré. He is one of the founders of Solid State Physics. His concept of Brillouin Zones in crystalline solids is still the basis for the understanding of the electronic properties of solids.

After the collapse of France, Brillouin emigrated to the United States. He was associated with both Harvard University and Columbia University. His major research interest in this period was the relationship between Statistical Thermodynamics and Information. In the following I will discuss his classic book: *Science and Information Theory* (1956) [2].

Brillouin was a master of "all things heat." Three types of heat include sound (phonons), light (infrared photons) and moving electrons. Another of his most famous books is *Wave Propagation in Periodic Structures* (1946) [3]. This is a

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Fig. 20.1 Léon Brillouin [1] (with permission from Belin)

complete academic discussion of types of heat in solids. Phonons are characterized by both energy (and frequency) and momentum. (Heat is characterized by both energy and momentum.) Not all motion in a crystalline solid is "propagating." Brillouin discusses both "acoustic modes" and "optic" modes. The optic modes are local vibrations. There are two types of acoustic modes: longitudinal and transverse. In solids with three different mechanical moduli, it is possible to have two different transverse modes. These real coherent mechanical excitations can actually be "seen" with Brillouin scattering. Light (photons) can be scattered by phonons and can either destroy or create phonons. The scattered light spectrum contains one peak due to creation of a phonon and one due to annihilation of a phonon. Light waves also are characterized by energy (frequency) and momentum. During the scattering process, both energy and momentum are conserved.

Phonons propagate with a velocity determined by the density of the medium and the mechanical moduli. They also suffer loss! (All propagating waves suffer loss.) This loss can be measured in many ways, but the width of the peaks in the Brillouin spectrum are determined by the loss. One source of loss is "viscosity." (This effect dominates the loss in liquids.) Another source of loss for longitudinal waves is conduction of heat, since the waves are adiabatic. Brillouin also identified what can be a major source of loss: transfer of energy to "optic modes." (local vibrational processes). (I intensively studied this type of loss in molecular liquids.) One reason why Brillouin should have been awarded the Nobel Prize was his explanation of the full dynamics of crystalline solids.

The heat capacity of crystalline solids decreases to 0 as the substance is cooled. While Nernst intuited that this would be true, based on sound thermodynamic arguments, the microscopic basis for this fact required a deeper understanding of the microscopic dynamics of the crystal. Einstein studied the theoretical properties of a system composed of independent harmonic oscillators. Brillouin extended

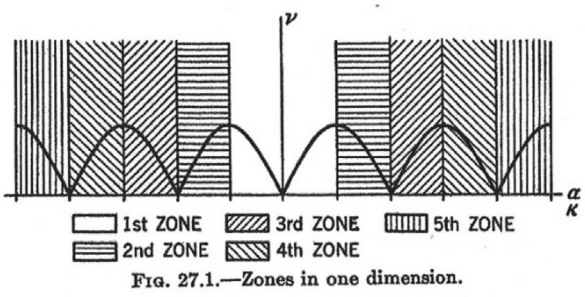


Fig. 20.2 Brillouin zones in one dimension [3]

this to a full description of a crystalline solid. At very low temperatures, only the acoustic modes matter. The heat capacity is then predicted to depend on T^3. This is exactly what is observed.

At higher temperatures (k_BT) the detailed crystal structure impacts the "phonon density of states." Brillouin was the author of both the concept of the phonon and the detailed calculations of collective mechanical modes. One of the blessings of the French academic system was the sophistication of the mathematics taught to the elite students. The monumental achievements of René Just Haüy (1743–1822) in crystallography were made possible by his deep understanding of the analytical geometry of Descartes. The monumental achievements of Brillouin were made possible by his deep understanding of the tensor mathematics of Auguste Bravais (1811–1863) (Fig. 20.2).

One of the key concepts needed to understand the dynamics of crystals is the relationship between the "direct lattice" for the crystal and the "reciprocal lattice" for the collective excitations. One of the concepts that won Brillouin universal acclaim is the "Brillouin Zone." These constructs are transparent in the reciprocal lattice. A collective excitation (phonon) is periodic in the geometry of the Brillouin zone for that lattice (Fig. 20.2).

The analysis of two-dimensional lattices was also completely understood by Brillouin. The shape of the Brillouin zones for a hexagonal lattice is shown in Fig. 20.3. In three dimensions, the primary lattices all fall within the 14 possible Bravais forms. This geometry was fully developed in the nineteenth century (1848). Brillouin analyzed these forms and calculated the Brillouin zones for the reciprocal lattices. The Brillouin zones resemble the rhombohedrons analyzed by Haüy. Results for a cubic lattice are shown in Fig. 20.4.

Brillouin's Law can be stated concisely as: "For any kind of waves (elastic, electromagnetic, or wave mechanical De Broglie waves) propagating in a medium with periodic structure, discontinuities are found in the relation between the frequency ν and the wavevector $\vec{a}$." This is one of the key concepts in solid state physics. For X-rays this criterion produces the observed Bragg-Laue spots. Another key concept is the number of vibrational modes, $N(\nu)$, as a function of frequency. The classic Debye function assumes a single rise with a cutoff, but real materials have

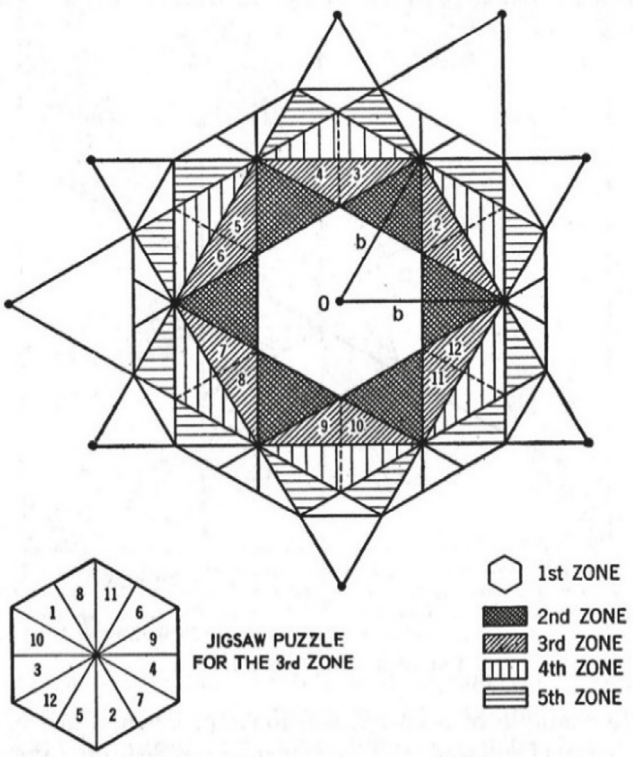


FIG. 31.3.—Zones for a hexagonal lattice.

Fig. 20.3 Brillouin zones in a hexagonal lattice [3]

both longitudinal and two transverse modes. For an anisotropic lattice, the two transverse modes have different functions. For a real material the "sharp" cutoff is not observed, but can be "softened" due to more accurate calculations (Fig. 20.5).

The dynamics of real crystals can now be calculated based on the exact lattice structure and the measured moduli. While Hooke knew that "heat was a kind of motion," Brillouin knew what kind!

After Brillouin, migrated to America he pursued the foundation of Information Theory. He was part of a movement that included leaders like Claude Shannon (1916–2001). Brillouin applied information theory to Thermodynamics! Entropy has bedeviled many scientists. Boltzmann showed that entropy could be understood in statistical terms and introduced the "partition function: Ω." In these terms $S = k_B \ln \Omega$. Brillouin showed that the partition function could also be expressed in terms of the amount of information contained in a system.

One of his most important contributions to the understanding of heat is his "exorcizing of Maxwell's demon." Maxwell envisioned a gaseous system with two chambers and a passageway controlled by the demon. He postulated that the demon

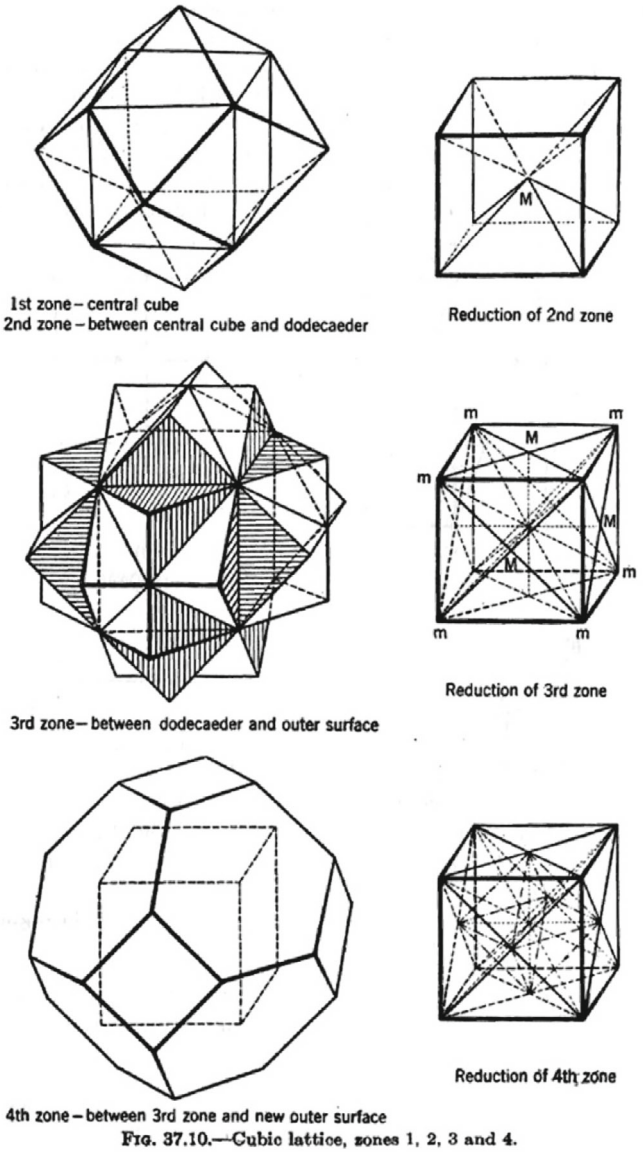


FIG. 37.10.—Cubic lattice, zones 1, 2, 3 and 4.

Fig. 20.4 Cubic lattice Brillouin zones [3]

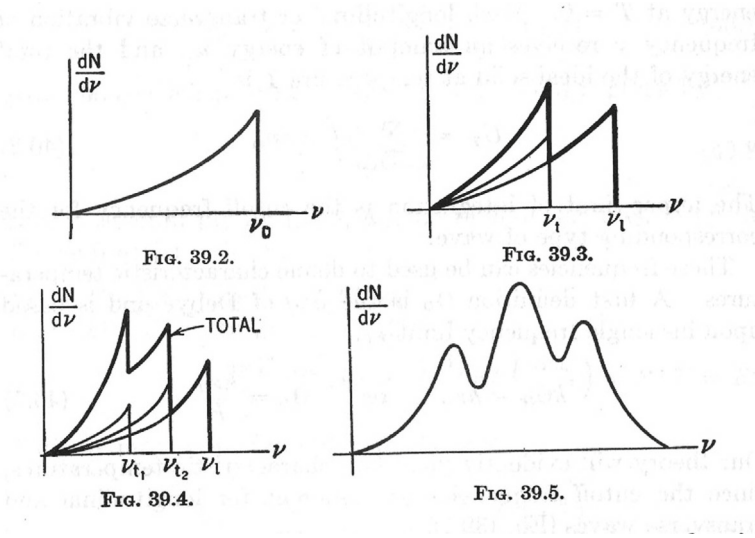


Fig. 20.5 Phonon density of states for: Debye function, isotropic solid theory, anisotropic solid theory, and experimental [3]

could select particles and allow them to pass from one container to the other. By clever selection he could corral the fast particles in one chamber and the slow particles in the other. This clearly violates the Second Law of Thermodynamics, since the change in entropy for such a process would be negative.

Brillouin was influenced by all the great physicists in his time. Jean Perrin received the Nobel Prize for his work on Brownian motion. Langevin was a master of all things fluid and is known for the Langevin Equation that allows a "random force" to be introduced to the classical equations of Newton. Planck explained the properties of "black-body radiation." Brillouin gathered all the known physics and produced a new "view" of the actual physical situation.

The boxes are initially in contact with a "heat bath" at $T = T_0$. Among other things this produces a system with black-body radiation in the chambers. Brillouin asked the question: How could the demon "see" the particles in a sea of photons? He then proposed a more sophisticated "measurement device" that could detect the presence of the particle. But such a device would produce heat! (All information is obtained at a cost!) He also noted that the particle could only be detected when it was "very near the portal."

Brillouin made the connection between information and "negentropy." He quantified this concept in terms of "bits" of information. Information can be used to decrease the entropy, but it "costs" more to obtain the information than the reduction. The Second Law survived yet another challenge to its universality. One of his inspirations for this approach was Leo Szilard (1898–1964), one of the famous "Martians of Science" [4]. Szilard was able to quantify the amount of entropy change associated with one "bit" of information: $\Delta S = k_B \ln 2$. When a genius

is able to talk to all the key thinkers, major improvements in our understanding of physical reality are possible.

Brillouin learned well from Perrin, Einstein, Smoluchowski and Langevin. Our physical reality involves "fluctuations." In the context of the Langevin equation, the random fluctuating force, $\vec{F}_r(\vec{r}, t)$, must average to 0. But its mean-squared value remains and is proportional to $k_B T$. Any fluctuation might deviate from the long-term average locally, but entropy is not an instantaneous quantity: it is the long-time average of the full system. Fluctuations take the "hard-edges" off the ideal models. While the average energy of a system may be insufficient for some event, there exists a "possibility" that a local fluctuation will achieve the required energy. When the temperature (also a long-time average over the whole system) is raised, not only does the average energy increase, the distribution of local energies broadens.

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Max Born: The Importance of Phonons and Electrons in the Science of Heat

21

Abstract

The detailed dynamics of crystalline solids allows the calculation of both the heat capacity and the thermal conductivity. Max Born provided a solid foundation for this subject in his magisterial monograph, *Dynamic Theory of Crystal Lattices.* Metallic crystals exhibit heat capacities comparable to non-conducting substances, but have much larger thermal conductivities. This is due to the transport of heat by "free electrons." The theory of electrons in metals introduced by Fermi and Dirac is presented. The empirical relation between the electrical conductivity and the electronic contribution to the thermal conductivity is discussed.

Although Max Born (1882–1970) was perhaps best known for his Nobel Prize in 1954 for "fundamental research in quantum mechanics, especially in the statistical interpretation of the wave function," he turned everything he touched into gold. He was a brilliant mathematician and astounded his professors at Göttingen (Klein, Hilbert and Minkowski) with his thesis on the fundamentals of solid-state continuum mechanics. Like Brillouin, he understood both the mathematical and the physical basis of the dynamics of crystals. He published his first book on this subject in 1915 (*Dynamik der Kristalgitter*) [1] and wrote an English version in 1922 (*Atomic Theory of Solid States*). The groundwork for this subject was published in *Physikalische Zeitschrift* in 1912 [2].

Albert Einstein tackled the difficult problem of the temperature dependence of the heat capacity of diamond in 1907 [3]. A crystal composed of N atoms will have $3N$ mechanical degrees of freedom. At sufficiently high temperature the heat capacity will approach 6 cal/mol K. At low temperature the heat capacity approaches 0 with a T^3 dependence. Einstein modeled the crystal as $3N$ harmonic oscillators after the work of Max Planck. He obtained the expression for

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the constant volume heat capacity, C_V:

$$C_V \cong Nk_B \left(\frac{\Theta}{T}\right)^2 \frac{\exp(\Theta/T)}{(\exp(\Theta/T) - 1)^2} \tag{21.1}$$

where Θ is determined by the "characteristic frequency" of the oscillators. (At low T, C_v and C_p are comparable, see Chap. 19) While this formula is a transparent application of the Planck theory and gives an approximate explanation for the observed heat capacity, Born attempted to improve the model by allowing a distribution of oscillator frequencies, consistent with his work on vibrations in crystals. While the calculation of this distribution of vibration frequencies is now possible with a computer, Peter Debye implemented the spirit of Born's approach. The key measurable quantity for a real solid is the sound velocity. Another key concept adopted by Debye was the maximum in the possible vibration frequency imposed by the existence of real atoms of finite size. The Debye function for the heat capacity of the fictive crystal is then:

$$C_V = 9Nk_B\left(\frac{T}{\Theta}\right)^3 \int_0^{x_m} \frac{e^x x^4}{(e^x - 1)^2} dx \tag{21.2}$$

The Debye theory does a creditable job of fitting heat capacity data, but is not quantitative at low temperatures (Fig. 21.1): The last word from Born on this subject is the book, *Dynamic Theory of Crystal Lattices* (1954) written with Kun Huang (1919–2005) [4].

21.1 Thermal Conductivity in Solids

In the gas phase, heat is diffused by the physical diffusion of the gas particles. The rate of heat diffusion, and the thermal conductivity, depends on the concentration of particles, the energy carried by the particles, the average speed of the particles, the mean-free path of the particles and the Brownian diffusion law (Chap. 15).

In a solid, the thermal conductivity depends on the speed of sound, the mean-free path of the phonons, and the phonon density of states, which determines the heat capacity per unit volume. A good illustration of the phonon density of states appears in Kittel [6] (Fig. 21.2).

Measurements of the thermal conductivity of quartz, sapphire and diamond reveal new realities [6] (Fig. 21.3). At room temperature, diamond has the highest thermal conductivity because it has the highest sound velocity. In this temperature range, the mean-free path is determined primarily by phonon–phonon scattering. As the temperature decreases, the effect of phonon–phonon scattering is reduced and the conductivity increases. Figure 21.3 shows that the thermal conductivity reaches a maximum and then decreases to 0 at $T = 0$ K. The final decrease occurs because the heat capacity per unit volume of the solid goes to 0. The intermediate maximum occurs because actual crystals are finite in size and contain defects

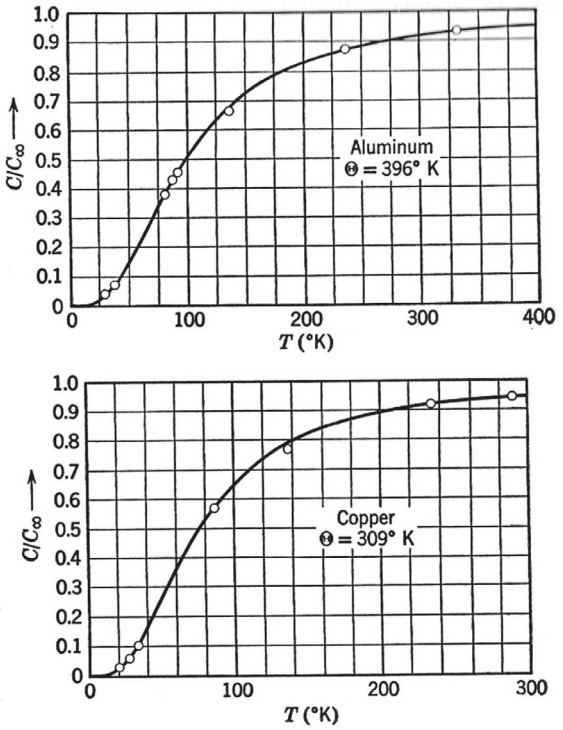


Fig. 21.1 Heat capacities of aluminum and copper as a function of temperature [5]

on some scale. Natural diamonds all contain defects that scatter the phonons and reduce the mean free path. Synthetic sapphires are much more perfect crystals. While the sound velocity is lower, the mean free path stays high. Only the decrease in the heat capacity creates the maximum. Quartz has a much lower sound velocity and a much more imperfect crystal structure with many defects.

21.2 The Role of Electrons in the Heat Capacity and the Transport of Heat

Unlike atomic solids like diamond, metallic crystals have another possible source of heat capacity, mobile electrons. Yet the measured heat capacities of most metals approach the classical limit. Precise measurements of the additional heat capacity due to the electrons in metals confirm this impression. The theory of the low temperature constant volume heat capacity, C_V, in metals can be expressed as [3]:

$$C_V(T) = C_V(\text{lattice}) + C_V(\text{electronic}) = \alpha T^3 + \gamma T \tag{21.3}$$

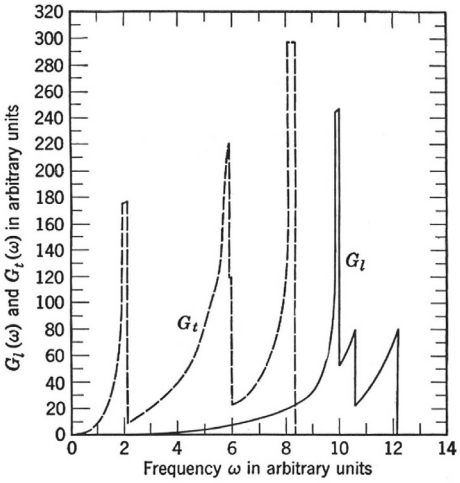


Fig. 6.5. The frequency spectrum of lattice vibrations in sodium. [According to calculations by A. B. Bhatia, Phys. Rev. **97,** 363 (1955).] The distribution functions $G_l(\omega)$ and $G_t(\omega)$ are predominantly associated with longitudinal and transverse waves, respectively.

Fig. 21.2 Phonon density of states from Kittel [6]

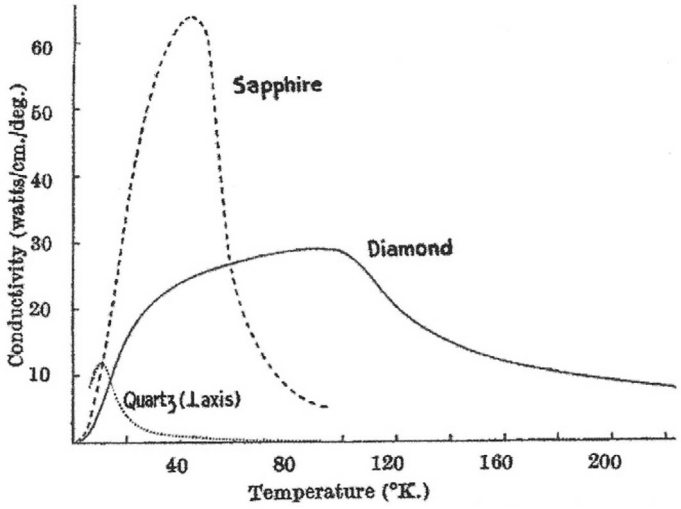


Fig. 21.3 Thermal conductivities of quartz, sapphire and diamond (from Kittel [6])

Measurements on silver confirm this form (Fig. 21.4).

The electronic contribution to the heat capacity at room temperature is minimal. Yet, the thermal conductivities vastly exceed the value determined by the speed of sound. The thermal conductivity of copper as a function of temperature is shown in Fig. 21.5 [6]. Ordinary silicate glass has a sound velocity comparable to copper at room temperature, but a thermal conductivity of only 1 W/m K. The increased thermal conductivity of the copper is due to the electrons.

The understanding of the conductivity due to the electrons required new concepts and the development of quantum mechanics. The first experimental evidence is found in the measurement of the electrical conductivity of metals (the inverse of the resistivity) At very low temperatures, the resistivity becomes very small (the conductivity becomes very large). Over most of the range the electrical conductivity decreases as $1/T$. The decrease in the conductivity is associated with

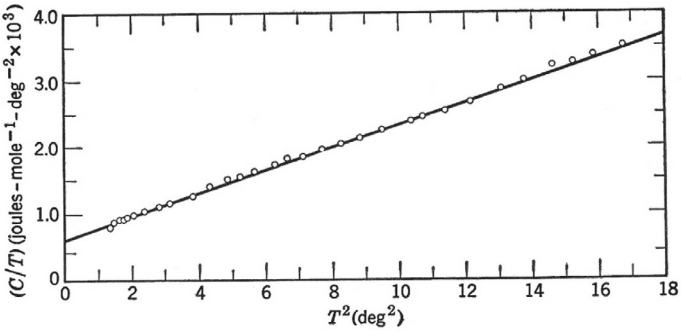


Fig. 21.4 Plot of C/T versus T^2 for silver at very low temperatures [6]

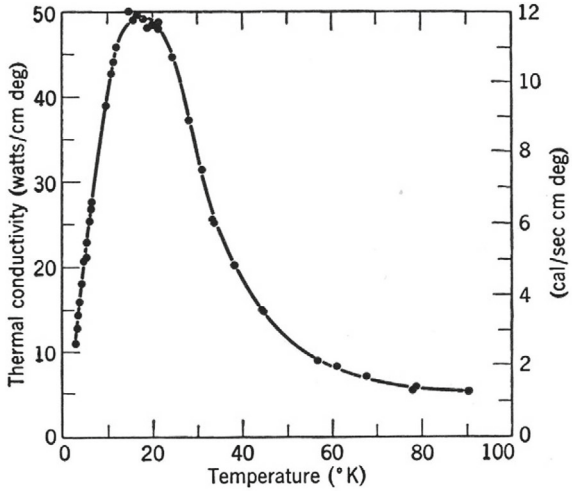


Fig. 21.5 Thermal conductivity of copper as a function of temperature [6]

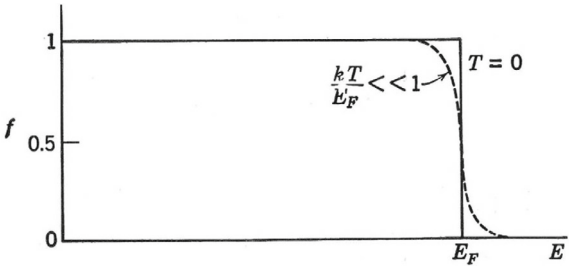


Fig. 21.6 Graph of the Fermi–Dirac distribution (Eq. 21.4) as a function of temperature for both $T = 0$ and for a temperature at which the temperature is still low enough that $k_B T/E_F$ is still small. (E_F/k_B for copper is 82000 K) (This explains why the electronic contribution to the heat capacity is so low: 273/82000 is very small!) [6]

the decrease in the electron mean free path. Both phonons and electrons scatter electrons.

The electrical conductivity can be expressed as [6]: $\sigma = Ne^2\tau/m$, where N is the number density of free electrons, e is the electron charge, m is the electron mass and τ is the mean free transit time of the electron. The first major challenge is to calculate the number density of "free electrons." This required the theory developed by Enrico Fermi (1901–1954) and Paul Dirac (1902–1984). Each metal is characterized by an energy, called the Fermi energy, E_F, that sets the energy at which all the electrons are not free at low temperatures. The Fermi–Dirac Distribution is given by:

$$F(E) = \frac{1}{\exp\left(\frac{(E-E_F)}{k_B T}\right) + 1} \tag{21.4}$$

A typical graphical example is given in Kittel [6] (Fig. 21.6).

Once the electronic conductivity has been obtained, the electronic contribution to the thermal conductivity can be calculated from the Wiedemann–Franz Law [7]:

$$\kappa_e = \sigma LT, \text{ where } L = \left(\pi^2/3\right)(k_B/e)^2 = 2.44x10^{-8}V^2/K^2 \tag{21.5}$$

L here is called the Lorenz number.

This combination of precise experiments and careful phenomenological physics produces a satisfying understanding of electronic thermal conductivity in terms of the conductivity of the free electrons. (Franz could never have understood it this way, since electrons were not discovered in 1853!).

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Thermal Conductivity in the 21st Century

22

Abstract

The study of the nature of heat continues to be an active area of research in the twenty-first century. Both improvements in theory and dramatic improvements in the laboratory have been reported. The many forms of "imperfections" in solids have been explored. Thermoelectric devices are now an important part of industrial practice. But, the fundamental truth about heat remains the same: Heat flows from a hot body to a cold body!

A fitting final chapter is based on the edited volume *Thermal Conductivity: Theory, Properties, and Applications* (2004) by Terry M. Tritt [1]. It is restricted to solids, but the thermal conductivity of gases and liquids was well-understood in the twentieth century. With the appearance of many new types of solids, both substances with ever higher thermal conductivity and ever lower thermal conductivity (insulators), new concepts have emerged.

Chapter 1.1 is a review of the "Theory of Thermal Conductivity" by Jihui Yang. He reminds his readers that "Heat energy can be transmitted through solids via electrical carriers (electrons or holes), lattice waves (phonons), electromagnetic waves, spin waves, or other excitations." The total thermal conductivity is the sum of the conductivities of each "channel."

For a system composed of "particles," the thermal conductivity κ is expressed as

$$\kappa = (1/3)\, C\, v\, l \tag{22.1}$$

where C is the heat capacity per unit volume, v is the mean velocity of the particles, and l is the mean-free path. This formulation allows the theorist to focus on the three key concepts separately. The heat capacity is a measurable thermodynamic property, for gases, liquids and solids. The velocity can also be measured

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for particles in a dilute gas, sound in a liquid or solid, or other carriers of the energy. The trajectory is modeled as a "random walk," whether it occurs in a gas, liquid or solid.

The thermal conductivity due to electrons in metals is conveniently expressed in terms of the "electrical conductivity," σ, the Lorenz number L_0, and the temperature, T:

$$\kappa_e = L_0 \sigma T \tag{22.2}$$

The electron mean-free path is determined both by the physical structure of the solid and by the scattering of electrons by phonons. At very low temperatures, it is convenient to define an "electronic thermal resistivity," ($W_e = 1/\kappa_e$). The resistivity can be separated into two contributions: (1) scattering by thermal phonons, W_i, and (2) scattering by structural defects, W_0. Careful annealing of the metal can highly reduce W_0. It can be shown that:

$$W_0 = r_0/L_0 T \tag{22.3}$$

Thus, at very low temperature:

$$\kappa_e \approx (L_0/\rho_0)T \tag{22.4}$$

In order to discuss the resistivity due to scattering by phonons, it is necessary to remind ourselves of the discussions in Chapters 19, 20 and 21. It is convenient to identify a measure of the modulus of the matrix, expressed as a temperature, θ_D, called the Debye Temperature. The "ideal resistivity" due to the phonons can then be expressed as:

$$\rho_i = A\left(\frac{T}{\theta_D}\right)^5 J_5\left(\frac{\theta_D}{T}\right) \tag{22.5}$$

where A is a very complicated constant based on many known constants and J_5 is the fifth order function:

$$J_5\left(\frac{\theta_D}{T}\right) = \int_0^{\frac{\theta_D}{T}} \frac{x^5 e^x}{(e^x - 1)^2}\, dx \tag{22.6}$$

Actual data for the thermal conductivity of silver as a function of temperature is shown in Fig. 22.1 [2]. The thermal conductivity continues to rise as the temperature falls until the mean free path becomes comparable to the texture of the residual defects.

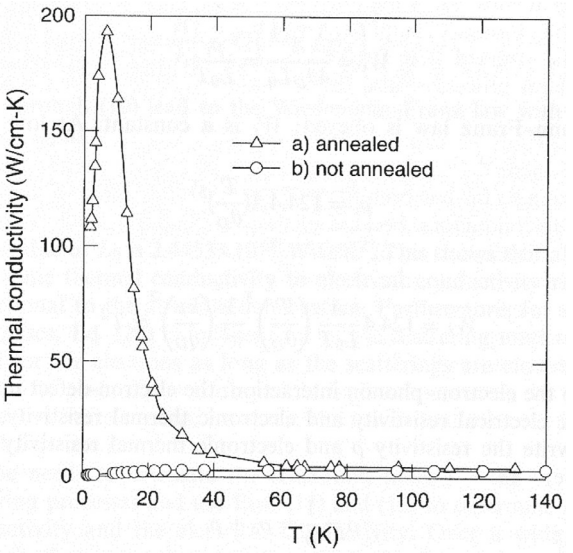


Fig. 22.1 Thermal conductivity of metallic silver as a function of temperature for a raw, polycrystalline sample and a highly annealed crystal [2]

Heat is also transported directly by the phonons. Yang presents an explicit expression for the contribution of the lattice phonons in the Debye approximation: (22.4)

$$\kappa_L = \left(\frac{k_B}{2\pi^2 v}\right)\left(\frac{k_B T}{\hbar}\right)^3 \int_0^{\frac{\theta_D}{T}} \tau(x)\left(\frac{x^4 e^x}{(e^x-1)^2}\right) dx \tag{22.7}$$

where $x = \hbar\omega/k_B T$ and the relaxation times may be a function of the energy of the phonon and the temperature of the medium. Yang astutely recognizes that the differential specific heat in this approximation can be expressed as:

$$C(x)dx = \left(\frac{3k_B}{2\pi^2 v^3}\right)\left(\frac{k_B T}{\hbar}\right)^3 \left(\frac{x^4 e^x}{(e^x-1)^2}\right) dx \tag{22.8}$$

where the mean-free path is then: $l(x) = v\,\tau(x)$. This allows the overall lattice thermal conductivity to be expressed as:

$$\kappa_L = \left(\frac{1}{3}\right) \int_0^{\frac{\theta_D}{T}} C(x)\, v\, l(x) dx \tag{22.9}$$

Both the differential heat capacity and the mean-free path then contribute as an average, but the form of the thermal conductivity retains its classical expression from Eq. 22.1.

Energy may also be lost by the phonon due to exchange with other lattice vibrations, including "optic modes." These processes, called "Normal processes, or N-processes" contribute to a lower thermal conductivity by draining energy away from direct transport of heat.

22.1 Thermal Conductivity of Metals

There is an enormous range of measured thermal conductivities for metals. Chapter 1.2, written by Ctirad Uher, explores both the full range of observed conductivities and the concepts needed to understand them. Since most metals are used as alloys in modern technology, the influence of the structure and dynamics of alloys is also considered.

Uher constructed a table of known thermal conductivities based on the classic Landolt-Börnstein compilation [3]. For the "noble metals," (Au, Ag, Cu) the thermal conductivity is dominated by the conduction of electrons. Uher's stated goal is to identify trends and to aid engineers in making good estimates of the thermal conductivity of metallic systems.

22.2 Electronic Heat Capacity

In Sect. 22.2, three key concepts are used to think about the thermal conductivity of metals: (1) specific heat, (2) electron mobility and (3) electron mean-free path. The electronic specific heat depends on the Fermi–Dirac Distribution for the valence electrons:

$$f(E,T) = \frac{1}{\exp^{\frac{(E-E_F)}{k_B T}} + 1} \tag{22.10}$$

where E_F is the Fermi energy discussed in Chapt. 21 (see Eq. 21.3). Another key aspect of the electron contribution is the "density of states" D(E). The specific heat per unit volume of electrons, c_V, can then be expressed as:

$$c_V = \int_0^\infty (E - E_F)\, D(E) \left(\frac{\partial f(E,T)}{\partial T} \right) dE \tag{22.11}$$

Metals are characterized by a specific "valence," the number of electrons that can participate in chemical reactions and carry heat: Z. After appropriate mathematical and physical laws are applied, the electronic specific heat per mole can then be expressed as:

$$\overline{C}_e = \frac{\pi^2}{2} Z\, k_B\, N_A \frac{T}{T_F} = \gamma T \tag{22.12}$$

TABLE 2 Comparison of Experimental and Calculated (free-electron) Values of the γ Coefficient of the Electronic Specific Heat for Selected Metals.[a]

Metal	Valence	Free-electron γ (10^{-3} J mole^{-1}K^{-2})	Experimental γ (10^{-3} J mole^{-1} K^{-2})
Na	1	1.09	1.7
K	1	1.67	1.7
Ag	1	0.64	0.66
Au	1	0.64	0.67
Cu	1	0.50	0.69
Ba	2	1.95	2.72
Ca	2	1.51	2.72
Sr	2	1.80	3.64
Co	2	0.61	4.98
Fe	2	0.64	5.02
Ni	2	0.61	7.02
Al	3	0.91	1.30
Ga	3	1.02	0.63
Sn	4	1.39	1.84
Pb	4	1.50	2.93
As	5	1.30	–
Sb	5	1.63	0.628
Bi	5	1.79	0.08

a. Experimental values are taken from Ref. 2.

Fig. 22.2 The "gamma" coefficient for some metals compared to the prediction of the value from (22.9)

This form for the electronic specific heat was discussed in Chapter 21. Many metals have been analyzed using this paradigm. Uher constructed a table (Fig. 22.2) of some results organized in terms of the number of valence electrons. These theoretical predictions were then compared to experimental results like those shown in Fig. 21.4 for silver.

The theory works well for the noble metals. It underestimates the effect for "transition metals," and overestimates the effect for "semi-metals" like bismuth. There must be something very special about nickel (Ni).

22.3 The Importance of the Boltzmann Equation for Understanding the Electronic Transport of Heat

The Boltzmann Equation was introduced as Eq. 15.2. It applies to all time-dependent distribution functions. In Sect. 3, Uher presents a lucid discussion of the use of the Boltzmann Equation in understanding electron transport in metals. He stresses that the geometry of the crystalline matrix is an essential part of the description of metals. Another key concept is "reciprocal space." Each "particle" is characterized by a "Bloch vector:" $\vec{k}$. The Bloch energy, $E\left(\vec{k}\right)$, allows a "group

velocity" to be calculated:

$$\left(\frac{1}{h}\right)\left(\frac{\partial E\left(\vec{k}\right)}{\partial \vec{k}}\right) \tag{22.13}$$

The key element of the Boltzmann Equation is the distribution function: $f\left(\vec{r}, \vec{k}, t\right)$. Uher identifies three "influences" that change this local distribution: (1) electrons may simply diffuse out of the region centered at $\vec{r}$, (2) electrons may be acted upon by electric fields or by thermal gradients, and (3) electrons may be "deflected" by phonons or by lattice imperfections. "After some algebra" he presents an expression for the "perturbed distribution function" that relaxes to the equilibrium state with a "relaxation time" $\tau\left(\vec{k}\right)$:

$$f\left(\vec{k}\right) = f^0\left(\vec{k}\right) + \left(-\frac{\partial f^0}{\partial E}\right)\vec{v}\left(\vec{k}\right)\tau\left(\vec{k}\right)\left\{e\left(\vec{\varepsilon} - \left(\frac{1}{e}\right)\nabla_r E_F\right) + \left(\frac{E - E_F}{T}\right)(-\nabla_r T)\right\} \tag{22.14}$$

where the gradient symbol, ∇_r, is the ordinary spatial gradient vector. While this expression looks formidable, it allows any good theorist to proceed directly to a discussion of electron transport in metals.

The existence of Brillouin zones also allows electrons to be scattered. The Fermi surfaces are actually quite complex in metals. Both longitudinal and transverse phonons can scatter electrons, since electrons also have angular momentum. Uher discusses this issue in terms of the difference between the Debye and Fermi "spheres." At high temperatures, high energy phonons can produce large changes in the electron trajectory and relax the fluctuation. The relaxation time for such processes is proportional to $1/T$. At temperatures well below the Debye temperature, electron–phonon scattering produces only small changes in direction and many events are needed to fully relax the fluctuation. The relaxation time now changes as $1/T^3$, as observed. Learning to think in reciprocal space and to imagine the complex Brillouin zones is challenging, and historians should be glad that there are competent solid-state physicists. The temperature dependence of the thermal conductivity for four very different metals is shown in Fig. 22.3.

22.4 Thermal Conductivity of Insulators and Glasses

Chapter 1.3 focuses on materials where acoustic phonons carry most of the heat. A detailed discussion of the "resistance to phonon propagation" is presented. Two acoustic phonons can annihilate one another with the creation of a new third phonon that satisfies conservation of energy and momentum. In a solid, the matrix can also participate and either add or subtract energy. Such processes are called

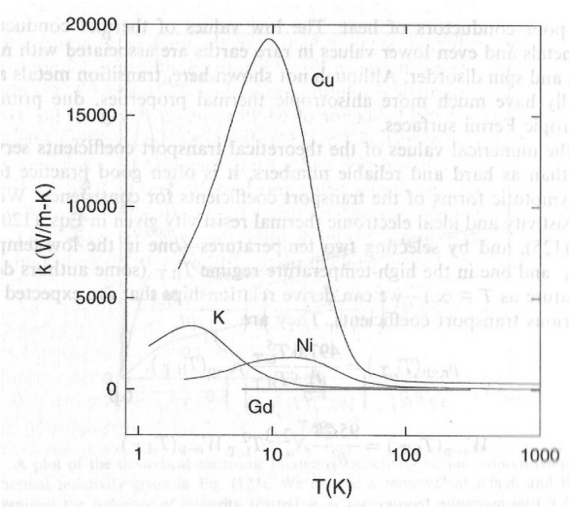


Fig. 22.3 Thermal conductivities for copper (Cu), a noble metal, potassium (K), an alkali metal, nickel (Ni), a transition metal, and gadolinium (Gd), a rare-earth metal. The temperature axis is logarithmic. There is a maximum for gadolinium as well around 25 K, but on the linear scale it is hard to see. The peaks occur at approximately $\theta_D/15$

"Umklapp processes." Another type of process starts with one phonon and produces two phonons with conserved energy and momentum. There can also be Umklapp processes that either add or subtract energy and momentum to the second form. Phonon resistivity is dominated by U-processes in insulating solids.

A transparent formula for the inverse relaxation time associated with loss due to U-processes is:

$$\frac{1}{\tau_U} = A\,\omega^2\,T\,\exp\left(-B\left(\frac{\theta_D}{T}\right)\right) \tag{22.15}$$

where A and B are material specific (experimental) constants. For temperatures large relative to the Debye temperature, the thermal conductivity scales as $1/T$, as observed for many well-ordered insulators. At low temperatures, scattering by imperfections dominates the loss and the mean-free path, λ, is constant. An instructive figure, presented as a log–log graph, follows the thermal conductivity, κ, and the mean-free path, λ, as a function of T (Fig. 22.4): The maximum in the thermal conductivity occurs near $\theta_D/10$.

Chemical atoms can have many different isotopes. This fluctuation in mass can lead to scattering of phonons, and hence to reduction in the mean free path. Elegant experiments with highly isotopically purified diamonds (99.999% ^{12}C) have obtained much higher thermal conductivities (41,000 $Wm^{-1}\,K^{-1}$) [4].

Molecular solids can introduce disorder due to fluctuations in packing and intrinsic conformational fluctuations. Acoustic phonons can also interact with "optic modes" of crystalline solids or individual molecules. Local, non-propagating vibrational modes exist in all atomic solids. For inorganic ionic solids, these polar vibrations can interact strongly with phonons. For "molecular solids," many vibrational modes exist and can transfer energy with these processes. Amorphous solids

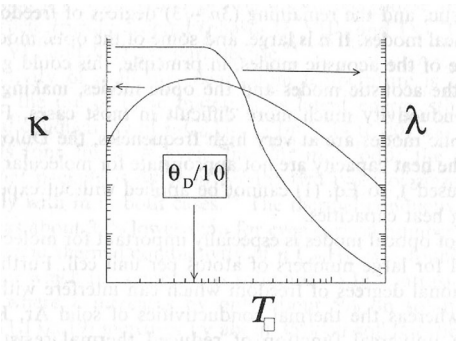


Fig. 22.4 Schematic view of the thermal conductivity and the phonon mean-free path as a function of temperature [3]

(glasses) are intrinsically disordered. Phonon mean-free paths must remain small for wave vectors near the range of the disorder.

22.5 Thermal Conductivity of Semiconductors

One of the most active areas of research in the last 50 years is the study of semiconductors. These materials come in two forms: (1) Binary or Ternary compounds, and (2) Doped insulators. Both kinds exhibit higher energy bands of energy for the electrons. Doped semiconductors also exhibit a new form of "carrier:" holes. These structures can carry heat!

As covered in Chap. 1.4, semiconductors exhibit the Seebeck effect: A temperature gradient produces an electrical potential difference: (22.12).

$$S = -\frac{\Delta V}{\Delta T} \tag{22.16}$$

The Seebeck coefficient is positive if the carrier of heat is holes, and negative if the carrier is electrons. A table of Seebeck coefficients is shown as Fig. 22.5.

In some semiconducting systems, both electrons and holes contribute to the heat flow. One of the key relationships presented in this chapter is the electrical thermal conductivity of a doped semiconductor, such as bismuth-telluride:

$$\kappa_e = \kappa_{e,1} + \kappa_{e,2} \frac{\sigma_1 \sigma_2}{(\sigma_1 + \sigma_2)} (\alpha_2 - \alpha_1)^2 T \tag{22.17}$$

where 1 and 2 are electrons or holes, σ, is the electrical conductivity, and α, is the Seebeck coefficient.

A remarkable relationship between the lattice contribution to the thermal conductivity and easily measurable properties was presented:

$$\kappa_L T = \left(\frac{R^{\frac{3}{2}}}{3\gamma^2 \varepsilon_m^3 N_A^{\frac{1}{3}}} \right) \left(\frac{T_m^{\frac{3}{2}} \rho^{\frac{2}{3}}}{M} \right) \tag{22.18}$$

Fig. 22.5 Seebeck coefficients for elements from bismuth to selenium [5]

Material	Seebeck coefficient *relative to platinum* (μV/K)
Selenium	900
Tellurium	500
Silicon	440
Germanium	330
Antimony	47
Nichrome	25
Iron	19
Molybdenum	10
Cadmium, tungsten	7.5
Gold, silver, copper	6.5
Rhodium	6.0
Tantalum	4.5
Lead	4.0
Aluminium	3.5
Carbon	3.0
Mercury	0.6
Platinum	0 (definition)
Sodium	-2.0
Potassium	-9.0
Nickel	-15
Constantan	-35
Bismuth	-72

where γ is the Gruneisen parameter (related to the mechanical moduli), M is the average atomic mass, and ε_m is a known fraction of the lattice constant. Real data supports this as a good qualitative guide (Fig. 22.6).

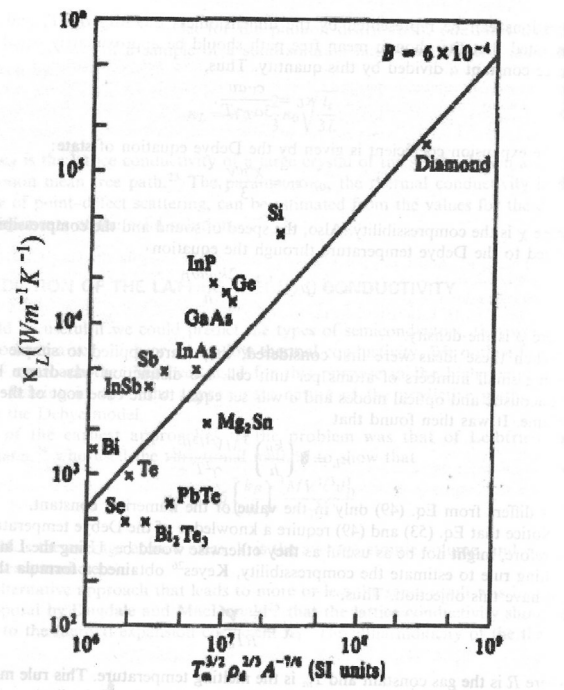


Fig. 22.6 The quantity $\kappa_L T$ (in spite of the error in the graph as shown) versus the material property product $T_m^{\frac{3}{2}} \rho^{\frac{2}{3}} (A \equiv M)^{-\frac{7}{6}}$. Again, diamond is the largest due to its high modulus. Materials with large Atomic weights have lower thermal diffusivities

22.6 Concluding Reflections

One of the most important conclusions from this study is that the "history of heat" is not finished. One example of this conclusion is the work of Steven Hawking on black holes. Are black holes really completely dark? Hawking believes in the Fourier heat law. How can black holes "evaporate?" While quantum tunneling ideas allow energy to "leak" out of a black hole, classical Thermodynamics can help us understand the "temperature" gradients between celestial regions.

Even in 2025, we are hardly sure that all forms of heat are known. Every form of heat involves energy "on the move." Electromagnetic radiation is the most common form of heat in the universe. Gamma rays are found in all parts of the known universe. Visible light is still being studied with various forms of "telescope." Infrared light (thermal radiation) is an important part of the universe. One of the key Nobel Prizes in the twentieth century was awarded for the characterization of the "microwave background radiation." Microwave astronomy is one of the most active current fields of research.

Energy can be carried by all massive particles that can exist independently. Electrons are emitted by our sun, along with many other massive particles. One of the more interesting forms are the "neutrinos." There are three forms that interconvert and have been "weighed." How important are neutrinos in the energy balance of the universe? On earth, neutrons are a very important part of the "Heativerse."

In the nineteenth century, geologists were surprised to discover that the center of the Earth is very hot. Where does this energy come from? It was assumed that all thermal energy on Earth comes "from the sun." Nuclear potential energy can be converted to "heat" in the form of many emitted particles. The neutrons have been commercialized as a major source of power for human culture. What if we could commercialize neutrinos?!

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