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HISTORICAL DEVELOPMENT IN THE THOUGHT OF THERMAL SCIENCE—HEAT AND ENTROPY

PREFACE AND CHAPTERS 18–20 (250 YEARS AFTER JAMES WATT AND 200 YEARS AFTER SADI CARNOT)

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ABSTRACT

This paper is an English excerpt of the Japanese book "*Historical Development in the Thought of Thermal Science—Heat and Entropy*" by Yoshitaka Yamamoto (first edition, Gendai-Sugakusha, Kyoto, 1986; revised edition, Chikumashobo, Tokyo, 2009). The subtitle "*250 Years after James Watt and 200 Years after Sadi Carnot*" was added to this excerpt by the translator, because the separate condenser for the steam engine was invented (patented) by Watt in 1769 and the historical paper "*Réflexions sur la Puissance Motrice du Feu (Reflections on the Motive Power of Fire)*" was published by Carnot in 1824. In the *Fourier Lecture* at IHTC-16, the translator presented one of the most important and interesting parts of Yamamoto's masterpiece, in which he thoroughly studied the development of thermal science in the seventeenth–nineteenth centuries and shed light on its true nature; this excerpt comprises Chapters 18–20, about one-tenth of the original book. In Chapter 18, Carnot's original problem setting of the motive power of heat is discussed in conjunction with Watt's pioneering work on the steam engine. In Chapters 19 and 20, the essence of Carnot's theory is described, and its profound significance in physics is analyzed in detail.

KEY WORDS: History of thermal science, James Watt, Sadi Carnot, Heat, Caloric theory, Steam engine, Motive power, Carnot cycle, Thermodynamics

PREFACE TO THE FIRST EDITION

Through the fevered Age of Great Voyages in Western Europe, human activity extended to the entire globe and discovered an entirely renewed world. On the basis of this world view, modern Europe advocated and developed heliocentrism and modern physics.

Modern physics was launched from the mechanisms proposed by Galileo and Descartes. It succeeded in providing a quantitative understanding of nature by regarding natural objects as homogeneous inactive bodies having only a geometrical shape and motion; this was a giant leap from Aristotelian physics, which focused principally on qualities. Simultaneously, it achieved a breakthrough from Aristotle's dualistic world view (i.e., a terrestrial world and celestial world), which was deduced from daily experiences that motion on the ground inevitably decelerates and ceases unlike the eternal and regular motion of heavenly bodies. Contrary to Aristotle's view, the modern mechanism treated celestial and terrestrial bodies on an equal footing, and such an approach was initially realized by neglecting the friction and drag associated with motion on the ground.

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It was Newton who overcame the limitation of the primitive mechanism. He recognized that the deceleration of motion by friction and drag is inevitable in nature, and furthermore introduced the concept of a force acting between bodies; this concept was necessary to compensate for deceleration. However, Newton also regarded ordinary matter as being passive and inactive, so forces were considered to be exerted by means of 'aether' as an active agent. This was one of the means of treating activity in the natural world, which newly introduced a dualistic materialism into the monistic one previously homogenized by the primitive mechanism.

The 'aether' of Newton as an active agent soon became the 'air' of Hales, 'materia ignis' of Boerhaave, 'electric matter' of Franklin, 'phlogiston' of Stahl, and finally the material of heat or 'calorique' of Cleghorn, Lavoisier, and others. Therefore, the caloric theory in the late eighteenth century was not a simple alternative to the dynamical theory of heat but connoted the pan-thermal world view, which regarded heat as the ultimate source of natural activity. It was an alternative, or at least a complement, to the mechanism in the seventeenth century. Furthermore, the material theory of heat, namely the considerations of heat as a special material, after the establishment of fundamental calorimetry by Black, paved the way for quantification in thermal science through its conservation and equilibrium. Although caloric theory itself was proved to be incorrect in the nineteenth century, we should note that its impact on thermal science and its legacy were profound.

Affected by the pan-thermal world view as well as caloric theory, and stimulated by the development of steam engines since Watt, in 1824, Carnot first proposed and solved the problem of whether the motive power (work) produced from heat has a limitation governed by principles. According to Carnot, to produce motive power from heat, a temperature difference between the heat source and environment is necessary, and its maximum efficiency is determined by their temperatures.

On the other hand, Mayer and Joule insisted that heat and work are equivalently interchangeable and their total is conserved. Such an approach advanced the unification of heat and work into energy, and apparently contradicted Carnot's principle that the conversion from heat to work is realized under a special condition, i.e., the existence of a temperature difference. Although the conservation of heat on which Carnot's work was based was later rejected, it is impossible to extract work by simply cooling a uniform-temperature body, even though such extraction of work does not violate the law of energy conservation.

By resolving the contradiction between Carnot and Mayer/Joule, Clausius and Thomson established almost perfect thermodynamics. Its principle is based on the argument that in nature there exist irreversible processes—entropy production in addition to energy conservation. Previously, to understand terrestrial phenomena in the same manner as planets and to construct a unified view of the cosmos, the mechanism neglected friction, drag, and diffusion/dissipation due to conduction/mixing. Clausius's and Thomson's thermodynamics, however, affirmed that such phenomena are essential natural principles.

The creation of thermodynamics was a giant step toward understanding terrestrial phenomena. Looking back over the history of thermal science, from the very beginning, it developed with the aim of understanding the phenomena on earth, which is a unique environment for humanity and also a huge thermal engine. Thermal science has retained its profound significance to this day, even though mainstream physics has shifted from macroscopic to microscopic subjects. The existence of humanity depends on the entropy balance of the globe.

The purpose of this book is to clarify the scope of thermal science and its importance in modern times by historically and demonstratively reviewing the development of thought on thermal science from the birth of modern physics to the early twentieth century. This book is basically a history of ideas that was also written with the aim of its use a textbook on thermal science. I sincerely hope that this book will be read from various viewpoints.

November 1986

Yoshitaka Yamamoto

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IMPORTANT PERSONS IN THIS BOOK

Born in the sixteenth century
Galileo Galilei (1564–1642)
Pierre Gassendi (1592–1655)
René Descartes (1596–1650)
Born in the seventeenth century
Robert Boyle (1627–1691)
Robert Hooke (1635–1703)
Isaac Newton (1642–1727)
Thomas Savery (ca.1650–1715)
Thomas Newcomen (1664–1729)
Herman Boerhaave (1668–1738)
Stephen Hales (1677–1761)
John Theophilus Desaguliers (1683–1744)
Colin Maclaurin (1698–1746)
Born in the eighteenth century
Benjamin Franklin (1706–1790)
William Cullen (1710–1790)
David Hume (1711–1776)
Joseph Black (1728–1799)
James Watt (1736–1819)
William Irvine (1743–1787)
Antoine Laurent Lavoisier (1743–1794)
Pierre-Simon Laplace (1749–1827)
Benjamin Thompson, Count von Rumford (1753–1814)
Lazare Carnot (1753–1823)
William Cleghorn (1754–1783)
John Dalton (1766–1844)
Jean-Baptiste Joseph Fourier (1768–1830)
Thomas Young (1773–1829)
Charles Bernard Desormes (1777–1838)
Louis Joseph Gay-Lussac (1778–1850)
Nicolas Clément (1779–1841)
Siméon Denis Poisson (1781–1840)
Michael Faraday (1791–1867)
William Whewell (1794–1866)
Nicolas Léonard Sadi Carnot (1796–1832)
Émile Clapeyron (1799–1864)
Born in the nineteenth century
Henri Regnault (1810–1878)
Carl Holtzmann (1811–1865)
Julius Robert von Mayer (1814–1878)
James Prescott Joule (1818–1889)
Hermann Ludwig Ferdinand von Helmholtz (1821–1894)
Rudolf Julius Emanuel Clausius (1822–1888)
William Thomson, 1st Baron Kelvin (1824–1907)
Julius Thomsen (1826–1909)
Pierre Eugène Marcellin Berthelot (1827–1907)
James Clerk Maxwell (1831–1879)
Josiah Willard Gibbs (1839–1903)
August Horstmann (1842–1929)
Ludwig Eduard Boltzmann (1844–1906)
Jacobus Henricus van't Hoff (1852–1911)
Max Karl Ernst Ludwig Planck (1858–1947)
Walther Hermann Nernst (1864–1941)

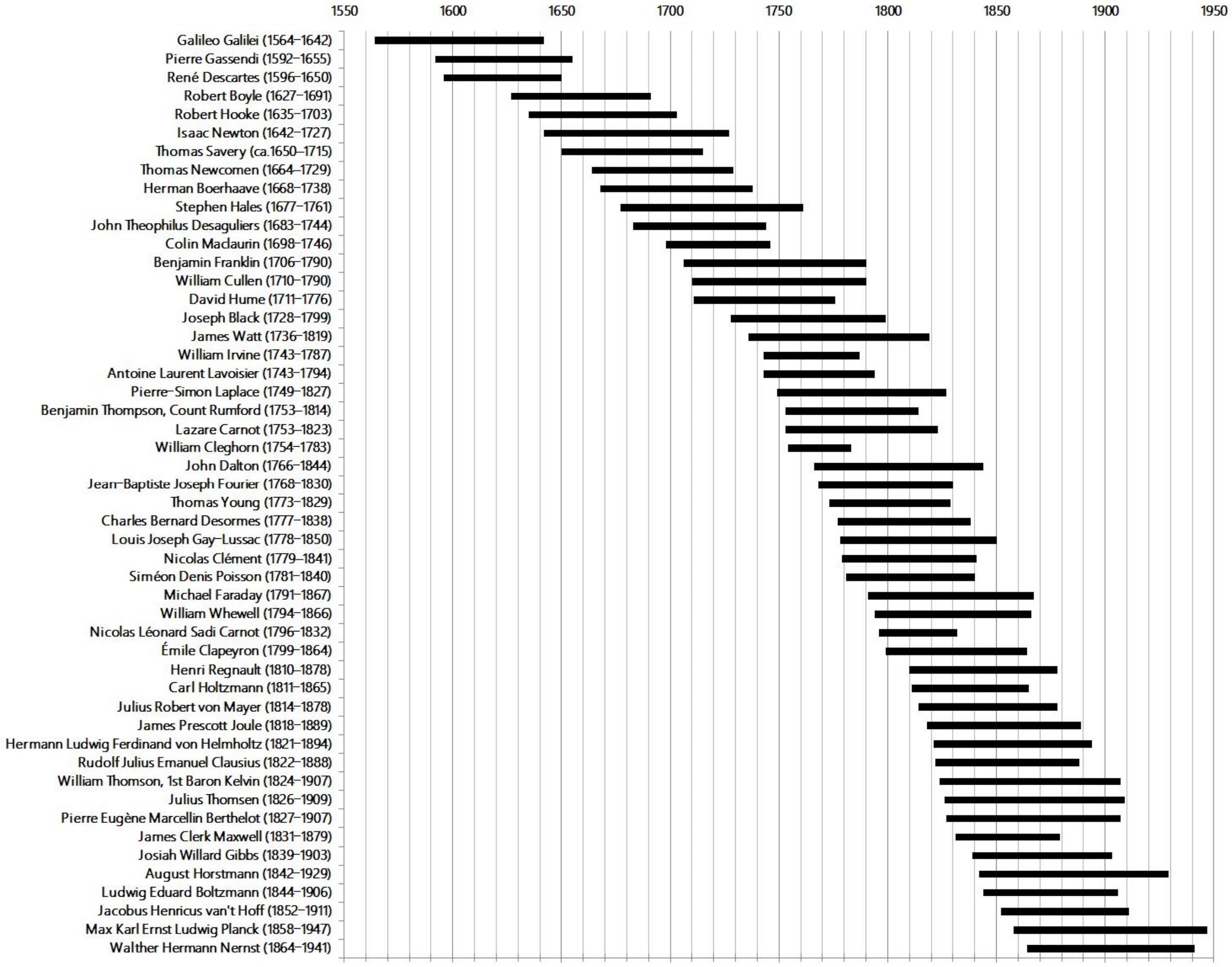

Fig. 1 Dates of important persons in this book. Note that this year, 2018, marks the 250th anniversary of Fourier's birth and the 200th anniversary of Joule's birth. (This section and Fig. 1 have been supplemented by Yoshida.)

CHAPTER 18 SETTING OF A NEW PROBLEM—"MOTIVE POWER" OF HEAT —CARNOT AND WATT

CONTENTS

I. Neglect of Carnot's paper during his lifetime

It was on August 24, 1832 that Sadi Carnot (Fig. 18.1) died of cholera at his age of 36. Although there is no connection, only three months prior to his death, the mathematician Évariste Galois was also killed before his 21st birthday. France experienced the successive early deaths of two great geniuses in physics and mathematics. Without doubt, the driving force of their work was the French intellectual atmosphere of that age, as if "the whole of Europe was illuminated by the light of science which emanated from Paris during the first third of this century"[1].

It was many years later, however, that the significance of their pioneering studies was understood and recognized by people; at that time, people, science, and society were all immature.

Sadi Carnot's short life is only known from a biographical sketch written in 1878 by Hippolyte Carnot (1801–1888), who was Sadi's younger brother and a French statesman [2]. Sadi's and Hippolyte's father was Lazare Carnot (1753–1823), who was a French politician known as "the Organizer of Victory" in the French Revolutionary Wars. Since he acted as a republican even in the anti-revolution period, he was purged and forced into exile; although he was a famous statesman, he was also an eminent mathematician and an engineer with expertise in applied mechanics. Sadi, who was born in 1796, graduated from the École Polytechnique in Paris, 1814. After becoming an army officer, he started research on physics and engineering perhaps being influenced by his father. Although he was isolated from the circle of the scientific elite such as Laplace (1749–1827), Gay-Lussac (1778–1850), and Poisson (1781–1840) as well as the French scientific establishment, he was acquainted with Clément (1779–1841), one of the first chairs in chemistry at the Conservatoire des Arts et Metiers in Paris.

According to Hippolyte Carnot, "He had such a repugnance to bringing himself forward that, in his intimate conversations with a few friends, he kept them ignorant of the treasures of science which he had accumulated"[2]. Despite his reticence, however, he was a quarter of a century ahead of the physicists at that time.

He left us with only three manuscripts; "*Réflexions sur la Puissance Motrice du Feu* (*Reflections on the Motive Power of Fire*) (1824), hereafter referred to as **the *Réflexions***"[3][1], which was published during his lifetime (Fig. 18.2), "*Notes sur les Mathématiques, la Physique et autres sujets* (1878)," which was published nearly half a century after his death, and "a draft of the *Réflexions*," which was discovered in 1964. His other remaining manuscripts left behind were burned to prevent cholera infection.

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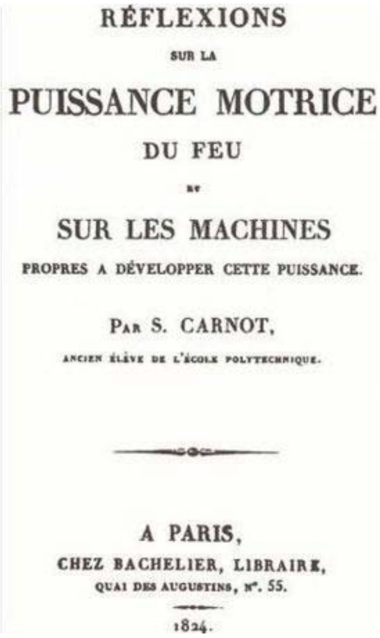
[1] Since reference [3] in this chapter is frequently referred to throughout this paper, it is expressed as [C, page number in Fox's English version (1986)], for example, [C, pp. 66-67].

Fig. 18.1 Sadi Carnot (1796–1832) at the age of 17.



RÉFLEXIONS
SUR LA
PUISSANCE MOTRICE
DU FEU
ET
SUR LES MACHINES
PROPRES A DÉVELOPPER CETTE PUISSANCE.

PAR S. CARNOT,
ANCIEN ÉLÈVE DE L'ÉCOLE POLYTECHNIQUE.

A PARIS,
CHEZ BACHELIER, LIBRAIRE,
QUAI DES AUGUSTINS, Nº. 55.
1824.

Fig. 18.2 Cover page of "*Réflexions sur la Puissance Motrice du Feu*" (1824).

In physics, if a problem has been properly defined, its solution is generally near at hand. In this sense, it is no exaggeration to say that the birth and consolidation of thermodynamics and its foundations were almost entirely due to a single paper: the *Réflexions*—a booklet of 118 pages, a small number of copies of which were published in 1824.

The paper, however, was neglected by physicists and engineers of the age, and completely forgotten after Carnot's death. "Possibly the most astonishing fact about Sadi Carnot's work is that it was received in complete silence by the world of French science"[4]. "A few days after its publication, Carnot's book was formally presented to the Académie des Sciences; this was at the meeting of Monday, June 14, 1824. It was presented by Girard, a prominent engineer. (omit) Among the Academicians present were Arago, Fourier, Laplace, Ampère, Gay-Lussac, Poinsot, Fresnel, Legendre, Poisson, Cauchy, Dulong, as well as Navier and Prony. Later this review was printed in the *Revue Encyclopédique* (23, 411, 1824). (omit) To summarise, the *Réflexions* received adequate publicity before the most eminent physicists and engineers of the Académie and the same enthusiastic report was published in a well-known journal. In spite of this auspicious beginning, one may look in vain for the slightest mention of Carnot's work in any of the journals"[4]. "In fact, Carnot's book made hardly a ripple on the surface of the main stream of science"[5].

That is, as Herivel [6] wrote, "It is too fanciful to suppose that many of the members may have allowed their attention to wander away from the *work* of the son to the *life* of the father? Some would have remembered with a sudden start the friends and relations on whose death warrants had figured the name of Lazare Carnot."

The exception is "in a manuscript book of notes taken by a student who attend the course of lectures given by Clément on Applied Chemistry at the Conservatoire des Arts et Métiers in 1824–25 and later years. The lectures were apparently open to the public"[7]. As Kuhn [8] pointed out, the mainstream of the Paris Académie had traditionally been interested in pure mathematical science since D'Alembert (1717–1783), Laplace, and Lagrange (1736–1813), while Lazare and Sadi Carnot belonged to the relatively minor stream based on practical engineering.

In 1834, ten years after Carnot's death, the engineer Émile Clapeyron (1799–1864) took up the *Réflexions* and gave it graphical and mathematical expressions in *Mémoire sur la Puissance Motrice de la Chaleur* (Cf. Reference [2] in Chapter 20). The *Réflexions*, however, still continued to be neglected. Kerker [9] wrote "F. Arago, as *sécrétaire perpetuelle* of the Academy of Sciences, read a 97-page *éloge* of Lazare Carnot in 1837, *Comptes Rendus*. 1837, 5; 294. There is no mention of Sadi in this biography which Arago submitted for publication without change in 1850, *Mémoires de l'Académie des Sciences*. 1850 (2), 22; 1. Arago's neglect of Sadi is all the more remarkable because of his interest in the history of the steam engine. First published in 1829 in *L'Annuaire du Bureau de Longitudes*, this "*Notice Historique sur les Machines à Vapeur*" was reissued in 1830, 1837 and 1860. (The 4th edition forms volume V of Arago's *Œuvres Complètes*.) The purpose of this 117-page work is to negate the assertion by many Englishmen that the steam engine was entirely an English invention. Arago emphasizes, especially, the role of Papin, but the contributions of Carnot are completely ignored, both in this work and in the biography of Lazare." Also, de Pambour's *Théorie de la Machine à Vapeur* (1939), which was well known to engineers and translated into English, does not refer to the *Réflexions* or reflect its influence. Furthermore, "Most surprisingly, the lithographic edition of course on steam engines given by Clapeyron at the *Ecole des Ponts et Chaussées* in 1844–45 makes no mention of the *Réflexions* nor uses its ideas"[10]. It was in 1844 that James Prescott Joule (1818–1889) disputed Carnot's theory on the basis of anti-caloric theory.

In the end, it was William Thomson (later Lord Kelvin) (1824–1907) who, after Clapeyron, rehabilitated the *Réflexions*, making it widely known among physicists. The following episode, however, clearly demonstrated the ignorance of the *Réflexions* by the scientific community at that time:

In 1844 or 1845 Thomson, who was born in the year that the *Réflexions* was published, learned about it for the first time from Clapeyron's paper. After he was elected a fellow of Peterhouse, Cambridge, he moved to Paris. "The perusal of this *mémoire* incited Thomson to refer to the original tract of Carnot. In vain did he inquire for it in the Library of the Collège de France. No one could tell him even where a copy might be seen. But a copy he must have, even if he searched all Paris to find it. (omit) *I (= Thomson) went to every book-shop I could think of, asking for the Puissance motrice du feu, by Carnot. "Caino ? Je ne connais pas cet auteur." With much difficulty I managed to explain that it was "r" not "i" I meant. "Ah! Ca-rrr-not! Oui, voici son ouvrage," producing a volume on some social question by Hippolyte Carnot; but the Puissance motrice du feu was quite unknown.* (omit) Not until the end of the year 1848 did he see the book, a copy of it being sent by Professor Lewis Gordon"[11]. In this way, the *Réflexions* finally reached a reader with a stature comparable to its author, in other words, a reader who could understand its significance, 24 years after its publication.

Compered with the understanding in France, other countries were far behind. In 1850, the German Rudolf Clausius (1822–1888), who developed the second law of thermodynamics almost simultaneously with Thomson, testified the following: "I have not been able to procure a copy of this work; I know it solely through the writings of Clapeyron and Thomson, from which latter are taken the passages hereafter cited"[12].[2]

In 1872, Carnot's paper was republished in *Annales Scientifiques–École Normale Supérieure* (pp. 393–457). On the other hand, "*Notes sur les Mathematiques, la Physique et autres sujets*" was first published in 1878 as an appendix of the *Réflexions*.

II. Carnot's premise and problem setting

Various reasons why Carnot's paper was neglected by physicists at that time have been conjectured by researchers, for example, the method of publication was not effective, or Carnot intentionally did not use analytical expressions to develop his concept. Although these are, of course, contributing factors, the critical reason is its contents, that is, his problem setting was essentially different from those of the physicists of that time.

The year of 1824 when Carnot published the *Réflexions* was one year after the completion of analytical calorimetry by Laplace and Poisson during the heyday of caloric theory. Caloric theory, especially the theory of specific heat and latent heat, succeeded in forming a paradigm. Carnot himself made the following comment on the 'amount of caloric.'

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[2] In this connection, there was a perversion that Carnot conceptually distinguished 'calorique' and 'chaleur'; he regarded the former as the quantity conserved in a reversible cycle, and thus equivalent to entropy. For the background of this incorrect interpretation, Clausius's testimony was misapplied as "Clausius did not know that Carnot had defined 'calorique' in a manner equivalent in principle to his own definition of entropy, a concept of Clausius introduced in 1865"[13].

"We think it unnecessary to explain here what is meant by the terms 'amount of caloric (calorique)' or 'amount of heat (chaleur)' (we use the two terms interchangeably) or to describe how to measure these quantities with a calorimeter. Nor shall we explain the meaning of latent heat, temperature, specific heat. etc. The reader should be familiar with these terms from elementary treatises on physics or chemistry"[C, pp. 66-67].

As demonstrated above, at least in the *Réflexions*, he accepted the paradigm of caloric theory with specific heat and latent heat, and developed his theory on the basis of its premises.

Note that the analytical calorimetry developed by Laplace is a dynamical theory which understands thermal phenomena in terms of 'molecules of caloric' and the force acting on them; attempts to break away from such dynamical reductionism, however, were also made. In Fourier (1768–1830)'s "*The Analytical Theory of Heat*," which was published in 1822 (two years prior to the *Réflexions*), the following description can be found:

"From what precedes it is evident that a very extensive class of phenomena exists, not produced by mechanical forces, but resulting simply from the presence and accumulation of heat. This part of natural philosophy cannot be connected with dynamical theories, it has principles peculiar to itself, and is founded on a method similar to that of other exact sciences"[14].

Without doubt, Carnot studied the above-mentioned "principles peculiar to itself." Actually, the caloric theory of Carnot was one based on the pure 'concept of functions.' Briefly, the purpose of the basic outline of his caloric theory was simply to approve the conservation of heat. The following description by Carnot clearly demonstrates how pure his caloric theory was:

"In our proof, we make the implicit assumption that when a body has undergone its various changes and after passing through a number of stages, has returned precisely to its original state (its state here being defined in terms of its density, temperature, and mode of aggregation), it contains the same quantity of heat as it did at the start. This is tantamount to assuming that the quantities of heat lost and gained in the different processes cancel one another out. This assumption has never been called into question; it was originally just taken for granted, but it has since been amply verified by numerous calorimetric experiments. To reject the assumption would be to overturn the entire theory of heat, which rests upon it."[C, p. 76].

This description on the conservation of heat directly expresses $\oint dq = 0 \ \ (13.3)''$. This is the best expression along with that of Poisson's (16-III).[3] This is completely different from the description based on the substantialism frequently repeated since Cleghorn (1754–1783) and Lavoisier (1743–1794), in which a caloric is neither an arising nor a ceasing peculiar elastic fluid having repulsion with itself but bonds with ordinary substances.

From only this feature, however, Carnot's paper can also be regarded as an extension of the analytical calorimetry purified by Poisson, which cannot have been so unfamiliar to the pivotal members of French academia. The critically novel factor which prevented them from understanding Carnot's paper was the unique style of Carnot's problem setting itself. That is, what is the theoretical limitation on the operational ability of heat? Carnot addressed this problem as follows:

First, "The question whether the motive power of heat is limited or whether it is boundless has been frequently discussed. Can we set a limit to the improvement of the heat engine, a limit which, by the very nature of things, cannot in any way be surpassed? Or, conversely, is it possible for the process of improvement to go on indefinitely?"[C, p. 63].

Second, "is the motive power of heat fixed in quantity, or does it vary with the working substance that is used? Does it vary with the intermediary material that we subject to the action of heat?"[C, p. 66].

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[3] However, as described later, Carnot finally rejected the conservation of heat and claimed the first law of thermodynamics.

Here, 'motive power (puissance motrice)' means 'work' in terms of modern physics, and its magnitude is the product of the force and the distance in the direction of the force. Actually, Carnot clearly defined it as follows: "The expression 'motive power' is used here to mean the useful effect that an engine is capable of producing. The effect can always be expressed in terms of a weight being raised to a certain height, it is measured, of course, by the product of the weight and the height to which the weight is considered to have been raised."[C, p. 63].

At that time, however, those who recognized the importance of motive power (work) and had grasped its concept clearly were researchers of applied mechanics and engineers rather than those of mathematical physics. In France, this concept was developed and established in mechanics by Lazare Carnot, Hachette (1769–1834), Navier (1785–1836), and Poncelet (1788–1867) from the eighteenth to early nineteenth century, while, in England, the same process was under way with the improvement and commercialization of the steam engine by James Watt (1736–1819) in the late eighteenth century [15]; Watt and his business partner Matthew Boulton (1728–1809) defined horsepower as a unit of power, while a unit of work [kgw·m] was first introduced by Poncelet and Navier.

The idea of not only studying the theoretical limitation of the operational ability of heat but also regarding heat as the source of motive power was motivated by the requirements of engineering and technology stimulated by the development of the fire (steam) engine. This was completely different from previous thermal science, i.e., caloric theory based on substantialism starting from natural philosophy (especially chemistry). This is the crucial point where Carnot's theory is distinguished from the previous caloric theory.

Thermal energy has been utilized since the time when humans first learned to make and control fire. The usage, however, was limited to direct use such as for heating, cooking, pottery manufacturing, and metallurgy, with the exception of guns. On the other hand, hydraulic power and animal power were used for motive power. The invention of the fire engine provided a means of converting heat to motive power. Prior to that time, humans used fire but also used various tools and machines independently of fire; the invention of fire engine integrated them both. Consequently, new issues regarding the relationship between heat and motive power were raised for engineers.

On the other hand, the central concern of the thermal science developed by Black (1728–1799), Lavoisier, Dalton (1766–1844), Gay-Lussac, and Laplace was always clarification of the change in substances with heat. That is, its main theme and purpose were to explain the expansion/contraction of matter, phase transitions, and exothermic/endothermic chemical reactions (especially combustion) as the union or separation of caloric with matter. It promoted the measurement of specific heat and contributed to the theory of the speed of sound and adiabatic changes.

Regardless of the sophistication of this approach, however, it did not go beyond 'calorimetry'; the relationship between heat and 'motive power' was of little concern. For example, at that time, regarding adiabatic changes, which typically indicate the relationship between heat and work from our modern viewpoint, the direct cause of generation/absorption was considered to be the change in volume itself. That is, people of that time did not consider that in the process of compression, mechanical work is necessary for heat generation. Also, they did not realize that, in the expansion process, they should distinguish the cases with and without work for an external system. As already stated in Chapter 15-I, Dalton wrote "Now a condensation of volume is a certain mark of diminution of capacity and increase of temperature, whether the condensation be the effect of chemical agency, as in the mixture of sulphuric acid and water, or the effect of mechanical pressure, as with elastic fluids"(*New System of Chemical Philosophy*, pt. l, p. 50, 1808, https://archive.org/details/newsystemofchemi01daltuoft [accessed May 17, 2018]), and stressed that there is no relationship between temperature changes and mechanical work.

Carnot's concern about the quantitative relationship between heat and motive power was overlooked by not only Dalton but also Lavoisier, Laplace, and Gay-Lussac. Carnot's proposition was, so to speak, a Copernican revolution, even if it was based on caloric theory. This is the real reason why Carnot's paper was neglected by academic physicists of the day.

III. Caloric theory and cosmology based on heat

The origin of caloric theory could be ascribed to the 'pneuma' of Anaximenes and the 'fire' of Heraclitus proposed in ancient times, but it can more directly be ascribed to the 'aether' of Newton. Although there is no need to dwell on Newton, let us briefly review his concept.

Classical mechanics was inaugurated when Newton introduced the concept of action at a distance between material bodies. The key concept of the cosmic system considered by Newton was the gravitational force among planets. This concept of force was far from the previous mechanism, in which materials were considered to be passive. In Descartes' mechanism, there was no origin of motion other than that given by God, and there was no action between materials other than caused by direct contact.

On the other hand, Newton did not base his work simply on his mechanism. For him, observed motion and changes could not be understood from the viewpoint of passive materials. That is, "they (= these particles) are moved by certain active Principles, such as is that of Gravity, and that which causes Fermentation, and the Cohesion of Bodies" (*Optics*, p. 376, https://archive.org/details/opticksortreatis1730newt [accessed May 17, 2018]), "And if it were not for these Principles, the Bodies of the Earth, Planets, Comets, Sun, and all things in them, would grow cold and freeze, and become inactive Masses" (*ibid.*, p. 375). It was the aether and spirits that Newton regarded as such active agents.

As a result, the aether was considered not only to be an intermediate force but also to be responsible for the expansion of materials, the reflection and refraction of light, electromagnetic phenomena, and even the functions of muscles and nerves of animals. In the final analysis, all actions in nature were ascribed to the aether. Its background was a 'pan-aetherial' view of nature, in which nature is considered as a process of circulation consisting of the evaporation/condensation and bonding/separation of aether, the essential driving force and ultimate material (Chapter 6-V).

Newton's philosophy was based on Cambridge neoplatonism, which regarded ordinary materials as passive and inactive, while active materials belonged to spirits (God); for Newton, nature was ascribed to the providence of God as an infinite spirit which is omnipresent in space. Consequently, aether and spirits as active agents were rather understood as a spiritual reality which embodies and/or expresses God's activity.

In the development of materialism during the Age of Enlightenment after Newton, the 'spiritual reality' for aether given by neoplatonism gradually disappeared, while dualism, consisting of ordinary passive materials and active principles, was retained. Thus, in the eighteenth century, through the 'air' of Hales (1677–1761), the 'materia ignis' of Boerhaave (1668–1738), and the 'electric matter' of Franklin (1706–1790), materials of heat such as the 'fire' of Cleghorn and the 'calorique' of Lavoisier were born. In all these materialisms, 'air,' 'fire,' and 'calorique' were regarded as active substances distinguished from ordinary materials, and because of such special features, their conservation law held true.

Consequently, on the basis of this historical background, caloric theory does not simply mean that heat is a material. *It was based on, from the very beginning, the "pan-thermal" view of nature in which heat is regarded as the origin of all the activity in nature, namely the motive force for material circulation and vital phenomena*.

On the other hand, owing to the progress in hydrology, meteorology, and oceanography in the seventeenth and eighteenth centuries, water circulation (evaporation of ocean water, formation of clouds, rainfall and snowfall) and atmospheric circulation (trade winds and westerlies) were understood to be caused by a thermal driving force. Thus, *a cosmology based on heat, which regards both the earth and the solar system as a heat engine, was formed*. The most typical statement of such cosmology based on heat can be found in the paper "*On Fire*" by Cleghorn, one of the pioneers of caloric theory. Let us cite its rather lengthy introduction:

"If we consider how important a part fire plays in Nature and how widespread it is, nothing will seem more deserving of the attention of philosophers. Inert matter acted on by fire puts on new forms. From it plants have drawn their life and living creatures their breath. It has given wings to the winds and movement to the waters, and it has raised the mountains that tower above the earth. What beautiful, what splendid things are thus displayed and brought into being! The earth continually changes its appearance. Now the fields are hard with frost and stiff with snow: now they smile and are bedecked with flowers, grass and leaves. Now the rivers are frozen into ice; now they flow down through the lands. Nations are terrified by clouds that blot out the day by the violent whirlwind, and the hearts of men are filled with terror.

How many and how beautiful are the things that fire produces in the sea! It produces vapours, which, driven aloft, form the rainbow by refracting the rays of light and those meteors that strike wondering men dumb with amazement. From the vapours raised into the air are formed the clouds which adorn the heavens and which, dispersed in showers, maintain the springs and rivers.

Heat is indispensable to the life of animals, to whom Nature has given the wonderful power of preserving their own temperature unchanged in the changing temperatures of the air. The same power exists in some measure also in plants: for experiments show that their juices resist the strength of cold below the freezing point; and no one doubts that they diminish the heat in hot countries. But if the external heat is increased or decreased to such an extent that the temperature of animals or plants is greatly changed, they soon perish.

Nor does fire seem to be confined within the bounds of this earth. It is probable that it flows through the whole solar system and extends to Saturn, the most distant of the planets. By analogy we conclude also that the fixed stars, which shine without number in the heavens, are bodies similar to the Sun and pour forth fire and light to other planets wheeling around them.

On this ordinance of God all thing, animate and inanimate, depend. If fire ceased to be, air would lose its spring, water its fluidity, animals their life, and all Nature would become a desolate and inert mass; if it increased greatly, the whole earth would dissolve, all things would disperse into vapour, and Nature would sink into chaos"[16].

This was written in 1779. No additional explanation is necessary. According to Cardwell [17], writing about the seventeenth and eighteenth centuries, "Indeed, a kind of cosmic machine of a second type came to be recognized. In asserting this we are extending the seventeenth century notion of a cosmic machine of the sort that was central to the thoughts of Galileo, Descartes and Newton: a strictly mechanical piece of clockwork. Fundamental to the new and complementary cosmic machine was heat."

IV. Carnot's view of nature and of society based on heat

In Carnot's paper, published about half a century after Cleghorn's paper, the pan-thermal view of nature was also enthusiastically claimed. Both Carnot's viewpoint and the accented point, however, were essentially different from those of Cleghorn. To compare them, the first part of Carnot's paper is cited below:

"It is generally known that heat can be the cause of motion and that it possesses great motive power. The steam engines in widespread use today are visible proof of this.

We must attribute to heat the great movements that we observe all about us on the Earth. Heat is the cause of currents in the atmosphere, of the rising motion of clouds, of the falling of rain and of other atmospheric phenomena; likewise, of the waters which furrow the surface of the globe and which mankind has succeeded in exploiting in some small measure. Heat is the cause too of earthquakes and volcanic eruptions.

From this vast reservoir we can draw the moving force that is indispensable to us. By providing us everywhere with fuel, nature has given us the means to produce at any time and in any place both heat and the motive power to which heat gives rise. It is the purpose of heat engines to develop this power and to harness it for our use.

The study of these engines is of the utmost interest. Their importance is immense, and their use is increasing daily. They seem destined to bring about a great revolution in the civilized world. The heat engine is already at work in the exploitation of our mines, for driving our ships, digging out our ports and rivers, forging steel, fashioning wood, milling grain, spinning and weaving cloth, transporting the heaviest loads, etc. It seems that one day it must become a universal source of power and in this respect supplant animals, water and wind. Over the first of these sources of power the heat engine has the advantage of economy; over the other two, the invaluable advantage that it can be employed and remain in uninterrupted use irrespective of either time or place.

If one day the heat engine is so perfected that it becomes cheap to erect and economical to run, it will combine all the qualities we could wish, and advance industrial techniques to an extent that can scarcely be predicted"[C, p. 61].

Carnot's view was the same as the previous cosmology based on heat as far as he also regarded heat as the motive force for the circulation of materials in nature. The crucial difference, however, is that Carnot extended the view to that of society.

While Cleghorn just (passively) praised the universality of the activity of heat in nature, Carnot attached great importance to the motive power of the heat engine, and consistently contemplated how to control and use the power for human society. It can also be said that, regarding heat, Carnot left the natural philosophical viewpoint and introduced political and economic viewpoints. The contrast between Cleghorn and Carnot demonstrates that a half-century including the French revolution and industrial revolution caused a change in the views of nature and of society, namely, the recognition of the superiority of humans to nature.

As previously stated, after the revolution, the French government promoted science and technology. Victor Hugo (1802–1885) wrote about the dream which fascinated the young after the revolution in "*Quatrevingt-Treize*" (*Ninety-Three*), in which a young Republican who had formerly been an aristocrat speaks as follows:

"Utilize nature, that gigantic auxiliary; enlist every breeze, every waterfall, every magnetic current, in your service. This globe has a subterranean network of veins, through which flows a marvellous circulation of water, oil, and fire; pierce this vein of the globe, and let the water feed your fountains, the oil your lamps, and the fire your hearths. Consider the action of the waves,—the ebb and flow of the tides. What is the ocean? A prodigious force wasted. How stupid is the earth, to make no use of the ocean!"[18].

At the time of the French revolution, young intellectuals must have been fascinated by the dream of enhancing productivity by controlling and exploiting nature, as well as (or much more than) by the idea of freedom, equality, and fraternity. It is reasonable to claim that, after the revolution, Saint-Simon (1760–1825)'s industrialism, a technocrat's dream, had been realized. Furthermore, it was correctly thought to be the heat engine (steam engine) that had achieved the dream. In 1839, Marc Seguin (1786–1875), who was later regarded as one of the pioneers of the first law of thermodynamics, wrote the following:

"The old world has shaken off the yoke of its old habits. It is refreshing and remaking itself. So look, everything is changed around us—the towns, the face of the countryside, the course of the rivers, the work of the peoples, the production of the soil and industry, the distribution of property—everything has taken a new face. And just where the direct force of the material power of men has shown itself insufficient to accomplish its work and to persevere in progress; where his will seems to be broken against insurmountable obstacles, just there a drop of water turned into steam acts to supplement his weakness, to create for him a power of which we cannot now, nor yet for a long time to come, measure the extent.
From now on with the help of this agent these prodigies have been accomplished, and the wonders which our fathers would not have thought realizable with the united efforts of all their magicians have become the ordinary run of things"[19].

Also, as can be understood from the above citation, the influence of the progress in the heat engine on Carnot would have been profound and direct. In "*The Industrial Revolution in the Eighteenth Century: An Outline of the Beginnings of the Modern Factory System in England*," Paul Mantoux wrote, "With the steam engine, science first made its appearance, and the empirical period of the industrial revolution was followed by the scientific one"[20]. Thermodynamics was established following the development of the steam engine.

Actually, it goes without saying that Carnot's problem, "The question whether the motive power of heat is limited," was stimulated by the earlier development of the heat engine, and conversely it was aimed at further improving the heat engine.

Furthermore, to solve the problem, Carnot used the improvement of the steam engine by James Watt as a clue, and directly attempted to grasp its process theoretically. This is because Watt's improvement of the steam engine was based on his purposive consideration, which clarified the essential features of the heat engine, unlike those based on ad hoc experience and intuition by craftsmen of the day. As a result, in the early nineteenth century, the heat engine had already been conceptualized, making it suitable for theoretical consideration. That is, since Watt practically pursued an ‘ideal engine,’ he could provide an object which was indispensable and most suited to the work of Carnot, who also theoretically pursued an ‘ideal engine.’

V. Development of steam engine and its defects before Watt

Here, let us briefly look back on the development of the steam engine.

Huygens (1629–1695) was the first person to invent a prototype of the internal combustion engine using gunpowder as its fuel. Controlling the reaction of gunpowder, however, was so difficult that Papin (1647–1713) used steam as an alternative working fluid. In his steam-driven water-lifting machine, a cylinder filled with water was heated, and a piston lifted by steam was then cooled by water. The subsequent downward motion of the piston was employed to lift water through the use of a lever. Although their engines can be demonstrated as desk machines, they could not be applied to practical use.

At the time, an effective means of removing and lifting spring water from mines was an important problem. That is because of the increased demand for metals owing to the modernization of weapons and the development of a money economy, which made water drainage in European mines on urgent issue. Many lifting pumps were depicted in “*De re Metallica*” by Agricola (1494–1555) in German and “*The Various and Ingenious Machines*” of Ramelli (1531–ca.1610) in Italy. Also, it is said that of “the fifty-five patents for inventions granted during the reign of Elizabeth, 1561-99, one in seven is for the raising of water”[21]. Since these hydro-, wind-, animal-, and human-power machines, had many limitations and were inefficient and uneconomical, an alternative was strongly required. This was a particularly critical problem in England in the eighteenth century.

The first commercially used steam powered device was an engine to raise water invented by Thomas Savery (ca.1650–1715) in England, as shown in Fig. 18.3. First, by opening cock O1, steam generated in boiler L is introduced to container P1. When P1 is occupied by the steam, the lower valve R3 is shut and the upper valve R1 is opened. Next, cock O1 is shut, and the outside of P1 is cooled by water. Then, the steam inside P1 is condensed, the space inside P1 becomes nearly vacuum, valve R1 is closed, valve R3 is opened, and water is lifted from underground through pipe T. Next, cock O1 is opened, and the water inside P1 is exhausted from pipe S by the force of the steam, and the system returns to the initial state. In P2, a similar process to that in P1 follows with a half-cycle delay. (This device originally only had P1 then was improved to continuously lift water by using the dual system as shown in Fig. 18.3.) That is, this operation consists of lifting water (from T to P1 and P2) by atmospheric pressure and exhausting water (from P1 and P2 to S) by steam pressure, where the former process involves water suction due to vacuum.

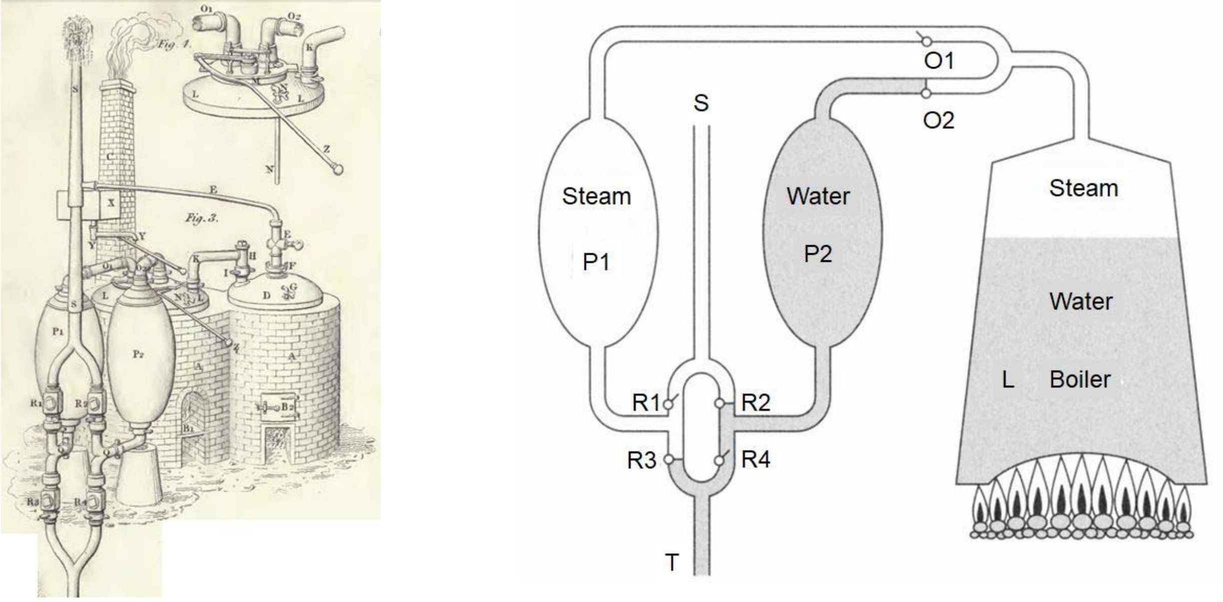

Fig. 18.3 Thomas Savery’s steam engine
(from Farey, J., *A Treatise on the Steam Engine: Historical, Practical, and Descriptive*, (1827) https://archive.org/details/treatiseonsteame01fareuoft [accessed May 17, 2018]).

This device had a defect that it could not work in principle more than 10m column of water, in addition to the practical limitations owing to the immature high-pressure technology at the time and the low efficiency associated with cooling from the outside of the container. Therefore, this device could not practically contribute to lifting water in mines.

On the basis of Papin's idea, Thomas Newcomen (1664–1729) separated the cylinder and boiler. Newcomen's practically useful engine was completed at the beginning of the eighteenth century. In 1712 the valve operations were automatized, which is considered to have revitalized the coal mines in Newcastle.

In Newcomen's engine (Figs. 18.4 and 18.5), a piston rod and a pump rod are connected to both ends of a beam oscillating about a central pivot. When a cylinder is filled with steam of nearly atmospheric pressure, the beam is

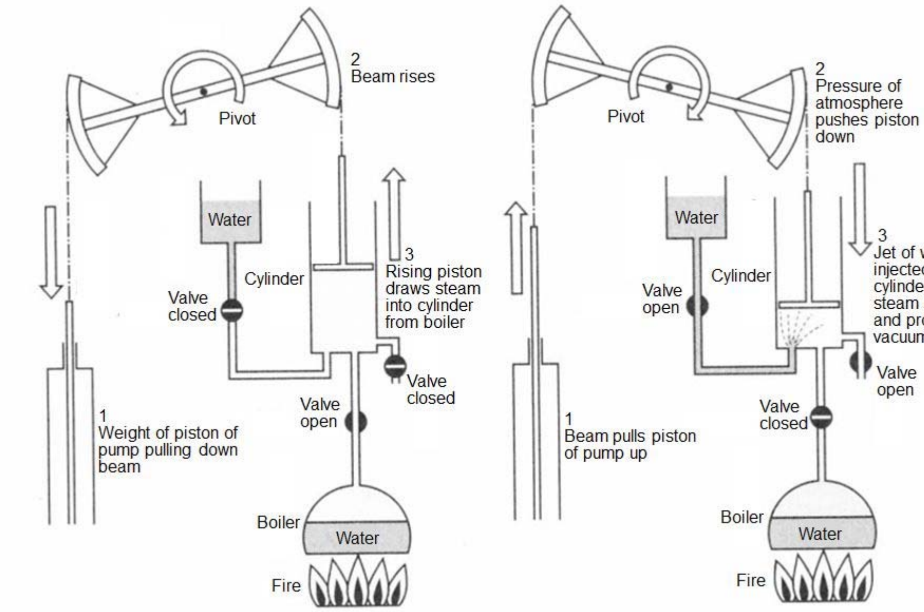

Fig. 18.4 Mechanism of Thomas Newcomen's steam engine. (I have added an exhaust valve to the figures in Lilley, S., *Men, Machines and History: A Short History of Tools and Machines in Relation to Social Progress*, London: Cobbett Press, pp. 76-77, (1948) and Bernal, J.D., *The Extension of Man: A History of Physics before the Quantum*, Cambridge: The M.I.T. Press, p. 261, (1972).)

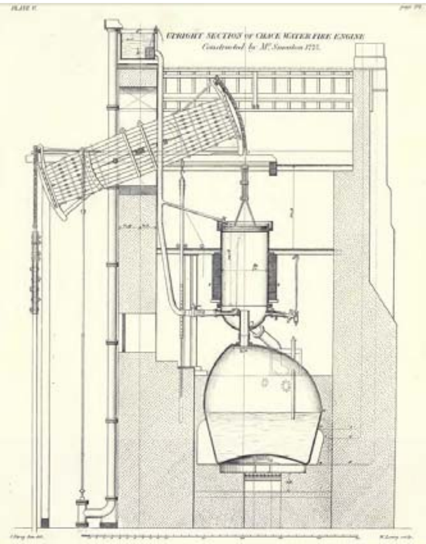

Fig. 18.5 Newcomen's steam engine designed by John Smeaton. Cooling water is stored in the upper left tank. Water exhausted from the cylinder is returned to the boiler (from Farey, J., *ibid*., (1827)).

counterweighted at the other end by the weight of the pump rod so that it tends to pull the piston up, drawing steam after it into the cylinder. When the cylinder is full, the steam is turned off and cold water is sprayed into it so that a vacuum is formed; the weight (pressure) of the atmosphere drives the piston to the bottom of the cylinder, and water is lifted on the opposite side of the beam. Since the maximum steam pressure was roughly atmospheric pressure, this machine could be built using the primitive technology at that time.

At the time, the steam engine was called an "Invention for raising Water by Fire"[22]. Indeed, Hales also called it "the engine to raise water by fire"[22].

What distinguishes Newcomen's engine is that it was operated by atmospheric pressure so can be called 'an atmospheric engine.' Furthermore, at the time, it was understood that the vacuum inside the cylinder generated by steam condensation jacks up the piston, rather than that atmospheric pressure pushes down the piston; steam, i.e., heat, was considered to merely have the peripheral role of creating the vacuum. In other words, steam was considered to perform work not by expansion but by contraction. From this understanding, it was doubtful that the crucial fact that 'heat produces work' was correctly understood.

Regarding Newcomen's engine, John Smeaton (1724–1792) later tried to improve its efficiency by changing the shape and size of the boiler and cylinder, although no essential improvements were made until those by Watt a half-century later.

In 1763, James Watt became interested in Newcomen's engine. Since 1757, Watt had been making a mathematical instruments in a workshop at the University of Glasgow, where he became friendly with Joseph Black and John Robison (1739–1805), who later edited Black's lectures. Later, Watt said, "You (= Robison) must have been much misinformed concerning my attending Dr. Blacks Lectures. I never did so, and certainly would have possessed more solid knowledge of chemistry than I do, if I had been wise enough to have done so. Every thing I learnt from him was in conversation and by doing small mechanical jobs for him. These Conversations and those I had with you served to give me true notions in Science and to develope the powers of my Mind, such as they were"[23]. On the other hand, Black and Robison also described Watt as their colleague. Robert Dick Junior, who was Professor of Natural Philosophy at Glasgow University from 1751 to 1757, supported Watt, and also Black lent research funds for putting his steam engine into practical use.

The fact that in the university a craftsman and scientists could have discussions and cooperate was due to not only the intellectual atmosphere in Glasgow but also Watt's own temperament. Actually, his way of thinking and working was more of a scientist than that of a workman. "Robison, who met him for the first time in 1758 (he was then twenty-two), was struck by his extensive knowledge and by intellectual grasp: 'I saw a workman and expected no more: I found a philosopher' "[24]. He was surprised at the depth of Watt's learning and the width of his vision. Later, Robison acknowledged Watt when he edited Black's lecture notes he edited. A century later, Balfour Stewart, a physicist of Manchester, wrote, "In 1763 James Watt, who was philosophical instrumentmaker to the University of Glasgow"[25].

Watt encountered Newcomen's engine by chance when he was asked to repair a model of the engine in the University of Glasgow. During the repair, he detected an essential shortcoming of the engine. His memoirs clearly pointed out the defects:

"As I had not at that time paid much attention to the subject and had other avocations, it was then pursued no farther; but in the Winter of 1763, having occasion to repair a Model of Newcomen's Engine which belonged to the Natural Philosophy class of the University of Glasgow; when I had got it in working order, I found that the Boiler, though large in proportion to the Cylinder could not supply it with Steam to work at a proper rate unless the fire was violently urged with bellows.
I observed also, that the Cylinder which was about 2 Inches diameter, could only give power enough to work a pump of the same diameter and about 2 feet high, which effect was much less in proportion to the Cylinder than was generally performed by larger \Steam/ Engines.
On considering the causes of these defects it appeared, 1st that as Steam is condensed by the contact of bodies colder than itself and in proportion to the quantities of such cold bodies with which it comes into contact, and the

internal surface of any cylinder being many times greater in proportion to its contents than that of the large Engines employed in Collieries, much more Steam must be condensed before the Cylinder could be filled so as to permit the piston to rise; 2dly that as water was supposed to boil *in vacuo* at much lower heats than it did under the pressure of the atmosphere, a vacuum could not be produced in the cylinder unless that vessel were cooled by the injection below the point at which water would boil in an exhausted Vessel"[26].

That is, Watt considered one of the reasons why the miniature model required more heat than the real one to be as follows. The net amount of steam required for the operation (A) is proportional to the volume of the cylinder (V), while an amount of steam (ΔA) proportional to the inner surface area of the cylinder (S) is cooled by contact with the cylinder wall and is condensed without being used for work. As a result, the ratio of wasted steam is given by

$$\frac{\Delta A}{A} \propto \frac{aS}{V} \propto \frac{a}{l},$$

where l is the characteristic length of the model and a is a constant with the dimension of length, which means that the ratio increases with decreasing size of the model. By observing the miniature steam engine model, the essential defect of Newcomen's engine that a large amount of steam is lost per cycle was brought to the fore.

VI. Watts' improvement—separate condenser

The above conclusion was so logical that Shin-ichiro Tomonaga (1906–1979; Nobel Prize in Physics 1965) commented that "This fact clearly demonstrates that Watt was not merely a merchant but a scientist"[27].

At that time, Watt wrote, "But before anything could be known certainly about the best manner of Constructing Fire engines there were several facts necessary to be determined"[28]. Also, his later approach to the problem was akin to the style of a scientist rather than that of a craftsman.

He first found by measurement that the volume of water expands by a factor of 1600 when it evaporates, and he calculated the actual volume of steam supplied to the cylinder per unit time, i.e., volume of water consumed per unit time $\times 1600$. Watt compared this amount with the required net amount of steam, i.e., volume of the cylinder × cycles per unit time. As a result, he found that the former is about five times the latter, that is, most of the steam was consumed only to heat the cylinder wall.

To reduce the wasteful use of steam and therefore fuel, it is clear that the cylinder must be kept at as high temperature as possible.

Simultaneously, Watt found that not only does steam contains air but also that water cooling nearly reaches the boiling temperature ($212°$F) after it is injected into steam because a large amount of heat is released when steam condenses. Regarding this point, although it may be argued that Watt learnt about latent heat from Black rather than discovering it himself, it was not the case [29].[4]

As noted above, under atmospheric pressure, water boils at a temperature below its usual boiling point. Consequently, the high-temperature water produces so-called backpressure and, together with the air contained in the steam, destroys the vacuum and decreases the output power. Hence, to increase the output power using this mechanism, when the piston moves down, it is not sufficient to simply reduce the temperature inside the cylinder to lower than the boiling temperature; the temperature must be kept as low as possible.

To reduce fuel consumption, the cylinder and its inside should be maintained at a high temperature, while, for high mechanical performance, effective cooling is necessary in each cycle. This produces a dilemma if we adhere to the idea based on the above mechanism. Watt, however, found a method to simultaneously satisfy both

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[4] Later, in 1781, Watt measured the latent heat of evaporation of water by himself. The results were 945.5°, 922.5°, 935.5°, 963.5°, 942.5°, 960.5°, 940°, 937°, and 943.375° F, an average of 524° C. namely 524 cal/gr. This value is much more accurate than that obtained by Black 450° C (the actual value is 540 cal/gr). We can see that Watt was a remarkably skilled experimental researcher [30].

requirements by spatially and substantially separating the expansion process and contraction process. That is, the essence of Watt's improvement is that, by separating the condenser (cooler) from the cylinder, it is possible for the condenser to be operated with a sufficiently low temperature and for the cylinder to be steadily maintained at a high temperature. Although this is very simple from the present perspective, it was "the greatest single improvement ever made in the engine"[31].

Furthermore, to prevent the cylinder from cooling by coming in contact with the surrounding air, Watt introduced a new mechanism so that the piston could be pushed by the steam itself, resulting in a real steam engine. This improvement is said to have reduced the fuel consumption by "almost 75 per cent"[31]. Since steam contains air, an exhaust pump was added downstream of the condenser.

The details of the cycle and mechanism of Watt's engine are as follows. In Fig. 18.6, when the piston, moved upward by counterweighted beam, reaches the top of the cylinder, the gate valve (which separates the upper and lower parts of the cylinder) is closed and the outlet valve (which is connected to the condenser) is opened and the lower part of the cylinder is evacuated. Simultaneously, by opening the inlet valve (which is connected to the boiler), steam is introduced into the upper part of the cylinder. As a result, the piston is driven downward. When the piston reaches the bottom, the inlet and outlet valves are closed and the gate valve is opened, then steam spreads into both sides of the piston while the piston is driven up again by the counterweighted beam. In the first half of the process, when the vacuum pump is in operation, the working substance is pure water vapor in the upper part of the cylinder, while in the second half of the process, the piston is driven by gravity. This mechanism patented in 1769 is called single-acting engine because steam is the driving force during only half of the cycle (Fig. 18.7).

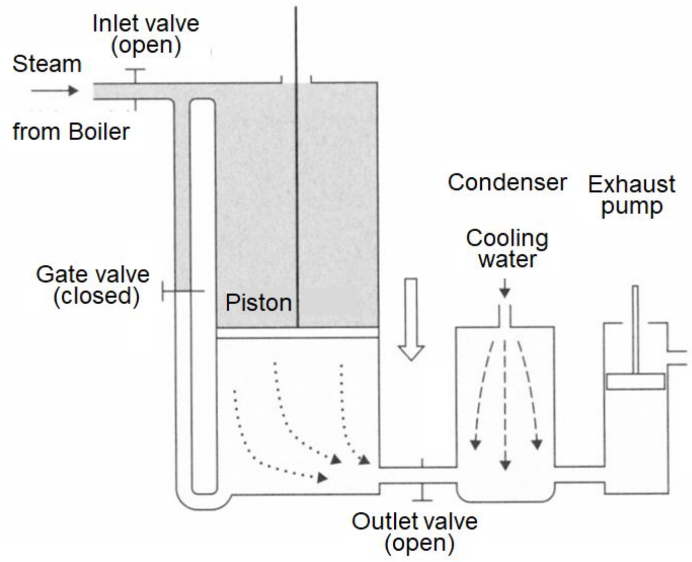

Fig. 18.6 Single-acting steam engine developed by JamesWatt.

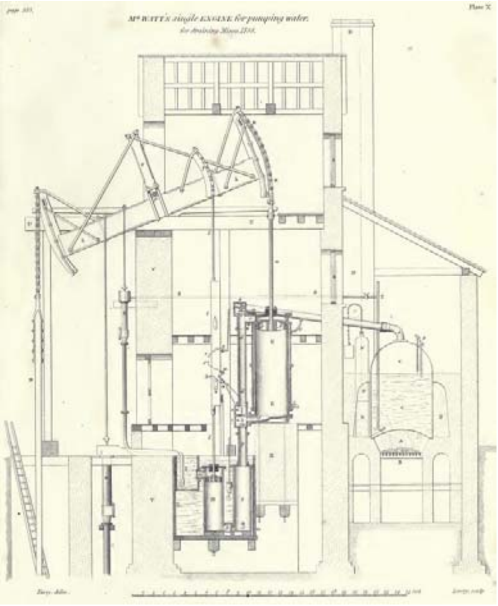

Fig. 18.7 Single-acting steam engine developed by James Watt.
A condenser and pump for the exhaust are equipped on the left side below the cylinder (from Farey, J., *ibid*., (1827)).

Furthermore, in 1782, Watt invented a double acting engine, which was operated by steam in both the upward and downward directions. In other words, a 100% steam engine or heat engine, whose operation was independent of atmospheric pressure and gravity, had been developed. It not only doubled the output power but also made rotating action possible instead of reciprocating action; as a result, its applicability was tremendously widened.

Watt and Boulton were highly successful in their commercialization of the steam engine. Boulton wrote the following in a letter to Erasmus Darwin (1731–1802; grandfather of Charles Darwin):

"Steam Engines of B & W construction differ from Newcomins in 6 principles
st
1. The acting power is Steam on ye piston. & Not the Atmosphere as in ye Com^{n} Eng^{ne}
2. The Steam is condensed in a separate Vessell, & Not in the Cylinder as in D°
3. The Cylinder is kept as hot as Steam, & Not alternately heated & coold as in D°
4. The air is extracted by an air pump at each Stroke & not blown out at Snifting Clak
5. The packing of the piston is preserved air & steam tight by oyls ... & not by Water
6. The Vacuum is alternately made above & below the piston & thereby obtain double power [32]

This description clearly shows, in a deeply satisfying way, how well Watt and Boulton understood their achievement.

VII. Watt's improvement—expansive principle

In the patent of 1782, one more improvement, which is very important in terms of thermodynamics, was based on Watt's expansive principle. Its idea was discussed in a letter written in 1769 [33].

Watt detected that when high-pressure and high-temperature steam freely expands from a cylinder to a low-temperature cooler, power potentially contained in the steam is wasted. Hence, Watt considered that by stopping the supply of steam from the boiler in the middle of the stroke, followed by adiabatic expansion of the steam, the steam will be gradually cooled while simultaneously carrying out work with the energy contained in the steam.

Since this point is very interesting, let us cite his rather lengthy description in the patent specification (1782):

"MY FIRST NEW IMPROVEMENT in steam or fire engines consists in admitting steam into the cylinders or steam vessels of the engine only during some certain part or portion of the descent or ascent of the piston of the said cylinder, and using the elastic forces, wherewith the said steam expands itself in proceeding to occupy larger spaces, as the acting powers on the piston through the other parts or portions of the length of the stroke of the said piston; and in applying combinations of levers, or other contrivances, to cause the unequal powers wherewith the steam acts upon the piston, to produce uniform effects in working the pumps or other machinery required to be wrought by the said engine: whereby certain large proportions of the steam hitherto found necessary to do the same work are saved. To explain which principle or improvement, I have delineated a section of a hollow cylinder at figure 1st (Fig. 18.8 in this paper) in the annexed drawing. (omit) These things being thus situated, and the piston placed as near as may be to the top of the cylinder, let the space of the cylinder under the piston be supposed to be exhausted or emptied of air, steam, and other fluids; and let there be a free passage above the piston for the entry of steam from the boiler, and suppose that steam to be of the same density or elastic force as the atmosphere, or able to support a column of mercury of thirty inches high in the barometer. Then I say that the pressure or elastic power of the said steam on every square inch of the area or upper side of the piston, will be nearly fourteen pounds avoirdupois weight, and that if the said power were employed to act upon the piston through the whole length of its stroke, and to work a pump or pumps, either immediately by the piston rod prolonged, or through the medium of a working beam or great lever, as is usual in steam engines, it would raise through the whole length of its stroke a column or columns of water, whose weight should be equal to ten pounds for each square inch of the area of the piston, besides overcoming all the frictions and vis inertia, of the water and the parts of the machine or engine. But supposing the whole distance from the under side of the piston to the bottom of the cylinder to be eight feet, and the passage which admitted the steam from the boiler to be perfectly shut when the piston has descended to the point K two feet, or one-fourth of the length of the stroke or motion of the said piston, I say that when the piston had descended four feet, or one-half of the length of the stroke, the elastic power of the steam would then be equal to seven pounds on each square inch of the area of the piston, or one-half of the original power; and that when the piston had arrived at the point P, the power of the steam would be one-third of the original power, or four pounds and twothirds of a pound on each square inch of the piston's area; and that when the piston had arrived at the bottom or end of its stroke, that the elastic power of the steam would be one-fourth of its original power, or three pounds and one-half pound on each square inch of the said area. And I further say, that the elastic power of the steam at the other divisions marked in the lengths of the said cylinder, are represented by the lengths of the horizontal lines or ordinates of the curve KL, also marked or delineated in the said cylinder, and are expressed in decimal fractions of the whole original power by the numbers written opposite to the said ordinates or horizontal lines. And I also say, that the sum of all these powers is greater than fifty-seven hundred parts of the original power multiplied by the length of the cylinder; whereby it appears that only one-fourth of the steam necessary to fill the whole cylinder is employed, and that the effect produced is equal to more than one-half of the effect which would have been produced by one whole cylinder full of steam, if it had been admitted to enter freely above the piston during the whole length of its descent"[34].

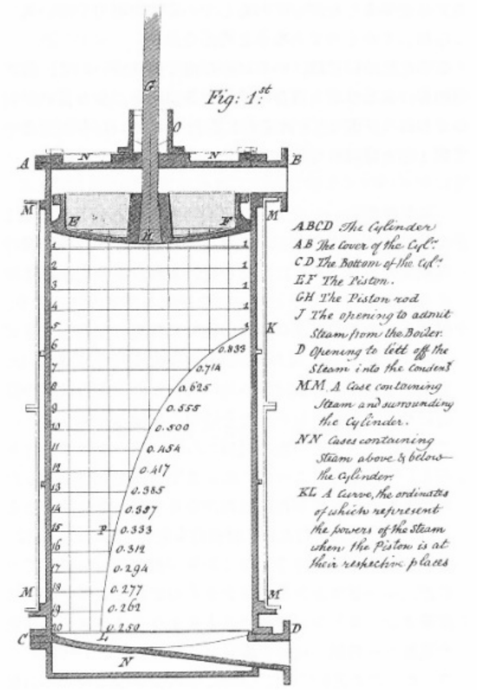

Fig. 18.8 Watt's diagram showing pressures of steam expanding in a cylinder (from his patent specification, (1782)).

In the *Réflexions*, Carnot highly appreciated the significance of Watt's expansive principle as follows: "Watt, who was responsible for nearly all the main improvements of the steam engine and who so perfected the engine that further advances would now be difficult, was also the first to use steam at progressively diminishing pressures"[C, p. 105]. That is, "The mark of a good steam engine, therefore, must be not only that it uses steam at a high pressure *but also that it uses it at pressures which are not constant but which vary substantially from one moment to the next and progressively decrease.*"[C, p. 104]. In other words, if high-pressure and high-temperature steam gradually performs work as its pressure and temperature decrease, then under a fully low-pressure and low-temperature condition it is guided to a condenser, the waste of energy is minimized. As discussed later, this leads to Carnot's theory that a **quasi-static reversible change** is ideal for maximizing work.

Although the aim of Watt's expansive principle was to improve fuel efficiency, from the theoretical viewpoint, it clarified that the role of steam in the steam engine is not 'to create a vacuum by condensation' but 'to work by expansion.' Also, by flexibly controlling and stopping the supply of steam into the cylinder, and thus by promoting the independence of the working substance, Watt's engine perfected the separation of the boiler and cylinder, the idea originating from Papin and Newcomen.

Combined with the invention of a separate condenser (cooler), Watt clarified the following three points. First, a heat engine consists of three elements, a furnace, cooler, and working substance; the working substance can freely be separated from and forced to come in contact with the furnace and cooler. Second, *to perform work, not only a high temperature but also a low temperature is necessary. That is, heat is carried by the working substance from a high-temperature region (furnace) to a low-temperature region (cooler)*. Third, *work is performed by the volume change of the working substance*. That is, the existence of a high temperature and a low temperature is a necessary but nor sufficient condition for performing work; to perform work, the potential power of the high-temperature working substance should be extracted by expanding its volume.

As described in the next chapter, these three points gave Carnot important hints when deriving his theory and are incorporated in his theory.

VIII. *P–V* diagram and expression for work

It should be noted that in Watt's description of expansive principle, he erroneously assumed that Boyle's law can be applied to adiabatic changes. Leaving this aside until later, what is important and interesting is that Watt actually recognized the importance of the *P–V* diagram and the concept of work.

Since the scale depicted on the side of the cylinder in Fig. 18.8 is the distance moved by the piston, it can also be regarded as the volume of the steam because the cross-sectional area of the cylinder is constant. On the other hand, the horizontal distance along the curve MKPL gives the pressure. Consequently, this figure is basically a *P–V* diagram, as widely used in later thermodynamics.

The *P–V* diagram was first introduced into thermal science in 1834 by Clapeyron, and it is often considered to originate from the indicator diagram of John Southern in 1796: "The practical solution of this problem is very simple and was found by John Southern in 1796. As one of Boulton and Watt's business acquaintances wrote: 'I am like a man parch'd with thirst in the Expectation of relief or a woman dying to hear (or tell) a Secret—to know Southern's mode of determining Power ...' It was simple enough. A sheet of paper is pinned to a board, which moves to and fro with the reciprocating motion of the piston; at the same time a spring-loaded pressure gauge causes a pencil, held in a lever arm, to move at right angles to the motion of the board. As a result the pencil automatically traces out the curve, relating the pressure of steam in the cylinder to the change of volume: that is to say it traces out the indicator diagram; and Gilbert's analysis showed that the area under the curve must be proportional to the work done or the power being developed by the engine"[35]. I, however, cannot understand why scientific historians did not attribute the origin of the *P–V* diagram to Watt's diagram in his patent specification of 1782.

In his specification, Watt wrote "that the sum of all these powers is greater than fifty-seven hundred parts of the original power multiplied by the length of the cylinder; whereby it appears that only one-fourth of the steam necessary to fill the whole cylinder (V_2) is employed"[35]. Here, Watt evaluated the work by expressing one tick of the cylinder length as the unit volume ($\mathit{\Delta} V = 1$ volume),

$$\sum_{i=1}^{20} P_i \mathit{\Delta} V = 11.54 \text{ (atm·volume)},$$

where P_i is one of the figures shown on the right side of Fig. 18.8. That is, Watt considered that the work done by the steam is expressed as $\int PdV$ or the area enclosed by the curve MKPL and both axes, which was calculated by numerical integration. Then, he compared it with the work under constant atmospheric pressure,

$$\sum_{i=1}^{20} P_i^{(0)} \Delta V = 1 \times 20 \text{ (atm·volume)},$$

and obtained the result of $11.54/20 = 57.7$ %. Thus, by using a quarter of the original amount of fuel, more than half of the work was available.

For more precise evaluation, since steam of pressure P_0 and volume V_1 is first supplied and then adiabatically expands to volume V_2, the total work is (erroneously assuming Boyle's law)

$$\int_0^{V_2} PdV = P_0 V_1 + \int_{V_1}^{V_2} PdV = P_0 V_1 \left\{ 1 + \ln\left(\frac{V_2}{V_1} \right) \right\} . \tag{18.1}$$

Comparing this with the work when steam of constant pressure P_0 and volume V_2 is supplied,

$$\int_0^{V_2} PdV = P_0 V_2 ,$$

for $V_2 = 4V_1$, the ratio of

$$\frac{V_1}{V_2}\left\{1+\ln\left(\frac{V_2}{V_1}\right)\right\} = 0.59 = 59\%$$

is obtained. Watt's numerical calculation result (57.7%) is in good agreement with the analytical value.

Clément first pointed out Watt's misconception about the application of Boyle's law (isothermal change of ideal gas) to the adiabatic process in 1819 [36]. However, Clément was also incorrect. He and Desormes (1777–1838) experimentally found the law for the adiabatic change of steam, which had been called Watt's law. Watt's law states that the absolute amount of heat (the sum of sensible heat and latent heat) contained in steam at saturated pressure is a constant independent of temperature, although it is uncertain whether or not Watt first discovered the law. For example, Dalton (1766–1844) wrote the following in *Chemical Philosophy*:

"I owe to Mr. Ewart the first hint of the idea respecting elastic fluids, which I have endeavoured to expand in the present section; he suggested to me some time ago, that it was probable steam of any low temperature, as 32°, of maximum density, contained the same quantity of absolute heat as the like weight of steam of 212° of maximum density; and that consequently if it could be gradually compressed without losing any heat, that is, if the containg vessel kept pace with it in increase of temperature, there would never be any condensation of steam into water, but it would constantly retain its elasticity"[37]. (Here, the unit of temperature is Fahrenheit, and 'steam of maximum density' corresponds to the state at the saturated pressure.) Dalton also wrote, "Since writing the above, Mr. Ewart informs me that the idea respecting steam, which I had from him, is originally Mr. Watt"[37].

In 1845, after graduating from Glasgow and Cambridge, William Thomson spent some time studying experiments on gases in Henri Regnault (1810–1878)'s laboratory. He wrote, "When, eighty-one years later, a student under Regnault in his laboratory in the college of France, I used to hear him speaking of "la loi de Watt," and telling us that it was the nearest approach to the truth which he found among the results of previous experiments, I felt some pride in thinking that the experiments on which it was founded had been made in Glasgow College"[38].

According to scientists who studied gas characteristics at that time, Watt's law was considered to be approximately correct. As Dalton wrote, on the basis of Watt's law, it was considered that saturated steam remains in the saturated state after an adiabatic change, and this fact was thought to provide the scientific rationale for treating saturated steam in the same manner as an ideal gas. Clément and Desormes were of the same opinion. In the *Réflexions* Carnot wrote,

"According to a law discovered by MM. Clément and Desormes—a law which they established by direct experiment—a given weight of steam always contains the same amount of heat at whatever pressure it is created. This is the same as saying that saturated steam will remain saturated whenever it is compressed or expanded mechanically in such a way that there is no loss of heat. *Steam in these conditions may therefore be treated as a permanent gas, subject to all the normal gas laws* (italicized by Yamamoto). [C, p. 90]

We shall see in Chapter 26-IV and V that the decision of whether the law of Clément and Desormes, i.e., Watt's law, is correct or not serves as a litmus test to ascertain whether the conservation of heat is correct or not.

Since the first law of thermodynamics is far ahead of the present subject, let us return to the concept of work.

"Watt and Boulton decided that their engine should be paid for by a royalty, or as they termed it a 'premium', based very appropriately on the saving in fuel effected by the engine as compared with the consumption of a common engine doing the same work. Boulton and Watt stipulated that they should receive one-third of the value of the fuel saved"[31] for 25 years, meaning that both the establishment of a unit of work and the accurate evaluation of work were crucially important. According to Cardwell [39], in Watt's litigation with Jonathan Hornblower (1753–1815) in 1792, Davies Gilbert (the sheriff for Hornblower) first obtained a mathematical expression for the work $\int PdV$. In particular, the analytical expression for the expansive principle, eq. (18.1), was first referred to by Robison in the 1797 edition of *Encyclopaedia Britannica*. We should, however, realize that Watt understood the quantitative concept and its expression for the work before them. Incidentally, it was Watt and Boulton who defined one horsepower as 33,000 (originally 32,572) $\mathrm{ft\,lbf/min}$.

In any case, Watt's patent specification of 1782 has much greater historical importance.

IX. High-pressure engine and its development in France

Since Watt only used low-pressure (atmospheric pressure) engines, he could not apply the expansive principle to actual devices. The advantage of the expansive principle only emerges when engines are operated at a high pressure; the practical realization of high-pressure engines started in the nineteenth century.

Watt's invention of the separate condenser was in 1765 and his expansive principle was patented in 1782. During the patent term, innovation leading to engines superior to Watt's engine was inhibited. After its expiration in 1800, however, the Boulton–Watt monopoly was broken, and in 1802, Richard Trevithick (1771–1833), an engineer from Cornwall, invented a high-pressure engine. In 1814, the Cornish engineer Arthur Woolf (1776–1837) produced a high-pressure engine based on the expansive principle.

In the Cornish mines, far from any coal mining areas, since the efficiency (ratio of output power to fuel consumption) of the steam engine was crucially important, Woolf's engine, whose efficiency was twice that of Watt's engine, had a significant impact. This success of the high-pressure engine demonstrated that there was plenty of scope for improving steam engines, although nobody could understand why the high-pressure engine could attain high efficiency [40].

The fact that the year in which Woolf's engine was perfected was1814 had special significance to Carnot, who graduated from École Polytechnique in the same year and was pondering over his future.

This is because in 1815 the Napoleonic Wars were over and diplomatic relations between England and France was restored. Much to the surprise of the French, the steam engine in England had achieved amazing progress. Attention was particularly directed to the high efficiency of the high-pressure engine [41], resulting in Woolf's engine plant being constructed as early as in 1815 in France. "on the Continent far more emphasis was placed on fuel economy than in Britain. From the very start the Woolf compound engine ... which made use of high pressure to operate two cylinders alternately and offered a fuel economy over the Watt engine of about 50 per cent found its greatest market in France"[42].

Consequently, after 1815, steam engines, particularly high-pressure engines, spread rapidly through France, and it is considered that by 1824, the year Carnot published his paper, about 300 steam engines were being operated in France.

Since the high-pressure engine could be readily downsized, it was suitable for use in transportation. In England, Trevithick produced the first steam locomotive in 1804. George Stephenson (1781–1848)'s steam locomotive was first practically applied to a traveling engine designed for hauling coal in 1814, and he also opened the public railway between Stockton and Darlington (21 km) in 1825.

Regarding steamboats, in 1807 the American engineer Robert Fulton (1765–1815) surprised the world by sailing a steamboat on the Hudson river from New York City to Albany, a distance of 240 km, in 32 hours. In France, although railways were introduced later, steamboats were already in operation by the 1810s. Victor Hugo wrote in "*Les Misérables*" that steamboats were operating on the Seine in 1817. In "*Une vie*" by Guy de Maupassant (1850–1893) a passage is contained in which the heroine went to Corsica on her honeymoon in 1819 on a steamboat [43].

The strong impression that steam engines had on French people was passionately expressed by Saint-Simonians who dreamed of the construction of an industrial society. Actually, "A substantial proportion of the first French railway-builders were fervent disciples of Saint-Simon"[44]. One of them, Michel Chevalier (1806–1879) described his dream as follows:

"By the aid of mechanical contrivances, this poor weak creature (= human), reaching out his hands over the immensity of nature, takes possession of the rivers, of the winds of heaven, of the tides o the ocean. By them, he drags forth from the secret bowels of the earth their hidden stores of fuel and of metals, and masters the subterranean waters, which there dispute his dominion. By them, he turns each drop of water into a reservoir of steam, that is, into a magazine of power, and thus he changes the globe, in comparison with which he seems an atom, into a labourious, untiring submissive slave, performing the heaviest tasks under the eye of its master. Is there any thing which gives a higher idea of the power of man, than the steam-engine under the form in which it is applied to produce motion on railroads? It is more than a machine, it is almost a living being; it moves, it runs like a courser at the top of his speed"[45].

Chevalier wrote this in 1836, and the following year another disciple of Saint-Simon, the financier, Émile Pereire (1800–1875), completed the first passenger railway between Paris and St. Germain in France.

In western Europe, which rushed headlong toward a highly industrialized society in the nineteenth century, the predominance of human beings over nature was first recognized; this presumptuous philosophy was based on the development of steam engines.

With this background, Carnot published the *Réflexions*. "If you were now to deprive England of her steam engines, you would deprive her of both coal and iron; you would cut off the sources of all her wealth, totally destroy her means of prosperity, and reduce this nation of huge power to insignificance"[C, p. 62]. This specific comment reveals Carnot's accurate recognition of the state of the art and the influence of the steam engine on his thinking.

In particular, the words "both coal and iron" are interesting. In the eighteenth century, the three generations of Abraham Darby (I (1678–1717), II (1711–1763), III (1750–1789)) in England produced marketable pig iron in a coke-fired furnace instead of one using charcoal. Their technology was completed almost at the same time as the improvement of the steam engine by Watt. Through this achievement, despite its limited supply of lumber, the mass production of iron became possible in England. For the new ironmaking process, a large supply of coal was required as well as high-performance blowers to supply air to large furnaces; both these requirements were met by Watt's engines. Thus, in England, the era of large-scale manufacturing started, and, in particular, the iron industry owed its existence to Watt's engines, as Carnot pointed out.

One of the motivations of Carnot's study was to clarify the reason why high-pressure engines were superior to low-pressure engines. This had been a major issue not only for Carnot but also for all the researchers and engineers of steam engines in France since 1815.

Only Carnot, however, could thoroughly investigate this issue from the principles, and a single paper of Carnot provided the basis for thermodynamics. Carnot's work was originally stimulated by a technical issue that was not of interest to physicists. Simultaneously, its approach was so fundamental and theoretical that it was not understood by engineers, and was therefore neglected.

In the next chapter, I will refer to the fact that in Carnot's investigation of heat engines, he depended on the analogy between heat engines and hydro-pressure engines.

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[42] Landes,. D.S., "Technological Change and Development in Western Europe, 1750–1914," in *The Cambridge Economic History of Europe*, edited by Habakkuk, H.J., and Postan, M., VI, The Industrial Revolutions and After: Incomes, Population and Technological Change (I), Part I, Cambridge: Cambridge University Press, pp. 410ff., (1965); Cf.
Cardwell, D.S.L., *ibid.*, p. 157, (1971).

[43] Hugo, V., *Les Misérables*, (1862), http://www.gutenberg.org/ebooks/135 [accessed May 17, 2018];
Maupassant, G., *Une vie*, (1883), http://www.gutenberg.org/ebooks/7114 [accessed May 17, 2018].

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Charléty. S., *Histoire du Saint-Simonisme (1825–1864)*, Paris: Hachette et cie., (1896) Paris, Paul Hartmann, (1931).

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CHAPTER 19 THEORY OF IDEAL HEAT ENGINE —CARNOT'S THEOREM

CONTENTS

I. Purpose of Carnot's paper

Carnot raised the problem of motive power not from the viewpoint of thermal science as a field of physics but from that of the technological development of steam engines. "Carnot owed far more to his contact with the world of power engineering than he did to the physics of his day"[1].

Nevertheless, it should be noted that, when both setting and solving the problem, he stuck to fundamentals and theory. As a result, his study was not limited to the technical theory of steam engines, and by clarifying the universal limitation in the relationship between heat and work, he developed a new field of physics.

Carnot's finding was that in steam engines, "The steam serves simply as a means of transporting the caloric" [2] [C, p. 65]. This can be also confirmed in the *Réflexions*, in which he wrote, "We draw a distinction here between the steam engine and the heat engine in general. The latter may employ any working substance, steam or anything else, in order to develop the motive power of heat"[C, p. 64], and he clearly distinguished 'heat engines (machine à feu)' and 'steam engines (machine à vapeur).'

Although Cardwell wrote, "The steam-engine, on the other hand, manifests in dramatic and clear form the capacity of heat to perform work"[3], such a comment is based on Carnot's recognition that the steam engine is a heat engine—*the true origin of power is not steam but heat*. Although this may sound obvious, it was not always so.

For example, in "*A Course of Lectures on Natural Philosophy and the Mechanical Arts*" by Thomas Young (1773–1829) in 1807 [4], which also deals with technical issues as indicated by its title, heat is discussed in Part 3 ("Physics"), while steam engines are discussed as an example of a pneumatic machine in Part 2 ("Hydrodynamics"); pneumatic machines include an air pump and "are principally dependent, in their operation, upon the properties of elastic fluids." That is, the power source of steam engines was considered to be the steam itself. Since Young, as described later, believed in the vibration (wave) theory of heat, he did not accept caloric, which might have made it difficult for him to ascribe the power source to heat.

Thus, it is considered that the problem of the motive power of heat was raised not by a proponent of the dynamical theory of heat but by Carnot, who believed that caloric theory was not paradoxical but natural.

In any case, solely by regarding steam simply as a means of transporting heat and by also regarding steam engines essentially as heat engines, Carnot's universal approach allowed the nature of heat to be studied as a source of power independent of the peculiarities of working substances and of the individual structures of devices.

By grasping and analyzing the status quo as follows: "The phenomenon of the production of motion by heat (la production du mouvement par la chaleur) has not been treated from a sufficiently general point of view"[C, p. 63], Carnot set out what needed to be achieved as follows:

"In order to grasp in a completely general way the principle governing the production of motion by heat, it is necessary to consider the problem independently of any mechanism or any particular working substance.

Arguments have to be established that apply not only to steam engines but also to any conceivable heat engine, whatever working substance is used and whatever operations this working substance is made to perform"[C, p. 64].

Such a surprisingly radical assertion may be the privilege of a young man in his 20s. Here, Carnot intended to establish "a complete theory (théorie complète)" based on a comprehensive universal principle at once. As guidance, the existing mechanical theory was referred to. Carnot illustrated a complete theory using mechanical theory.

"A mechanical theory permits a very detailed study of those machines that do not derive their motion from heat but are driven by men or animals, a fall of water, wind, etc. Every situation can be foreseen, and every conceivable movement is subject to some well-founded and universally applicable general principle. It is this which characterizes a complete theory"[C, p. 64].

Therefore, it was necessary to extend the theory of the heat engine to the mechanical theory. Actually, the mechanical theory in France had been almost completed by Lazare Carnot. In contrast, how random (au hasard) the improvement of the heat engines (particularly high-pressure engines after Watt) was!—The young Carnot was acutely aware of the lack of fundamental theory.

"but such a theory is plainly lacking in the case of the heat engine. It will only be achieved when the laws of physics are sufficiently extensive and general for us to be able to predict all the effects that are produced when heat acts in a particular way on any given substance"[C, p. 64].

Carnot achieved his objectives; he had taken the first step toward establishing a "universally applicable general principle" in thermal science. On the basis of these objectives, his paper, which "is perhaps the most original in physical science"(J. Larmor, *On the Nature of Heat*, P.T.R.S. (1916–18), p. 326), was published.

Although Carnot's paper was motivated by technical requirements, it was extremely fundamental and universal, and was not written for engineers nearly interested in short-sighted practicability. Consequently, it did not have any impact on them. Truesdell wrote that "It is easy to say, and it has often been said, that Carnot wrote for engineers, but I can find no evidence that any engineer ever read and applied his results"[5].

II. Carnot's preliminary theorem and its background

As described earlier, Carnot tackled the problems of "whether the motive power of heat is limited or whether it is boundless," and "is the motive power of heat fixed in quantity, or does it vary with the working substance that is used?" He sought clues to these problems by the analysis of actual steam engines. That is, "The production of motion in the steam engine always occurs in circumstances which it is necessary to recognize, namely when the equilibrium of caloric is restored, or (to express this differently) when caloric passes from a body at one temperature to another body at a lower temperature"[C, p. 64]. On the basis of his recognition of this simple but essential fact, he made the following premises:

The first premise is that "*Wherever there is a difference in temperature, motive power can be produced*"[C, p. 67]; this can be summarized to mean that *a temperature difference is a necessary condition to produce motive power*. The detailed description is as follows:

"So the production of motive power in a steam engine is due not to an actual consumption of caloric *but to its passage from a hot body to a cold one*. It is due, in other words, to a restoration of the equilibrium of caloric after that equilibrium has somehow been disturbed, for example by a chemical reaction such as combustion, or by some other means. We shall soon see that the same principle can be applied to any engine whose motion is due to heat"[C, p. 65].

The discovery that not only a high temperature but also a low temperature is necessary was Carnot's breakthrough.

The second premise is that "Obviously heat can only be a source of motion in so far as it causes substances to undergo changes in volume or shape"[C, p. 66]; this can be summarized to mean that *a change in the volume of substances is an indispensable condition for producing motive power*. That is, upon the direct contact between high- and low-temperature substances, only heat transport occurs and no work is done. Work is done not merely by heat transport but also through the cooling of the working substance accompanied by its expansion.[5] That is, "For there is nothing in nature that does not undergo changes in volume, contracting and then expanding as it experiences cold or heat; there is nothing which, in doing so, cannot act against a resisting force and there by develop motive power"[C, p. 66]. This is precisely the theoretical specification of Watt's expansive principle; the only difference is that Watt assumed the expansion process on the basis of Boyle's law, while Carnot correctly understood the temperature drop associated with the adiabatic process.

As a result of the above two premises, the maximum possible work with respect to a specified difference in temperature is obtained "if no changes in temperature occur unless they are caused by changes in volume; in other words, bodies at sensibly different temperatures should not come into contact with one another"[C, p. 77].

"Since any process in which the equilibrium of caloric is restored can be made to yield motive power, a process in which the equilibrium is restored without producing power must be regarded as representing a real loss (perte). Now, a moment's reflexion will show that any change in temperature that is not due to a change in the volume of a body is necessarily one in which the equilibrium of caloric is restored profitlessly. Hence the necessary condition for the achievement of maximum effect is *that the bodies used to produce motive power should undergo no change in temperature that is not due to a change in volume*. Conversely, whenever this condition is fulfilled, the effect produced will be a maximum"[C, p. 70].

Here, I will daringly refer to this as **Carnot's preliminary theorem**, although this name has not been used elsewhere.

Furthermore, as a corollary to this theorem, we can derive the following: an ideal engine which achieves the maximum work is simultaneously a reversible one because it does not include thermal conduction between regions with a finite temperature difference. This played a very important role in deriving Carnot's theorem. Here, 'reversible' is used with a narrow meaning that the process can be reversely operated by adding the same amount of work to the previously obtained work.

Carnot's idea for his preliminary theorem might have been directly stimulated by the development of heat engines, particularly the improvement of the steam engine by Watt. **The first premise**, i.e., to obtain work by using steam, not only a high temperature but also a low temperature is necessary, is exactly the same principle as used in the theoretical work understanding Watt's invention of the separate condenser—purification of the heat engine by separating the furnace and cooler. **The second premise** followed Watt's expansive principle, in which steam separated from a boiler expands, reducing its pressure and temperature, and enters a cooler after fully converting its potential activity to work.

Simultaneously, however, in the background of Carnot's argument, there was accumulated technology and theory on hydraulic machines, which were developed in parallel with the steam engine during the industrial revolution.

In particular, there was remarkable progress in the column-of-water engine (machine à colonne d'eau), which was invented in the eighteenth century by modeling Newcomen's engine. As shown in Fig. 19.1, a piston is operated by using hydro pressure instead of steam pressure, and hence it was also known as a water-pressure engine. This engine was popular in European countries with few coal resources but abundant flowing water

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[5] In 1821, the German physicist Seebeck (1770–1831) discovered the phenomenon that two junctions of a loop consisting of two dissimilar metals produces an electric current when the two junctions are kept at different temperatures. If a motor is operated by using this current, the temperature difference will produce work without a volume change. Carnot, however, did not know of this phenomenon. Also, we do not consider this phenomenon here.

with high drops. “Between 1750 and 1825, the column-of-water engine represented an ingenious and scientifically advanced method of harnessing water power”[6].

Carnot’s recognition that both high and low temperatures are necessary for heat to produce work was considered to be based on the analogy with the following column-of-water engines, which require a fall of water to produce work. This is confirmed from the following statement in the *Réflexions*: “From the ideas that have been established so far, we are sufficiently justified in comparing the motive power of heat with that of a fall of water. ...... The motive power of a fall of water depends on its height (chute d’eau) and on the amount of liquid. The motive power of heat likewise depends on the amount of caloric that is used and on what might be termed—in fact on what we shall call—the height of its fall (sa chute); it depends, in other words, on the difference in temperature of the bodies between which the passage of caloric occurs”[C, p. 72].

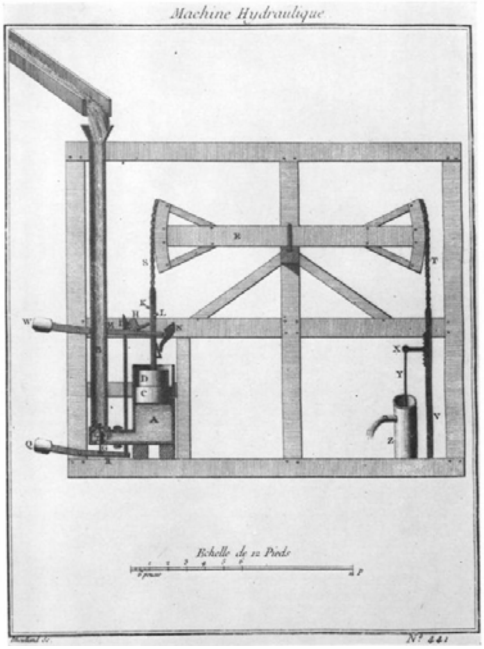

Fig. 19.1 Early column-of-water engine produced by Gensanne. (from Cardwell, D.S.L., *From Watt to Clausius: The Rise of Thermodynamics in the Early Industrial Age*, Ithaca: Cornell University Press, Plate VI, (1971))

After Carnot, this analogy became more popular. A textbook by Balfour Stewart (1866) contains the following description: “Carnot, a French philosopher, who was the first to study this subject, very ingeniously likened the mechanical capability of heat to that of water, remarking that just as water on the same level can produce no mechanical effect, so neither can bodies at the same temperature; and just as we require a fall of water from a higher to a lower level in order to obtain mechanical effect, so likewise we must have a fall of heat from a body of higher to one of lower temperature”[7].

Regarding the analogy with a current of water, there were other elements described below. One more basis of Carnot’s preliminary theorem was the studies by the French military engineer Jean-Charles Borda (1733–1799) and his father Lazare Carnot.

By the middle of the eighteenth century, it was known that an overshot water wheel based on gravitation is much more efficient than an undershot water wheel. The English engineer John Smeaton (1724–1792) found that the efficiency of an overshot water wheel is three times that of an undershot water wheel. Furthermore, he found that when the blades of an undershot water wheel receive an impact by a current of water, a major loss arises. Also, for an overshot water wheel, it is desirable that buckets filled with water are driven not by impact but by gravitation, as slowly as possible [8].

Similarly, Borda, who studied the output power of the water wheel, found that when fluid subjected to a sudden change becomes turbulent and loses its vis viva (kinetic energy), "Then the water, instead of suddenly impacting the blade, would enter without impact, as prescribed by Borda, and would slowly give up its momentum as it ascended the curve of the blade. The water would gradually slow down, stop, and then descend the blade, picking up its initial velocity, but in a direction opposite that of the wheel. If the wheel's velocity and the length of its blades were proportioned correctly, the water as it left the wheel would have a velocity equal to that of the wheel, but in an opposite direction, so that their relative velocity would be zero. Thus Borda's requirement that the water leave the wheel without velocity could be met as well"[9].

The principle of energy loss associated with inelastic collision was generalized by Lazare Carnot. In his "*Essay upon Machines in General*" (1782), he wrote,

"We may conclude from this, for example, that the method of producing the greatest possible effect in a hydraulic machine moved by a current of water, is not to adapt a wheel to it, the wings of which receive the shock of the fluid. In fact, two good reasons prevent us from producing in this way the greatest effects: the first is, as we have already said, because it is essential to avoid every kind of percussion whatever; the second is, because after the shock of the fluid there is still a velocity which remains to it as a pure loss, since we should be able to employ this remainder in still producing a new effect to be added to the first. In order to make the most perfect hydraulic machine, i.e. capable of producing the greatest possible effect, the true difficulty lies, 1st, In managing so as that the fluid may lose absolutely all its movement by its action upon the machine, or at least that there should only remain precisely the quantity necessary for escaping after its action; 2d, Another difficulty occurs in so far as it loses all this movement by insensible degrees, and without there being any percussion, either on the part of the fluid, or on the part of the solid parts among themselves: the form of the machine would be of little consequence; for a hydraulic machine which will fulfil these two conditions will always produce the greatest possible effect: but this problem is very difficult to resolve in general, not to say impossible; it may even happen that in the physical state of things, and in respect of their simplicity, there can be nothing better than wheels moved by shocks: and in this case as it is impossible to fulfil at once the two conditions most desirable, the more we wish to make, the fluid lose of its movement in order to attain the first condition, the stronger will be the shock; the more, on the contrary, we wish to moderate the shock in order to approach the second, the less will the fluid lose of its movement. We perceive that there is a medium, by means of which we shall determine, if not in an absolute manner, at least, having regard to the nature of the machine, that method which will be capable of the greatest effects"[10; Carnot, L.N.M., vol. 31, p. 300].

Sadi Carnot's statement[6] about the maximum work for a given heat is almost a counterpart of Lazare Carnot's statement about the maximum work for a water wheel. In the former, the contact between substances having a temperature difference reduces the power of the heat, and in the latter, the impact between the blades and the fluid with a velocity difference reduces the power of the water current. We can see the remarkable analogy between an ideal hydraulic machine which changes its state as slowly as possible and an ideal heat engine which operates through a quasi-static process.

When Sadi Carnot wrote, "A mechanical theory permits a very detailed study of those machines that do not derive their motion from heat"[C, p. 64], he must have recalled his father's study.

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[6] From only the following statement, the reason why a high-pressure engine is advantageous can be explained. "Since coal is able to produce temperatures above 1000° when it is burned, and since the water most commonly available to us in our climate is at roughly 10°, it is easy to obtain a fall of caloric of 1000°, though of this fall only 120° arc used in a steam engine. Even then, the 120° are not utilized to the full. There are always substantial losses caused by a failure to restore the equilibrium of caloric in a useful way. The reasons for the superiority of what we call high-pressure engines over engines operating at a lower pressure are now evident. The superiority lies essentially in their ability to utilize a greater fall of caloric. Since steam that is produced at a higher pressure is also at a higher temperature, and since the temperature of condensation always remains much the same, the fall of caloric is obviously greater"[C, p. 104].

III. Carnot cycle

On the basis of the preliminary theorem, Carnot proposed the so-called Carnot cycle, a thermal cycle for gas with the maximum efficiency which operates between a high-temperature furnace and a low-temperature cooler. He was wise enough to consider not only a single process but also an entire cycle to clarify the work done by heat; at that time, all other scientists and engineers considered only the expansion process directly producing work.

The most important feature of the cycle is as follows: When the working substance has returned to the initial state, the heat added at the furnace—and the heat exhausted to the cooler in a Carnot cycle—is considered to be completely used for work to the outside. If the state has not returned to the initial state, however, part of the heat may be used to induce a physical internal change of the working substance, or conversely, the physical internal change of the working substance may be used to produce work.

William Thomson in 1849 and Rudolf Clausius in 1850 highly appreciated Carnot's insightful view [11], while Ernst Mach (1838–1916) simply wrote, "We may remark that the choice of a cyclic process for the derivation of this theorem was a particular happy one (eine besonders glückliche)"[12]. Since Carnot intentionally considered the cycle, Mach's comment was inappropriate. On the basis of the preliminary theorem, in the operation of an ideal engine, the temperature of the working substance must be equal to that of the constant (high)-temperature furnace during heat absorption, and to that of the constant (low)-temperature cooler during heat discharge, in order not to include thermal conduction due to the finite temperature difference between the working substance and the device. Thus, the ideal engine must consist of isothermal and adiabatic processes. This cycle forms the skeletal structure of the heat cycle proposed by Carnot.

Strictly, of course, the temperature of the working substance must be lower than that of the furnace and higher than that of the cooler. "But the most minute difference in temperature is enough to bring about condensation, and, for the purpose of my argument, that is all that is necessary. It is just as in differential calculus, where we achieve rigorously demonstrated proofs by ignoring quantities that arc infinitesimally small relative to the ones that we retain in our equations"[C, p. 68].

In such a case, the working substance and the furnace or the cooler are effectively in thermal equilibrium, and heat is transported infinitely slowly, i.e., "*jiwa jiwa*" in Japanese (which means bit by bit) [13], from the furnace to the working substance and from the working substance to the cooler.

Similarly, when the working substance (for example, air) expands, its pressure must be higher than the external pressure, and when it contracts, its pressure must be lower than the external pressure. To prevent the loss of power during these processes, and more specifically to avoid the acceleration of the piston and the induced flow of the working substance (air), these processes must proceed as slowly as possible. To this end, the difference between the internal and external pressures must be infinitely small.

Here, we define the **quasi-static change** as the change under the conditions of an infinitesimally small difference from the external pressure as well as an infinitesimally small temperature difference from the heat source. In this case, inside the working substances, the state variables such as pressure and temperature—which were originally defined only for the equilibrium state—are also defined at every moment of the change. Furthermore, since the reverse process is also quasi-static, this process is reversible.

As the working substance, Carnot considered air (or gas) contained in a cylinder with a movable piston. The bottom of the cylinder is made of a material with perfect heat conduction, while the side walls and the piston are made of a material with perfect thermal insulation (Fig. 19.2).

To clarify the point to be discussed, let us consider the explanation by Clapeyron. First, the cylinder is set on the furnace, and air with the same temperature as the furnace (θ_+) is expanded by adding heat (q_+) (isothermal expansion: A → B). Second, the cylinder is separated from the furnace, its bottom is closed by an insulator, and the air is cooled to θ_- ($< \theta_+$) by expansion (adiabatic expansion: B → C). Third, the cylinder is set on a cooler, and air with the same temperature as the cooler (θ_-) is made to contract by extracting heat (q_+) (isothermal compression: C → D). Finally, the cylinder is separated from the cooler, the bottom is closed by an insulator, and the air is heated to θ_+ by compression (adiabatic compression: D → A).

In this operation, each process is quasi-static. Therefore, for the air, the pressure P, temperature θ, and volume V are defined at every moment; thus, the equation of state $P = P(\theta, V)$ holds and, furthermore, on the basis of Carnot's premise, the heat contained in the air is a state variable ($Q = Q(\theta, V)$). From these two relationships, if Q and θ return to their initial values, P and V will also return to their initial values. Consequently, the air returns to the initial state and a perfect cycle is achieved.

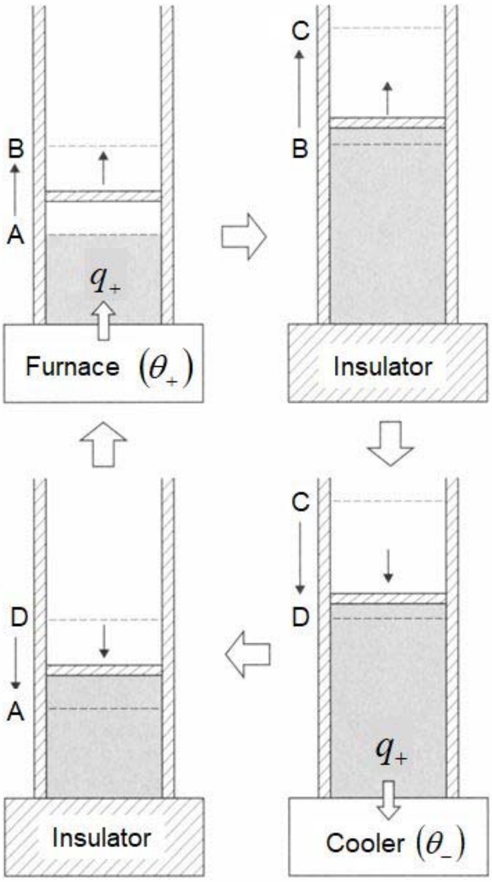

Fig. 19.2 Carnot cycle.

According to this explanation, it might be considered that the existence of the heat function $Q(\theta, V)$, i.e., the conservation of heat, is necessary to close the cycle; however, this is not always the case. Note that the above explanation is based on that of Clapeyron, which was different from that of Carnot.

Carnot started his cycle from a gas of volume V_0 with temperature θ_+ (A_0 in Fig. 19.3). The gas is isothermally expanded to B upon coming in contact with the furnace with the same temperature θ_+. From B, the gas is adiabatically expanded to C with temperature θ_-. From C, the gas is isothermally compressed to D with the initial volume V_0 by coming in contact with the cooler of temperature θ_-. Furthermore, from D, the gas is heated to temperature θ_+ by adiabatic compression; of course, the volume at A is less than V_0. From A, the air can be isothermally expanded to V_0 by coming in contact with the furnace of temperature θ_+, and the cycle is closed at A_0.

This is known as the **Carnot cycle**.

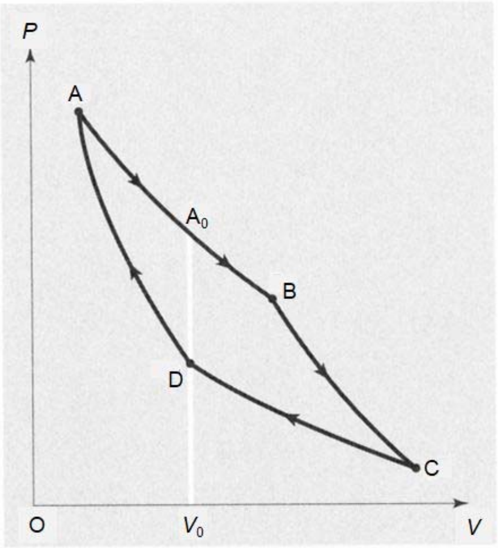

Fig. 19.3 *P–V* diagram of Carnot cycle.

Consequently, to close the Carnot cycle, the conservation of heat is not required. Let define the sum of the heat absorbed from the furnace during processes A → A_0 → B as q_+ and the heat discharged to the cooler in process C → D as q_-. Even if $q_+ \neq q_-$, this cycle is closed, which enabled the Carnot cycle to play a key role in the development of thermal science; the approach by Clapeyron detracts from the significance of Carnot's reasoning [14].[7]

Upon reading Carnot's original paper after studying thermodynamics, it may be considered that his description of the above five processes is somewhat convoluted as well as strange; however, we should recognize that such a description was necessary.

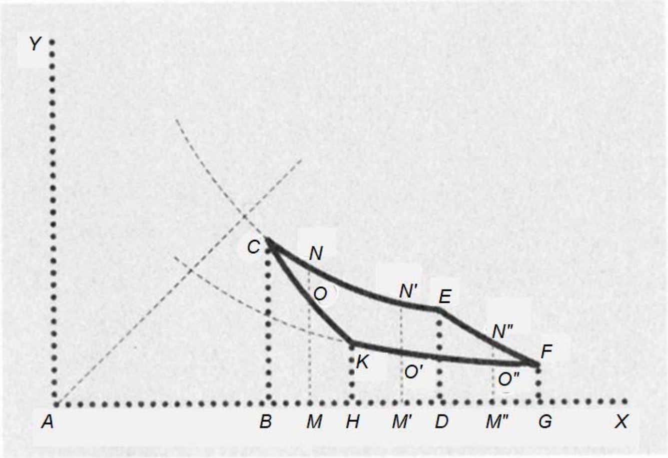

Fig. 19.4 Carnot cycle depicted in Clapeyron's paper.

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[7] If we know the *P-V* relationship for an adiabatic process—Poisson's formula $P^{1/\gamma}/\rho = \text{const.}$ or $PV^{\gamma} = \text{const.}$ (16.15)—, we can determine point D as the point which can adiabatically return to point A without using the relation $q_+ = q_-$, as employed by Clapeyron. Thus Clausius succeeded in removing the restriction of the conservation of heat. However, if we start from point D or B, the discussion is much simpler. Clapeyron's paper first expressed the Carnot cycle as an indicator diagram in the *P–V* plane as shown in Fig. 19.4. Clapeyron also pointed out that the area enclosed by the cycle lines is equal to the work.

Actually, in the *Réflexions*, Carnot's discussion was based on the conservation of heat, while he was much more careful about the necessary condition than Clapeyron by adding the following words: "We believe, nevertheless, that if the fundamental law that we set out to confirm is to be placed beyond all doubt, new tests are called for. The law is based on the theory of heat as we understand it today, and it must be admitted that we do not consider this as an entirely solid foundation"[C, p. 100].[8]

"In these different processes, the air in the cylinder exerts pressure on the piston. The pressure varies, since the elastic force of the air is affected by changes both in its volume and in its temperature. But it will be seen that for any given volume, that is, when the piston is in a particular position, the temperature is higher while the air is expanding than while it is being compressed. During expansion, therefore, the elastic force of the air is greater, and hence the amount of motive power produced is also greater than the amount that is expended in order to bring about compression. In this way, there will be a net production of motive power which can be put to some use. The air has thus been made to act as a heat engine; moreover, *it has been used in the most advantageous way possible,* since there has been no useless restoration of the equilibrium of caloric"[C, p. 75].

IV. Carnot's theorem

In this cycle (hereafter referred to as **C**), according to Carnot, heat q_+ flows from the furnace (θ_+) to the cooler (θ_-), work W is produced, and there are no other changes. Furthermore, the cycle is reversible from the corollary of the preliminary theorem, that is, "*The whole sequence of operations just described can be reversed, and carried out in the opposite order*"[C, p. 75]. In other words, if work W is provided from the outside, heat q_+ is pumped up from the cooler to the furnace. This point is crucial in the following discussion.

That is, the specific structure and the gas properties of the working fluid of a Carnot cycle are not important but the fact that the cycle is ideal and thus reversible is essential. (A Carnot cycle is reversible in a narrow sense because all four processes are reversible. In the following discussion, however, the cycle is required to be reversible only in the broad sense that it can be reversed irrespective of the above-mentioned four processes.)

Here, we go back to the original problems of "whether the motive power of heat is limited or whether it is boundless," and "is the motive power of heat fixed in quantity, or does it vary with the working substance that is used?"

To this end, we assume that there is a cycle (referred to as **C′**) between the temperatures θ_+ and θ_- whose efficiency is superior to the Carnot cycle **C**. That is, there is a cycle **C′** which can produce work W' (> W) for the same q_+. In this case, as shown in Fig. 19.5, by transferring the work W ($< W'$) generated by **C′** to the reversed cycle **C**, heat q_+ can be pumped from the cooler to the furnace. Overall, without any change in the furnace and cooler or the working substance, net work $W' - W > 0$ can be produced.

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[8] As demonstrated in a later chapter, in the recently discovered notes of Carnot's manuscript, he reached the first law of thermodynamics—he rejected the conservation of heat and he insisted that to generate the motive power, heat must be consumed. Medoza, who carefully studied his notes, wrote, "The remarkable change of opinion, from believing that the theory of heat was «beyond doubt» to feeling that «its basis is not unshakable solidity», again indicates that many of the doubts expressed in the *Manuscript Notes* must have begun to assail Carnot even while he was writing book"[15]. If this is the case, Carnot might have been so strongly prepossessed by the analogy between the heat engine and the water-column machine that he assumed that heat is conserved from the high-temperature furnace to the lower-temperature cooler even though he doubted caloric theory.

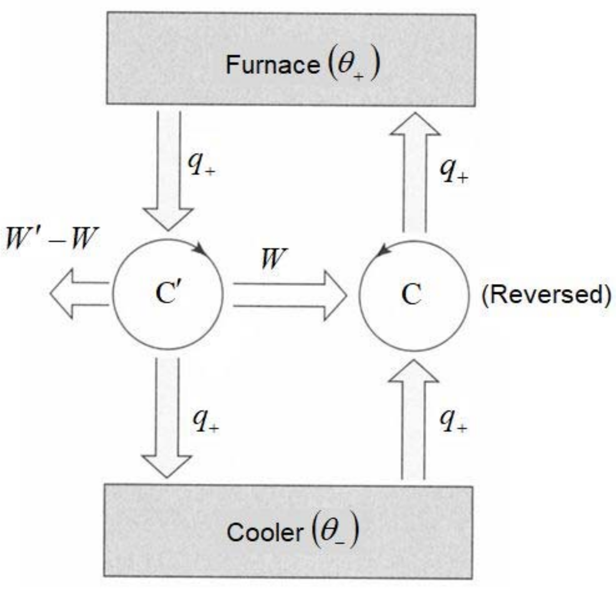

Fig. 19.5 Carnot's proof of his theorem.

Carnot said, "We should then have a case not only of perpetual motion (mouvement perpétuel) but of motive power being created in unlimited quantities without the consumption of caloric or of any other agent.[9] Creation of this kind completely contradicts prevailing ideas, the laws of mechanics (mécanique), and sound physics; it is inadmissible"[C, p. 69]. That is, if we regard the principle that a perpetual motion machine of the first kind is impossible as **the third premise** (for the first and second premises, see pp. 28-29 of this paper), we can conclude that the Carnot cycle attains the maximum efficiency independent of the properties of the working substance and the mechanism of the machine.

"We have chosen air as the substance with which to develop the motive power of heat, but it is clear that the argument would be the same for any other gas. Indeed, it would be the same for any body whose temperature can be changed through successive decreases or increases in volume, that is for any substance in nature or at least for any substance with which motive power can be developed. From this, the following general proposition may be stated:
The motive power of heat is independent of the working substances that are used to develop it. The quantity is determined exclusively by the temperatures of the bodies between which, at the end of the process, the passage of caloric has taken place. (La puissance motrice de la chaleur est indépendante des agens mis en œuvre pour la réaliser; sa quantité est fixée uniquement par les températures des corps entre lesquels se fait en dernier résultat le transport du calorique.)"[C, p. 76].

This is **Carnot's theorem**. It is the greatest discovery in the history of thermal science, from which thermodynamics began.

Note that the following three items are also important discoveries of Carnot in addition to his theorem: first, the concept of quasi-static and reversible changes; second, the consideration of his cycle; and finally, the proof by contradiction by considering a combination of the normal and reversed cycles.

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CHAPTER 20 STRUCTURE OF CARNOT'S THEORY AND ITS EXTENSION —THE START OF THERMODYNAMICS

CONTENTS

I. Premises of Carnot's theory

Carnot's theory states that there is an upper limit to the efficiency of a heat engine which is determined only by the temperature, irrespective of the working substance and the structure of the engine. In the previous chapter, a proof of the theorem was given on the basis of the Carnot cycle, and the emphasis was laid on the historical development, particularly in connection with the improvement of the steam engine by Watt. In this chapter, we focus on the internal logical structure of Carnot's theorem and its extension.

The basis of Carnot's heat theory in the *Réflexions* is the same as that in the work of Laplace and Poisson in Chapter 16 except that the taking temperature θ and volume V are considered as the variables; they are summarized by the following three premises:

Premise A: paradigm of specific heat and latent heat

For a unit mass of a material, the added heat q is related to the changes in temperature and volume as

$$dq = C_V d\theta + \Lambda_{\mathrm{D}} dV \,, \qquad (13.5)_{\mathrm{r}}$$

where C_V is the specific heat for a constant volume and Λ_{D} is the latent heat of expansion.

Carnot stated that "When a gaseous fluid is rapidly compressed, its temperature rises; and when, on the other hand, it is rapidly expanded, there is a fall in temperature. This is one of best demonstrated of all pieces of experimental evidence, and it will be taken as a starting-point for my proof"[C, p. 73]. and "if the gas is expanded, its temperature can be prevented from falling if we supply to it an appropriate quantity of caloric. We shall call the caloric that is used in these circumstances, where the temperature remains constant, the caloric due to the change in volume (calorique dû au changement de volume)"[C, p. 74].

The former statement means that in the case of a rapid change, i.e., $dq = 0$, then $d\theta < 0$ for $dV > 0$ and $d\theta > 0$ for $dV < 0$, hence $\Lambda_{\mathrm{D}}/C_V > 0$. The latter statement means that in isothermal heating, i.e., $d\theta = 0$, then $dV > 0$ for $dq > 0$, hence $\Lambda_{\mathrm{D}} > 0$. Therefore,

$$\Lambda_{\mathrm{D}} > 0 \,, \; C_V > 0 \,. \qquad (20.1)$$

This restriction is postulated as **Premise A**.

Premise B: existence of the equation of state

For a gas, the existence of an equation of state, i.e., a relationship among P, θ, and V, is assumed. That is,

$$P = P(\theta, V) \ . \tag{20.2}$$

In particular, for most ordinary gases, the Boyle–Gay-Lussac law, namely

$$P = R\frac{\alpha^{-1} + \theta}{V} \tag*{(20.2)′}$$

holds, where $\alpha^{-1} = 267°\mathrm{C}$, $R \equiv \alpha(PV)_{\theta=0°\mathrm{C},\ P=1\,\mathrm{atm}}$. As shown later in Fig. 20.3, this equation was used by Carnot himself. Carnot regarded this equation as being applicable to all gases; hereafter, the gas expressed by eq. (20.2)′ is called an 'ideal gas.'[10]

Premise C: conservation of heat

This means that a heat function exists as a state variable $Q(\theta, V)$. In other words, dq in eq. (13.5) is a total derivative, and the single-valued function

$$Q(\theta, V) = \int_{(\theta_0, V_0)}^{(\theta, V)} dq \tag*{(13.4)$_\mathrm{r}$}$$

can be defined; in this case, $dQ = dq$ holds.

In most of the books about the history of thermal science, **Premise A (paradigm of specific heat and latent heat)** and **Premise C (conservation of heat)** are inseparably linked to each other. Although this is historically true, it is not logically true. **Premise A** is not always associated with **Premise C**. Even if the conservation of heat does not hold (i.e., dq is not the total derivative), ex. (13.5) for dq is allowed; $q = \int dq$ is obtained if the integration path is specified for a quasi-static change. Or, one can understand that when the state changes along the curve $f(\theta(t), V(t))$ on the (θ, V) plane, $dq = C_V \dot{\theta} dt + \Lambda_\mathrm{D} \dot{V} dt$ can be determined [1].

Here, let us consider the condition required to realize a Carnot cycle.

In a Carnot cycle, the working substance isothermally expands when it comes in contact with the furnace of temperature θ_+, then it is cooled to θ_- by adiabatic expansion; it is isothermally compressed when it comes in contact with the cooler of temperature θ_-, then it is heated to θ_+ by adiabatic compression. Its *P*–*V* diagram is shown in Fig. 20.1 (Fig. 19.4).

Therefore,

$$\left(\frac{dP}{dV}\right)_Q < \left(\frac{dP}{dV}\right)_\theta < 0 \tag{20.3}$$

is necessary. (The subscripts indicate the variables which are kept constant; Q means adiabatic and θ means isothermal.)

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[10] In the following, the apostrophe is used to distinguish an equation for an ordinary gas (eq. (20.2)) and one for an ideal gas (eq. (20.2)′).

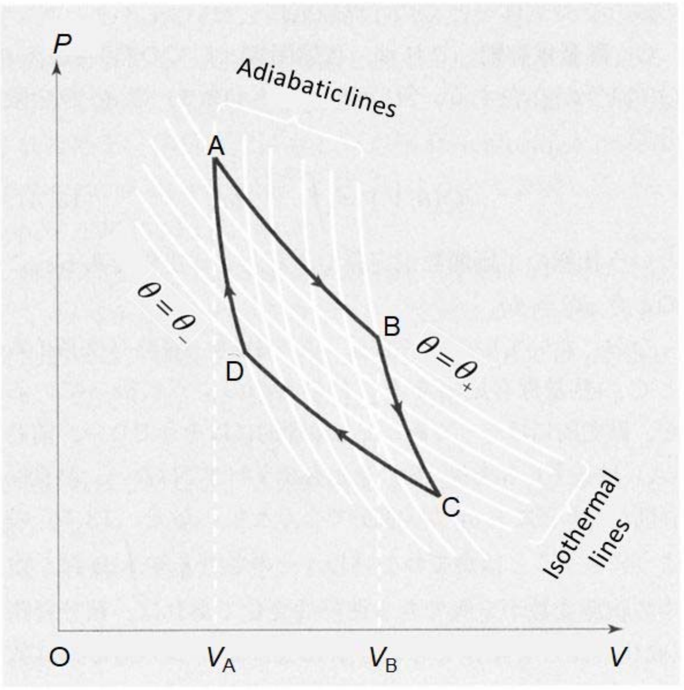

Fig. 20.1 Carnot cycle for ideal gas.

For an ideal gas,

$$\left(\frac{dP}{dV}\right)_\theta = -\frac{P}{V},$$

$$\left(\frac{dP}{dV}\right)_Q = -\frac{P}{V} + \frac{R}{V}\left(\frac{d\theta}{dV}\right)_Q,$$

and from eqs. (13.5) and (20.1), when Q is constant $(dQ = dq = 0)$, $(d\theta/dV)_Q = -\Lambda_{\mathrm{D}}/C_V < 0$, hence eq. (20.3) is proved, which enables the realization of a Carnot cycle.[11]

II. Analytical expression for Carnot's theorem

In a Carnot cycle (Fig. 20.1), according to Carnot, the working substance receives heat q_+ in the isothermal process A → B, and the same amount of heat is discharged to the cooler. Associated with the decrease in heat, the volume of the working substance changes and work $W = \oint P dV$ is generated. In general, the work for this case is expressed as

$$W = W(q_+, \theta_+, \theta_-, V_{\mathrm{A}}, V_{\mathrm{B}}).$$

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[11] It seems that Clapeyron, who first illustrated the Carnot cycle on the P–V plane, did not know Poisson's formula for an adiabatic process, eq. (16.15) $PV^\gamma = \text{const}$. Actually, he wrote, that regarding curve BC, "its pressure decreases more rapidly according to an unknown law", and regarding the curve DA, "the unknown law, of how the pressure varies when the volume of the gas is reduced"[2]. He, however, proved eq. (20.3), and therefore could depict a qualitatively correct diagram.

Strictly speaking, from eq. (13.5), for the isothermal process A → B, $q_+ = \int_{V_\mathrm{A}}^{V_\mathrm{B}} \Lambda_\mathrm{D} dV$; as a result, V_B is determined by V_A and q_+, and hence is not independent.
Here, Carnot's theorem demonstrates that the work generated by a Carnot cycle W is maximum when heat q_+ decreases from θ_+ to θ_- irrespective of the properties of the working substance and the mode of operation.

Then, *this theorem indicates that the work is independent of* V_A *and* V_B.

Or, returning to Carnot's proof (Chapter 19-IV), we can state the following. First, we assume that for a Carnot cycle in a different volume range $(V'_\mathrm{A} - V'_\mathrm{B})$, more work is generated. That is, for the same q_+, $W(V_\mathrm{A}) < W(V'_\mathrm{A})$. In this case, first we operate a normal cycle starting from V'_A, and second by using part of the generated work $W(V_\mathrm{A})$, we can operate the reverse cycle for V_A. As a result, we can obtain work $W(V'_\mathrm{A}) - W(V_\mathrm{A})$ without any change; however, this violates the principle that a perpetual engine is impossible, i.e., **the third premise**. Consequently, W is independent of the volume range of the working substance.

Furthermore, it can be deduced that in a Carnot cycle the work produced by using the amount of heat nq_+ is n times as great as W produced by using q_+. This is because Carnot's theorem includes the statement that a cycle with heat nq_+, and n cycles, each with q_+, are equivalent. That is, $W(nq_+,\theta_+,\theta_-) = nW(q_+,\theta_+,\theta_-)$. Hence, $W(q_+,\theta_+,\theta_-) \propto q_+$.

From the above discussion, Carnot's theorem is expressed as follows. The maximum efficiency of a heat engine operated between θ_+ and θ_- is determined as

$$\frac{W}{q_+} = \Psi(\theta_+,\theta_-) \ , \tag{20.4}$$

where Ψ is a universal function independent of the working substance; this is known as **Carnot's theorem: expression I**. Here,

$$\begin{aligned} \theta_+ > \theta_-, \quad & \Psi(\theta_+,\theta_-) > 0 , \\ \theta_+ \to \theta_-, \quad & \Psi(\theta_+,\theta_-) \to 0 . \end{aligned}$$

Furthermore, Carnot considered the case of $\theta_+ = \theta, \ \theta_- = \theta - \Delta\theta$, where $\Delta\theta$ is very small ($0 < \Delta\theta << \theta$) as shown in Fig. 20.2.

In this case, we let the produced work be ΔW and introduce the function

$$\lim_{\theta' \to \theta} \left\{ \frac{\Psi(\theta,\theta')}{\theta - \theta'} \right\} \equiv \frac{1}{\Theta(\theta)} \ . \tag{20.5}$$

Then, Carnot's theorem is expressed using a universal function $\Theta(\theta)$ as

$$\frac{\Delta W}{q_+} = \Psi(\theta, \theta - \Delta\theta) = \frac{\Delta\theta}{\Theta(\theta)} \ . \tag{20.6}$$

This is known as **Carnot's theorem: expression II**. Here, we call this universal function $\Theta(\theta)$ the **Carnot function**. The existence of this universal function is the key point of Carnot's theorem, and it is the ultimate basis of thermodynamics.

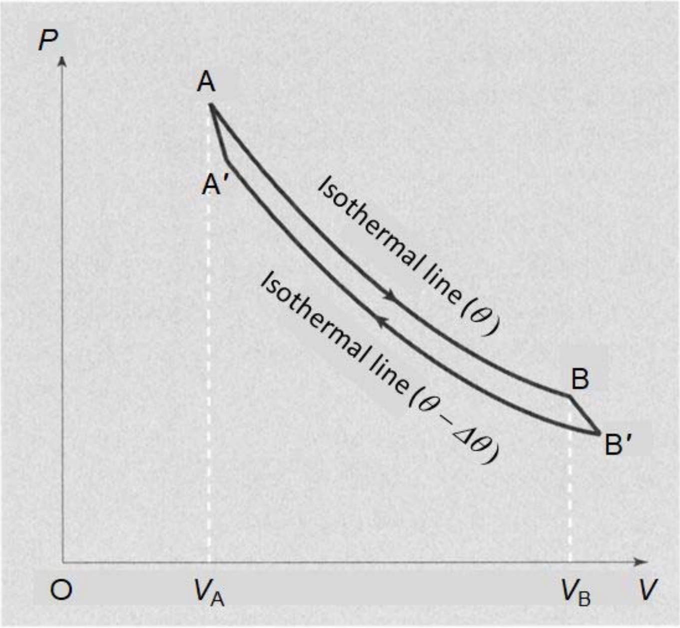
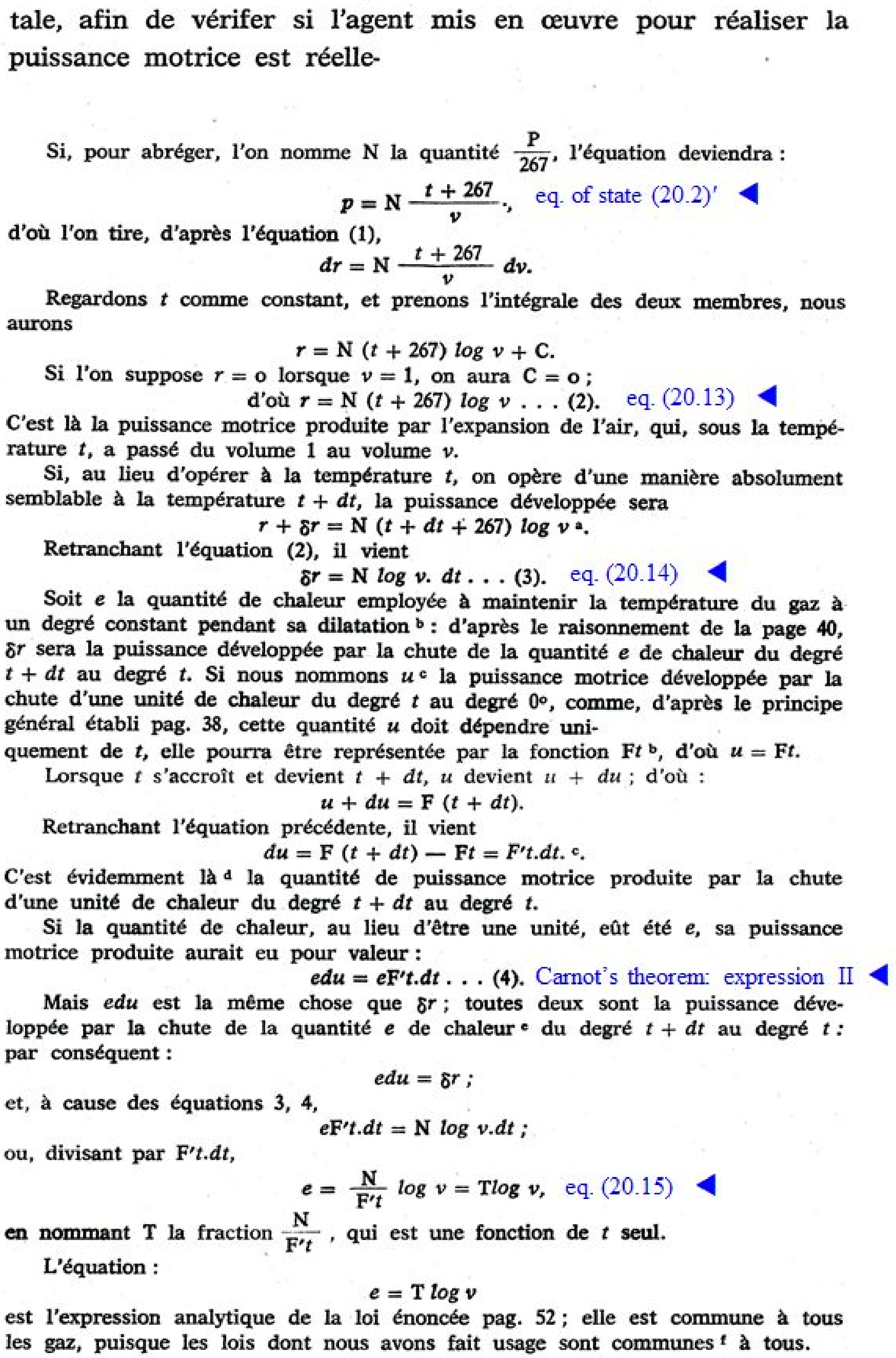


Fig. 20.2 Carnot cycle with infinitesimally small temperature difference.

It is often said that Carnot did not use mathematical expressions, but that is a misconception; he wrote the above equation in a footnote (Fig. 20.3). As shown in the figure, Carnot expressed $1/\Theta(\theta)$ as $\mathrm{F}'t$ and $R\Theta(\theta)$ as T. Although the Carnot function is usually denoted by $C(\theta)$ after Clapeyron or $1/\mu(\theta)$ after Thomson, I did not use $C(\theta)$ because it could be confused with specific heat. Actually, I wanted to use $T(\theta)$ similarly to Carnot; however, to avoid the possible misunderstanding that $T(\theta)$ is the absolute temperature, $\Theta(\theta)$ is used following Takabayashi's book "*History of Thermal Science*" in Japanese (first edition, Nihonkagakusya, Kyoto, 1948; second edition, Kaimeisya, Tokyo, 1999).



tale, afin de vérifer si l'agent mis en œuvre pour réaliser la puissance motrice est réelle-

Si, pour abréger, l'on nomme N la quantité $\frac{P}{267}$, l'équation deviendra :

$$p = N\frac{t + 267}{v}\cdot,$$ eq. of state (20.2)′ ◀

d'où l'on tire, d'après l'équation (1),

$$dr = N\frac{t + 267}{v}dv.$$

Regardons t comme constant, et prenons l'intégrale des deux membres, nous aurons

$$r = N\,(t + 267)\,log\,v + C.$$

Si l'on suppose $r = o$ lorsque $v = 1$, on aura $C = o$;

d'où $r = N\,(t + 267)\,log\,v\ .\ .\ .\ (2).$ eq. (20.13) ◀

C'est là la puissance motrice produite par l'expansion de l'air, qui, sous la température t, a passé du volume 1 au volume v.

Si, au lieu d'opérer à la température t, on opère d'une manière absolument semblable à la température $t + dt$, la puissance développée sera

$$r + \delta r = N\,(t + dt + 267)\,log\,v\ ^{a}.$$

Retranchant l'équation (2), il vient

$\delta r = N\,log\,v.\,dt\ .\ .\ .\ (3).$ eq. (20.14) ◀

Soit e la quantité de chaleur employée à maintenir la température du gaz à un degré constant pendant sa dilatation [b] : d'après le raisonnement de la page 40, δr sera la puissance développée par la chute de la quantité e de chaleur du degré $t + dt$ au degré t. Si nous nommons u [c] la puissance motrice développée par la chute d'une unité de chaleur du degré t au degré 0°, comme, d'après le principe général établi pag. 38, cette quantité u doit dépendre uniquement de t, elle pourra être représentée par la fonction Ft [b], d'où $u = Ft$.

Lorsque t s'accroît et devient $t + dt$, u devient $u + du$; d'où :

$$u + du = F\,(t + dt).$$

Retranchant l'équation précédente, il vient

$$du = F\,(t + dt) - Ft = F't.dt.\ ^{c}.$$

C'est évidemment là [d] la quantité de puissance motrice produite par la chute d'une unité de chaleur du degré $t + dt$ au degré t.

Si la quantité de chaleur, au lieu d'être une unité, eût été e, sa puissance motrice produite aurait eu pour valeur :

$edu = eF't.dt\ .\ .\ .\ (4).$ Carnot's theorem: expression II ◀

Mais edu est la même chose que δr ; toutes deux sont la puissance développée par la chute de la quantité e de chaleur [e] du degré $t + dt$ au degré t : par conséquent :

$$edu = \delta r\ ;$$

et, à cause des équations 3, 4,

$$eF't.dt = N\,log\,v.dt\ ;$$

ou, divisant par $F't.dt$,

$e = \frac{N}{F't}\,log\,v = T log\,v,$ eq. (20.15) ◀

en nommant T la fraction $\frac{N}{F't}$, qui est une fonction de t seul.

L'équation :

$$e = T\,log\,v$$

est l'expression analytique de la loi énoncée pag. 52 ; elle est commune à tous les gaz, puisque les lois dont nous avons fait usage sont communes [f] à tous.

Fig. 20.3 Part of a footnote of Carnot's paper; N denotes R, r denotes W, $1/F't = T/N$ denotes Θ, e denotes q_+.

III. Experimental determination of Carnot function

The core of Carnot's theory is that *there is the principle restriction on the work produced from heat*. Theoretically, it is reduced to the fact that *the Carnot function* $\varTheta(\theta)$ *is a universal function independent of the working substance*. Therefore, to examine whether Carnot's theory is correct, it is sufficient to directly determine $\varTheta(\theta)$ for various working substances and compare them. Thus, Carnot wrote, "In order to test our basic proposition, to test whether the nature of the working substance that is used for developing motive power really has no bearing on the amount of power produced, we shall consider a number of substances in turn. These substances are air, steam, and alcohol vapour"[C, p. 94].

As the first example, let us consider a cycle for a unit amount of air with an infinitesimally small temperature difference ($\varDelta\theta$), A → B → B′ → A′ → A (Fig. 20.2). In this case, the work done in the adiabatic processes (B → B′, A′ → A)[12] can be neglected because it is an infinitesimal higher-order quantity, and hence the net work done by the air is

$$\varDelta W = \int_{V_\mathrm{A}}^{V_\mathrm{B}} \{P(\theta) - P(\theta - \varDelta\theta)\} dV = \int_{V_\mathrm{A}}^{V_\mathrm{B}} \left(\frac{\partial P}{\partial \theta}\right)_V \varDelta\theta dV \cong \left(\frac{\partial P}{\partial \theta}\right)_V \varDelta\theta (V_\mathrm{B} - V_\mathrm{A})\,. \tag{20.7}$$

Here, as shown in Fig. 20.4, consider the intersection M of an adiabatic line through points A and A′ and an isobaric line through point B (temperature $\theta - \varDelta\theta_0$). If we consider the curve AB where the relationships $\varDelta\theta << \varDelta\theta_0$ and $\varDelta\theta_0 << \alpha^{-1} = 267°\mathrm{C}$ are satisfied, by using

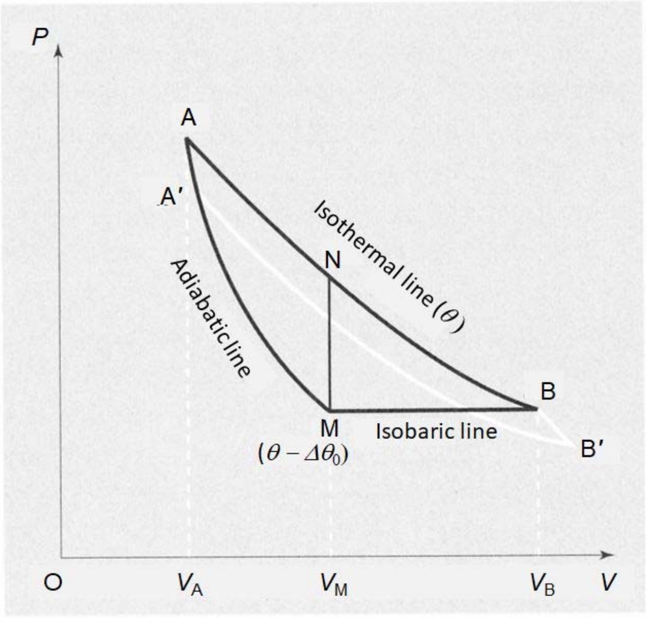


Fig. 20.4 Explanation of Carnot's calculation.

$$\begin{cases} \alpha(\theta) \equiv \dfrac{1}{V}\left(\dfrac{\partial V}{\partial \theta}\right)_P \cong \dfrac{V_\mathrm{B} - V_\mathrm{M}}{V\varDelta\theta_0} \\ \beta(\theta) \equiv -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial \theta}\right)_Q \cong \dfrac{V_\mathrm{M} - V_\mathrm{A}}{V\varDelta\theta_0} \end{cases}, \tag{20.8}$$

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[12] The difference between the work done to the outside in B → B′ and that from the outside in A′ → A.

the volume change is expressed as

$$V_{\mathrm{B}} - V_{\mathrm{A}} = \left(\alpha(\theta) + \beta(\theta)\right) V \varDelta\theta_0 \ . \tag{20.9}$$

(Here, since a small factor $\varDelta\theta_0$ is included in the R.H.S., V in the R.H.S. can be V_{A}, V_{B}, and V_{M}.)
On the other hand, if we assume the conservation of heat (the existence of a heat function) along the adiabatic process corresponding to MA, $Q(\mathrm{A}) = Q(\mathrm{M})$; since MB is an isobaric process, the heat absorbed by the air in process AB is expressed by using the specific heat at constant pressure as follows:

$$q_+ = Q(\mathrm{B}) - Q(\mathrm{A}) = Q(\mathrm{B}) - Q(\mathrm{M}) = C_P \varDelta\theta_0 \ . \tag{20.10}$$

Actually, even if we do not assume the conservation of heat, in the process M → A → B → M, $\oint dq$ is the second order of a minutely small quantity; since we now only consider the first order of a minutely small quantity, this result is obviously correct.[13]

Therefore, the Carnot function is obtained as

$$\Theta(\theta) = q_+ \frac{\varDelta\theta}{\varDelta W} = \frac{(C_P \varDelta\theta_0) \times \varDelta\theta}{(V_{\mathrm{B}} - V_{\mathrm{A}})(\partial P/\partial\theta)_V \varDelta\theta} = \frac{C_P}{\{\alpha(\theta) + \beta(\theta)\} V (\partial P/\partial\theta)_V} \ .$$

Here, if we assume that air is an ideal gas, $(\partial P/\partial\theta)_V = R/V = \alpha\,(PV)_0/V$ and $\alpha(\theta) = \left(\alpha^{-1} + \theta\right)^{-1}$, then $\theta = 0°\mathrm{C}$, we obtain

$$\Theta(0°\mathrm{C}) = \frac{C_P}{(\alpha + \beta(0))\alpha\,(PV)_0} \ . \tag{20.11}$$

$\theta = 0°\mathrm{C}$, $P = 1\,\mathrm{atm} = 10.4 \times 10^3\ \mathrm{kgw/m^2}$, $V(0) = 0.77\,\mathrm{m}^3$ for 1 kg of air, the measured value of Delaroche and Bérard for the specific heat of gases of $C_P = 0.267\,C_{\mathrm{water}} = 0.267\,\mathrm{kcal/°C}$ (Table 15.2), $\alpha = 1/267\,°\mathrm{C}$ of Gay-Lussac, and $\beta(0) = 1/116\,°\mathrm{C}$ of Poisson ((eq.15.6))[14], and obtained

$$\Theta(0°\mathrm{C}) = \frac{1}{1.39}\left(\frac{\mathrm{kcal°C}}{\mathrm{kgw \cdot m}}\right) .$$

For later discussion, we rewrite the above result as follows:

$$\Theta(0°\mathrm{C}) = \frac{1}{1.39} \times \frac{10^3}{9.8}\left(\frac{\mathrm{cal°C}}{\mathrm{J}}\right) = 307\left(\frac{\mathrm{cal°C}}{4.185\,\mathrm{J}}\right) .$$

(A factor of 4.185 was introduced to account for knowledge obtained later. If we introduce the precise values of $V(0) = 0.773\,\mathrm{m}^3$, $1\ \mathrm{atm} = 10.3 \times 10^3\ \mathrm{kgw/m^2}$, $C_P = 0.240\,\mathrm{kcal/°C}$, $\alpha = 1/273\,°\mathrm{C}$, and $\beta(0) = 1/109\,°\mathrm{C}$, we obtain

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[13] I consider this fact to be self-explanatory. However, there is a paper stating that the result expressed in eq. (20.10) is "surprenant" and needlessly studying the reason why it is correct [3].

[14] Strictly speaking, although $\beta(0) = 1/116\,°\mathrm{C}$ obtained by Poisson is the value at $7.5°\mathrm{C}$, Carnot regarded it as constant.

$$\Theta(0°\mathrm{C}) = \frac{1}{1.56}\left(\frac{\mathrm{kcal°C}}{\mathrm{kgw \cdot m}}\right) = 273\left(\frac{\mathrm{cal°C}}{4.185\,\mathrm{J}}\right).$$

Readers can anticipate what $\Theta(\theta)$ means.)

As the second example, Carnot considered a cycle in which 1kg of water at $\theta = 100°\mathrm{C}$ is evaporated and then liquefied by compressing it at $\theta = 99°\mathrm{C}$. In this cycle, both the temperature and pressure are constant in the evaporation and liquefaction processes, as shown as Fig. 20.5, which illustrates a Carnot cycle consisting of two isothermal and two adiabatic processes. For $m = 1\,\mathrm{kg}$, the variations in the volume and pressure are expressed as

$$\Delta V = V_{\mathrm{vapor}} - V_{\mathrm{water}} \cong V_{\mathrm{vapor}} = 1.7\,\mathrm{m}^3,$$
$$\Delta P = P(100°\mathrm{C}) - P(99°\mathrm{C}) = 0.36 \times 10^3\,\mathrm{kgw/m}^2,$$
$$q_+ = \Lambda_{\mathrm{E}} m = 550\,\mathrm{kcal},$$

where Λ_{E} denotes the latent heat of evaporation, the subscript E means evaporation, and

$$\Theta(100°\mathrm{C}) = q_+ \frac{\Delta\theta}{\Delta W} = \Lambda_{\mathrm{E}} m \frac{\Delta\theta}{\Delta V\, \Delta P} = \frac{1}{1.11_2}\left(\frac{\mathrm{kcal°C}}{\mathrm{kgw \cdot m}}\right) = 384\left(\frac{\mathrm{cal°C}}{4.185\,\mathrm{J}}\right).$$

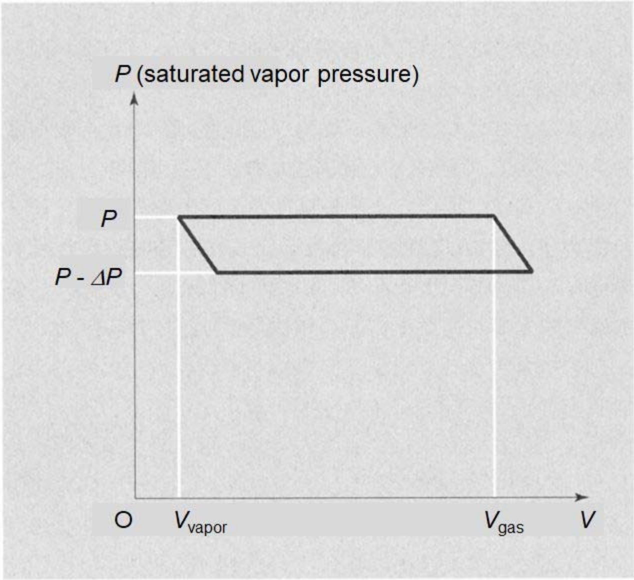

Fig. 20.5 Carnot cycle in the case of using steam.

As the third example, for 1kg of ethyl alcohol at its boiling point $\theta = 78.8°\mathrm{C}$, he obtained

$$\Theta(78.8°\mathrm{C}) = \frac{1}{1.23_0}\left(\frac{\mathrm{kcal°C}}{\mathrm{kgw \cdot m}}\right) = 347\left(\frac{\mathrm{cal°C}}{4.185\,\mathrm{J}}\right).$$

Simply by comparing values at different temperatures, however, it is impossible to clarify that $\Theta(\theta)$ is a universal function for air, water, and alcohol. Carnot himself recognized that “It would have been desirable to be able to make other similar comparisons, to calculate, for instance, the motive power developed by the action of heat on solids and liquids, by the freezing of water, etc. But, at present, physics does not provide the information we need for this purpose”[C, p. 100].

Clapeyron, who popularized Carnot's theory 10 years after it was published, also wrote, "The function C (Carnot function $\Theta(\theta)$) is, as we have seen, of great importance: it is the common link between the phenomena caused by heat in solid bodies, liquids and. gases"[4], and focused on its importance. Following Carnot, Clapeyron tried to determine the values of the function.

Clapeyron expressed the work for the cycle shown in Fig. 20.5 as

$$\varDelta W = \left(V_{\text{gas}} - V_{\text{liquid}}\right)\varDelta P = \left(V_{\text{gas}} - V_{\text{liquid}}\right)\frac{dP}{d\theta}\varDelta\theta\,.$$

where P is the saturated vapor pressure (a function of only θ). On the basis of the above equation, using $q_{+} = \varLambda_{\mathrm{E}} m$, and applying Carnot's theorem eq. (20.6), Claperon obtained

$$\frac{1}{\Theta(\theta)} = \frac{\varDelta W}{q_{+}\varDelta\theta} = \frac{V_{\text{gas}} - V_{\text{liquid}}}{m\varLambda_{\mathrm{E}}}\cdot\frac{dP}{d\theta}\,,$$

i.e.,

$$\frac{dP}{d\theta} = \frac{m\varLambda_{\mathrm{E}}}{V_{\text{gas}} - V_{\text{liquid}}}\cdot\frac{1}{\Theta(\theta)} = \frac{\varLambda_{\mathrm{E}}}{v_{\text{gas}} - v_{\text{liquid}}}\cdot\frac{1}{\Theta(\theta)}\,, \tag{20.12}$$

where $v_{\text{gas}} = V_{\text{gas}}/m$. This equation is called **Clapeyron's foumula**, which "was the first physico-chemical application of what we now call the second law of thermodynamics"[5].

Using this formula, Clapeyron evaluated $\Theta(\theta)$ for water, ethyl alcohol, diethyl ether (sulfuric ether: boiling point 35.5°C), and oil of turpentine (boiling point 156.8°C). In Fig. 20.6, Clapeyron's results are plotted by open triangles[15], while Carnot's are plotted by open circles.

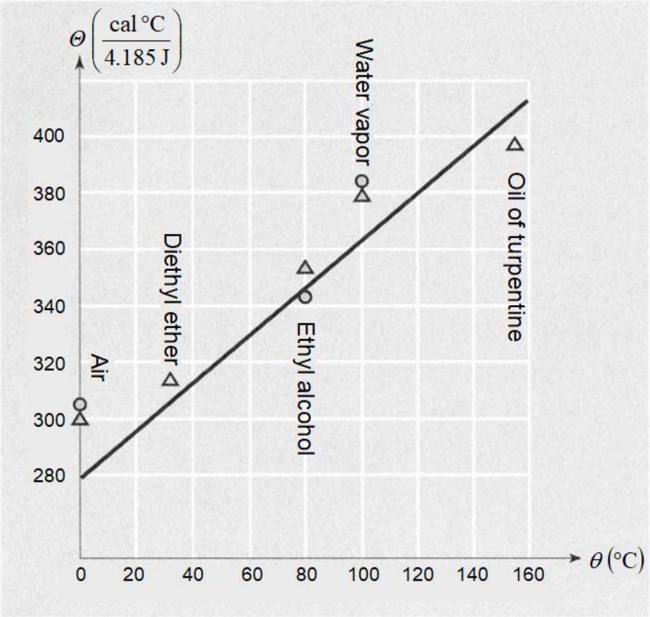

Fig. 20.6 Determination of Carnot function.
(open circles: Carnot, open triangles: Clapeyron, a straight line: Thomson)

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[15] Actually, Clapeyron obtained two kinds of values. Cf. Table 25.1 including the values evaluated by Helmholtz (1821–1894).

From these limited results, it is obviously impossible to confirm the universality of the Carnot function. Clapeyron himself stated, "Unfortunately there are no experiments which allow us to determine the values of this function at all values of the temperature"[6].

Another person who focused on the importance of the Carnot function was William Thomson in 1849. "The complete theoretical investigation of the motive, power of heat is thus reduced to the experimental determination of the coefficient $\mu\,(=1/\Theta(\theta))$; and may be considered as perfect, when, by any series of experimental researches whatever, we can find a value of μ for every temperature within practical limits. The special character of the experimental researches, whether with reference to gases, or with reference to vapours, necessary and sufficient for this object, is defined and restricted in the most precise manner, by the expressions (6) for μ, given above"[7].

For the sake of comparison, in Fig. 20.6, I included Thomson's results as a straight line, which he evaluated $\Theta(\theta)$ on the basis of Regnault's measurements and Clapeyron's formula for $\theta = 0-230°\mathrm{C}$. In view of the lower accuracy of Carnot's and Clapeyron's evaluations, we can safely conclude that the agreement with the results of Thomson is reasonable [8].[16]

IV. Extension of Carnot's theory and gas theorem

To confirm the correctness of a basic theory such as Carnot's theorem, however, a direct proof is not necessarily required. On the contrary, its extension, i.e., what is theoretically deduced from it, is more important.

Carnot wrote his paper with the aim of solving technological issues on thermal efficiency. Simultaneously, however, he was well aware of the main theme of research, which at that time was dominated by the central academy of France. He successfully demonstrated the effectiveness of his theory by applying it to the gas theory, i.e., a central issue of the day, which attracted interest from French top academics.

In fact, he succeeded in deriving several theorems which could not be explained by the simple calorimetry of the day, although some of them were incorrect. In other words, *for the first time, he demonstrated the power of thermodynamics*.

Later, Clapeyron wrote, "S. Carnot, avoiding the use of mathematical analysis, arrives by a chain of difficult and elusive arguments at results which can be deduced easily from a more general law which I shall attempt to prove"[9]. On the strength of this comment, it was later considered that Carnot did not use mathematics. Furthermore, Truesdell, who liked mathematical formulation, made the strong criticism, "Among physicists of the first rank, Carnot is the first who was not in at least equal measure a mathematician"[10]. It is indeed true that Carnot's paper is hard to read, and cannot avoid criticism for lacking in mathematics.

Actually, however, Carnot presented a mathematical discussion. Certainly, in the main text, he developed "a chain of difficult and elusive arguments" without mathematics, and only in the footnotes did he add very brief mathematical explanations; because of his poor description, he suffered an unreasonable amount of criticism. Figure 20.3 shows part of one of his footnotes.

Here, to provide a clear understanding, let us consider Carnot's gas theory on the basis of his footnote.

The work done when a gas expands by dV is given by $dW = PdV$. In particular, for an ideal gas, it is expressed as $dW = R\left(\alpha^{-1} + \theta\right)dV/V$. As a result, the work done by an ideal gas in an isothermal process A → B is given by

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[16] The unit used by Thomson is converted as follows:
$\left[\frac{1}{\mu}\right] = \frac{\mathrm{BTU\,°C}}{\mathrm{lbw \cdot ft}} = \frac{\mathrm{kcal \cdot °C}}{\mathrm{kgw \cdot ft}} = 334.8\frac{\mathrm{cal \cdot °C}}{\mathrm{J}}$. Note that Thomson expressed lbw simply as lb.

$$W(\theta)=\int_{V_\mathrm{A}}^{V_\mathrm{B}} R\left(\alpha^{-1}+\theta\right)\frac{dV}{V}=R\left(\alpha^{-1}+\theta\right)\ln\left(\frac{V_\mathrm{B}}{V_\mathrm{A}}\right) . \tag{20.13}$$

In a Carnot cycle with an infinitesimal temperature difference ($\Delta\theta$), the net work done is

$$\Delta W=W(\theta)-W(\theta-\Delta\theta)=R\Delta\theta\ln\left(\frac{V_\mathrm{B}}{V_\mathrm{A}}\right) . \tag{20.14}$$

The amount of heat q_+ which the gas absorbed in the process A → B is given by this equation and **Carnot's theorem**: **expression II** (eq. (20.6)), and is expressed by using the Carnot function as follows:

$$q_+=\Theta(\theta)\frac{\Delta W}{\Delta\theta}=R\Theta(\theta)\ln\left(\frac{V_\mathrm{B}}{V_\mathrm{A}}\right) , \tag{20.15}$$

where $\Theta(\theta)$ is a universal function, and hence q_+ is identical irrespective of the kind of gas if we consider ideal gases. Consequently, the following theorem is deduced. (The "gas" Carnot referred to was an ideal one.)

Gas theorem 1
"*When a gas passes from a particular volume and pressure to another specified volume and pressure, without undergoing a change in temperature, the amount of caloric absorbed or given out is always the same, whatever the gas on which the observation is made*"[C, p. 78].

Gas theorem 2
"*When the volume of a gas changes at a constant temperature, the amounts of heat absorbed or released by the gas will follow an arithmetical progression when the increases or decreases in volume follow a geometrical progression*"[C, p. 83]. (This means that if $q_+=q_0$ for $V_\mathrm{B}/V_\mathrm{A}=\lambda$, then $q_+=nq_0$ for $V_\mathrm{B}/V_\mathrm{A}=\lambda^n$.)

Of course, this theorem can be deduced from the first law of thermodynamics and the fact that the internal energy of an ideal gas is only a function of temperature. At that time, however, these facts were not known. It is surprising that such a general relationship for q_+ as eq. (20.15) can be obtained only from the constraint on the work generated by heat (Carnot's theorem). It was four years later that Dulong (1785–1838) experimentally found **gas theorem 1**. When Mayer (1814–1878) proposed the equivalent conversion between heat and work, this fact was one of the important bases.

Furthermore, Carnot considered the case of the isobaric process M → B and the constant-volume process M → N in Fig. 20.4. Assuming that heat is a state variable, he set

$$\begin{aligned}\mathrm{M}\rightarrow\mathrm{B}:\ C_P\Delta\theta_0&=Q(\mathrm{B})-Q(\mathrm{M}),\\ \mathrm{M}\rightarrow\mathrm{N}:\ C_V\Delta\theta_0&=Q(\mathrm{N})-Q(\mathrm{M}),\end{aligned}$$

and thus obtained

$$(C_P-C_V)\Delta\theta_0=Q(\mathrm{B})-Q(\mathrm{N}) . \tag{20.16}$$

However, since the right hand side is the amount of heat added in the isothermal process N → B, if the gas is regarded as ideal, it is concluded from **gas theorem 1** that the left hand side is independent of the type of gas. As a result, the following theorem is obtained:

Gas theorem 3
"*The difference between the specific heat at constant pressure and the specific heat at constant volume is the same for all gases*"[C, p. 80], [11].

Although the proof was based on the conservation law of heat, as described earlier, it is correct because the discussion was made for an infinitesimally small cycle.

Note that if we combine eqs. (20.15) and (20.16), because $V_\mathrm{M} = V_\mathrm{N}$, we obtain

$$(C_P - C_V)\mathit{\Delta}\theta_0 = R\Theta(\theta)\ln\left(\frac{V_\mathrm{B}}{V_\mathrm{M}}\right),$$

Substituting the first relationship of eq. (20.8), i.e.,

$$V_\mathrm{B} = (1+\alpha(\theta)\mathit{\Delta}\theta_0)V_\mathrm{M}$$

into the above equation gives

$$\alpha(\theta) \equiv \frac{1}{V}\left(\frac{\partial V}{\partial \theta}\right)_P = \frac{1}{\alpha^{-1}+\theta} .$$

Since $\alpha(\theta)\mathit{\Delta}\theta_0 < \alpha\mathit{\Delta}\theta_0 = \mathit{\Delta}\theta_0/267°\mathrm{C} << 1$, the right-hand side of the above equation becomes

$$R\Theta(\theta)\ln(1+\alpha(\theta)\mathit{\Delta}\theta_0) \cong R\Theta(\theta)\alpha(\theta)\mathit{\Delta}\theta_0 ,$$

and finally we obtain

$$C_P - C_V = R\Theta(\theta)\alpha(\theta) = \frac{R\Theta(\theta)}{\alpha^{-1}+\theta} . \tag{20.17}$$

This is the mathematical expression for **gas theorem 3**, which was first derived by Clapeyron [12].

Although Carnot derived various theorems, some of them were incorrect because he based them on erroneous experimental data; thus, I will omit them here.

Clapeyron presented full mathematical expressions corresponding to Carnot's discussion on the basis of the existence of the heat function as described below.

Let us consider a Carnot cycle with an infinitesimally small temperature difference and volume. In Fig. 20.2, imagine that state B is infinitesimally close to state A. By introducing $V_\mathrm{B} - V_\mathrm{A} = \mathit{\Delta}V$ in eq. (20.7), the net work is expressed as

$$\mathit{\Delta}W = \mathit{\Delta}V\,\mathit{\Delta}P = \left(\frac{\partial P}{\partial \theta}\right)_V \mathit{\Delta}\theta\,\mathit{\Delta}V . \tag{20.18}$$

In particular, for an ideal gas, for which $(\partial P/\partial\theta)_V = R/V$,

$$\mathit{\Delta}W = (R/V)\mathit{\Delta}\theta\,\mathit{\Delta}V . \tag{20.18$'$}$$

At this point we assume the existence of the heat function $Q = Q(\theta, V)$. Although Clapeyron expressed it as (P, V), let us write it as (θ, V) for convenience in the following discussion. In this case, the amount of heat absorbed in the isothermal process A → B is $q_+ = (\mathit{\Delta}Q)_\theta = (\partial Q/\partial V)_\theta \mathit{\Delta}V$. Therefore, substituting it into **Carnot theorem: expression II**, we obtain

$$\frac{\varDelta W}{q_+}=\frac{(\partial P/\partial\theta)_V\varDelta\theta\varDelta V}{(\partial Q/\partial V)_\theta\varDelta V}=\frac{\varDelta\theta}{\varTheta(\theta)} ,$$

which, for an ideal gas, leads to

$$\left(\frac{\partial Q}{\partial V}\right)_\theta=\varTheta(\theta)\left(\frac{\partial P}{\partial\theta}\right)_V=\varTheta(\theta)\frac{R}{V} . \tag{20.19}$$

By integrating this equation, the heat function for an ideal gas is obtained as follows:

$$Q(\theta,V)=f(\theta)+R\varTheta(\theta)\ln V ,$$

where $f(\theta)$ is an unknown function of temperature. As a result, the amount of heat absorbed in the isothermal process A → B is given by

$$q_+=Q(\theta,V_\mathrm{B})-Q(\theta,V_\mathrm{A})=R\varTheta(\theta)\ln(V_\mathrm{B}/V_\mathrm{A}) . \tag{20.20}$$

This is simply the eq. (20.15). Furthermore, if we consider the difference between the following two equations:

$$C_P=\left(\frac{\partial Q}{\partial\theta}\right)_P=\frac{df(\theta)}{d\theta}+R\frac{d\varTheta(\theta)}{d\theta}\ln V+\frac{R}{V}\varTheta(\theta)\left(\frac{\partial V}{\partial\theta}\right)_P ,$$

$$C_V=\left(\frac{\partial Q}{\partial\theta}\right)_V=\frac{df(\theta)}{d\theta}+R\frac{d\varTheta(\theta)}{d\theta}\ln V ,$$

using $\left(\frac{\partial V}{\partial\theta}\right)_P=\frac{R}{P}=\frac{V}{\alpha^{-1}+\theta}$, we again arrive at eq. (20.17). Thus, **gas theorems 1**, **2**, and **3** have been proved anew.

V. Further discussion and significance of thermodynamics

As shown above, Clapeyron proved the gas theorems firmly on the basis of the existence of the heat function. Consequently, after the conservation of heat was later rejected, these theorems were often regarded as having been obtained as a result of multiple errors cancelling each other out. On the other hand, a contrived interpretation in which the "caloric" referred to by Carnot should be regarded as entropy was historically proposed [13].

As stated earlier, however, **Premise A: paradigm of specific heat and latent heat** and **Premise C: conservation of heat** are different; most of Carnot's theory was obtained from **Premise A**, and thus **Premise C** is not necessary.

Even if the conservation of heat does not hold, provided we consider an infinitesimally small cycle,

$$\oint dq=\text{infinitesimal quantity of the second order}\cong 0 ,$$

thermodynamically correct results are often derived in practice.

Most of Carnot's mistakes are based on erroneously measured data relating to the pressure dependence of specific heat. Thus, using only **Premise A**, let us reconstruct Carnot's theory.

Consider a Carnot cycle with an infinitesimally small temperature difference and volume change. From **Premise A**, i.e., eq. (13.5),

$$q_+ = (\mathit{\Delta} q)_\theta = \mathit{\Lambda}_\mathrm{D} \mathit{\Delta} V \text{ .}$$

As described earlier, even if dq in eq. (13.5) ($dq = C_V d\theta + \mathit{\Lambda}_\mathrm{D} dV$) is not total a derivative, for a quasi-static change, the integration along a path can be expressed as $(\mathit{\Delta} q)_\mathrm{path}$. On the other hand, since $\mathit{\Delta} W$ is given by eqs. (20.18) and (20.18)′, from **Carnot's theorem: expression II**

$$\frac{\mathit{\Delta} W}{q_+} = \frac{(\partial P/\partial\theta)_V \mathit{\Delta}\theta \mathit{\Delta} V}{\mathit{\Lambda}_\mathrm{D} \mathit{\Delta} V} = \frac{\mathit{\Delta}\theta}{\Theta(\theta)} ,$$

we obtain

$$\mathit{\Lambda}_\mathrm{D} = \Theta(\theta)\left(\frac{\partial P}{\partial\theta}\right)_V . \tag{20.21}$$

In particular, for an ideal gas, the following important relation is derived:

$$\mathit{\Lambda}_\mathrm{D} = \Theta(\theta)\frac{R}{V} . \tag*{(20.21)′}$$

According to Truesdell, eqs. (20.21) and (20.21)′ deserve to be called the **general Carnot–Clapeyron theorem** [14].

From this, the amount of heat absorbed during an isothermal change is given by

$$q_+ = \int_{V_\mathrm{A}}^{V_\mathrm{B}} \mathit{\Lambda}_\mathrm{D} dV = R\Theta(\theta)\ln\left(\frac{V_\mathrm{B}}{V_\mathrm{A}}\right) , \tag{20.22}$$

which is identical to eq. (20.15).

If the heat function exists, these two equations are, of course, the same as eqs. (20.19) and (20.20), respectively. *Yet even if the conservation of heat does not hold and eqs. (20.19) and (20.20) are not available, eqs. (20.21) and (20.22) are correct because they were proved by using an infinitesimally small cycle*. (This point is explained in detail in Chapter 27-IV.)

Carnot wrote, "What is the cause of the difference between the specific heats at constant volume and at constant pressure? It is the caloric required to bring about expansion in the latter case"[C, p. 86]. That is, from eq. (13.5),

$$C_P \mathit{\Delta}\theta = (\mathit{\Delta} q)_P = C_V \mathit{\Delta}\theta + \mathit{\Lambda}_\mathrm{D}\left(\frac{\partial V}{\partial\theta}\right)_P \mathit{\Delta}\theta ,$$

$$C_P - C_V = \mathit{\Lambda}_\mathrm{D}\left(\frac{\partial V}{\partial\theta}\right)_P , \tag{20.23}$$

In particular, for ideal gases,

$$C_P - C_V = \mathit{\Lambda}_\mathrm{D} \times \frac{R}{P} = \mathit{\Lambda}_\mathrm{D} \frac{V}{\alpha^{-1} + \theta} . \tag*{(20.23)′}$$

This is obtained only from **Premise A: paradigm of specific heat and latent heat**. If Clapeyron's theorem (eq. (20.21)) is substituted into eq. (20.23), we obtain

$$C_P - C_V = \Theta(\theta)\left(\frac{\partial P}{\partial \theta}\right)_V \left(\frac{\partial V}{\partial \theta}\right)_P . \tag{20.24}$$

For ideal gases, it goes without saying that this is identical to eq. (20.17).

Additionally, if we apply the definition $\mathit{\Lambda}_{\mathrm{D}} = (\Delta q / \Delta V)_\theta$, to the evaporation of water (θ is constant during evaporation), we obtain

$$\mathit{\Lambda}_{\mathrm{D}} = \frac{m\mathit{\Lambda}_{\mathrm{E}}}{V_{\mathrm{gas}} - V_{\mathrm{liquid}}} .$$

On the other hand, in the generalized form of the Carnot–Clapeyron theorem (eq. (20.21)), the saturation vapor pressure is only a function of temperature, and we obtain

$$\mathit{\Lambda}_{\mathrm{D}} = \Theta(\theta)\frac{dP}{d\theta} .$$

From these two equations, we also arrive at Clapeyron's formula (eq. (20.12)); this was pointed out by Clapeyron in 1864 [15].

Further, if we denote $\beta(0) = \beta$ in eq. (20.11), we obtain

$$C_P = (\alpha + \beta)\alpha(PV)_0\Theta(0) = (\alpha + \beta)R\,\Theta(0) .$$

On the other hand, from eq. (20.17),

$$C_P - C_V = \alpha R\,\Theta(0) .$$

In addition to these two equations, if we take data measured by Gay-Lussac and the calculated values of Poisson, the ratio of the heat capacities becomes

$$\gamma \equiv \frac{C_P}{C_V} = \frac{\alpha + \beta}{\beta} = \frac{267 + 116}{267} = \frac{1}{0.70} , \tag{20.25}$$

which was shown by Carnot in the *Réflexions*. (This result is readily obtained if we set $\theta = 0$ and $k = \gamma - 1$ in eq. (15.4),

$$\beta \equiv -\frac{1}{V}\left(\frac{dV}{d\theta}\right)_Q = \frac{1}{\rho}\left(\frac{d\rho}{d\theta}\right)_Q = \frac{1}{k} \times \frac{\alpha}{1 + \alpha\theta} . \tag{15.4$_{\mathrm{r}}$)}$$

The above comprises all the results and extensions of Carnot's theory for the present moment.

Note that *Carnot's theory is crucially different from the previous caloric theory*. The significance of Carnot's theory—thermodynamics—is as follows.

For example, if we compare the equation of state for a gas eq. (20.2.2)′, i.e., the Boyle–Gay-Lussac law, with the Carnot–Clapeyron theorem (eq. (20.21)) and Clapeyron's formula (eq. (20.12)), we find an essential difference: even if the equation of state $PV = R(\alpha^{-1} + \theta)$ seems to be valid for various gases, it is only approximately valid, and, strictly speaking, the functions and constants vary depending on the gas. That is, the statement is true only within the measurement accuracy.

On the other hand, Carnot's statement expressed by eqs. (20.12), (20.21), and (20.24) means that although the latent heat $\mathit{\Lambda}$ and specific heat C may depend on the gas, *the relationship based on the universal function* $\Theta(\theta)$

is absolutely correct for all gases; this is the statement of Carnot, namely of thermodynamics. Because of this feature, thermodynamics is called 'the physics based on the principles.' Truesdell wrote, "Carnot was the first to see that a theory connecting heat and work imposes restrictions upon the constitutive function of bodies (Λ, C, P, etc.). The discovery of such restrictions has been the *essence of thermodynamics* from his day to ours"[16]. That is, only eqs. (20.12), (20.21), and (20.24) are called thermodynamic equations.

As shown above, Carnot can be credited with the birth of thermodynamics. His theorem (eqs. (20.4) and (20.6)) gave the expressions clarifying the quantitative relationship between heat and work performed by heat.

Twenty years later, Mayer and Joule found another quantitative relationship between heat and work (the first law of thermodynamics). Then, by unifying these two relationships which at first glance seemed to be incompatible, the basis of thermodynamics was established.

In the next chapter, prior to describing the work of Mayer and Joule, we will survey the present state of the kinetic theory of heat.

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[10] Truesdell, C., *ibid*., p. 136, (1980); Cf.
Truesdell, C., *ibid*., p. 80, (1980).

[11] Note that "gas theorems 1, 2, and 3" are renamed by Yamamoto. Carnot explained them in the order of 1, 3, and 2.

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