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GENERAL PROBLEMS OF TRANSPORT THEORY

DEVELOPMENT OF THE SCIENCE OF THERMODYNAMICS

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History of discovery of three basic laws of thermodynamics and their formulations are presented.

Keywords: *caloric, heat, work, heat engine, absolute temperature, energy, laws of thermodynamics, availability-exergy, entropy.*

The story of thermodynamics began in 1824 in Paris when a young military engineer **Sadi Carnot** (1796–1832), who graduated from the L′Ecole Polytechnique, published his book "Reflections on the Motive Power of Fire." By motive power was meant the work or the rate of its doing and by fire was meant heat. His aim was to discover the general operating principles of steam engines and other heat engines that provide work output. This book was ignored for more than 20 years. Steam engines invented by Arthur Wolf were used as driving machinery in ships, and Carnot was interested in those heat engines. His aim consisted of mechanically and thermally ideal engine operation. His ideal heat engine used a gaseous working substance. We can see the Carnot cycle (Fig. 1) in the present-day books on thermodynamics.

Carnot insisted that the forces driving an ideal heat engine are so small that they can be reversed with no additional external effect, and the engine can operate in the opposite direction. This heat engine provides work output and can be reversed, and the ideal machine requires work input and heat transfer from a lower temperature to a higher one. It is the so-called heat pump which is analogous to the pump that pumps water from a low level to a high one. Carnot concluded that ideal heat engines working between two reservoirs at temperatures T_1 (not absolute) and T_2 with heat input Q gives the same work output W and the working fluid can be air, steam, or even a liquid, i.e., W is independent of the working fluid. The Carnot principle became an indispensable source of inspiration for all of his successors.

The first man who addressed to the Carnot work was **Emile Clapeyron** (1799–1864), his former classmate. He published a paper in the Journal de L′Ecole Polytecnique in 1834 where he clarified how to calculate the efficiency function $F(t)$ that was only mentioned by Carnot. The Clapeyron paper was translated into German and English, and for approximately ten years it was the only link between Carnot and his followers. During the 1840s and early 1850s, two second-generation thermodynamicists, a German student at the University of Halle **Rudolf Clausius** (1822–1888) and a recent graduate of Cambridge University **William Thomson** (later Lord Kelvin, 1824–1907), became interested in the Carnot work.

In different ways Clausius, Rankine, and Thomson extended the Carnot work to the science on heat that Thomson eventually called thermodynamics. He defined an absolute temperature scale and later introduced the concept of energy. With the Clausius contributions to the Carnot heat engine, it was clear that heat is not only transferred in the heat engine from a high temperature to a low one, but is also partially converted into work. This conclusion was a departure from the Carnot water engine analogy.

James Prescott Joule (1818–1889) had no formal education and hardly any training in science at all. He believed that quantitative equivalences could be found among mechanical, thermal, chemical, and electrical effects. He studied such connections in a number of ways. He investigated, for example, the conversion of electrical effects into thermal, chemical, and mechanical ones and of mechanical effects into thermal and electrical ones. In 1840, he demonstrated accurately that heating a wire by an electric current is proportional to the square of the current I and to the electrical resistance R (so-called I^2R heating law). Then he began the measurements of the mechanical equivalent of heat, which is presently well known. The first such experiments were performed in 1843. In the Joule famous experiments, the wheel of an induction device was

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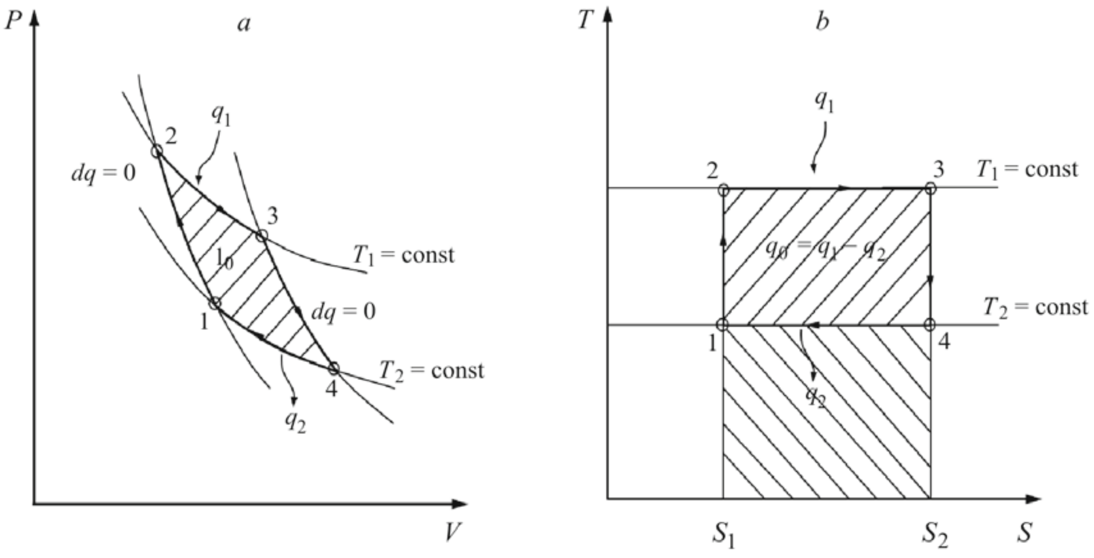

Fig. 1. Carno cycles as *P–V* (a) and *T–S* (b) diagrams.

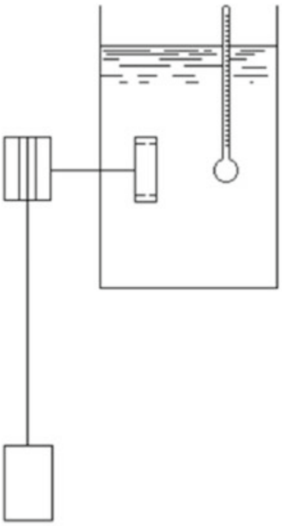

Fig. 2. Schematic of Joule′s paddle–wheel experiments.

driven by falling weights. The mechanical work was calculated in ft·lb, and heat was measured in British thermal units, or BTU. Here we should like to recall the fact that Daniel Gabriel Fahrenheit, a German physicist, engineer, and glass blower, had already invented the mercury-in-glass thermometer in 1714 and proposed a temperature scale which was named after him. The BTU is the measure corresponding to heat which is necessary to raise the temperature of one pound of water by one degree Fahrenheit (^{o}F). Joule performed several cyclic processes several times. His experiments showed that the work done in raising the weight is proportional to the heat delivered by the system to a calorimeter. As a result of this series of cyclic experiments (paddle–wheel) shown in Fig. 2, Joule determined the mechanical heat equivalent to be 896 ft·lb/BTU. Joule did thirteen experiments of this kind and reported an average value of 838 ft·lb/BTU which later was named Joule (J) by Thomson. These important experiments were expressed later as **the first law of thermodynamics** for a cyclic process in a closed system:

$$\mathrm{J}\oint \delta Q = \oint \delta W \,.$$

If any closed system is carried through a cyclic process, the net work delivered to the surroundings is proportional to the net heat taken from the surroundings. With the paddle–wheel device and water as the calorimeter liquid, Joule obtained J = 773.762, 776.303, and 776.997 ft·lb/BTU. He presented the results of his experiments in 1847 at an Oxford meeting of the British Association for the Advancement of Sciences. The communication was done in the presence of Thomson, Faraday, and George Stokes.

William Thomson, at that time Professor of natural philosophy at Glasgow University, had some reservations concerning the Joule work, but he also recognized that it could not be ignored. During three years after the Oxford meeting, Joule scored a prominent position in the British scientific establishment: he was elected a corresponding member of the Royal Academy of Sciences at Tulin and a fellow of the Royal Society. After these eventful years, Joule began very close and successful collaboration with Thomson.

William Thomson studied at Cambridge and published many papers on pure and applied mathematics during his undergraduate studies. He was elected to fellowship in the Royal Society. Thomson began to focus on the work of Carnot and on the Clapeyron paper on the Carnot method. In Carnot′s time, heat was considered as an indestructible uncreatable fluid material called "caloric." By 1840, this theory had a small but growing number of opponents, and Joule and Thomson were among them.

Thomson had already read the masterpiece "The Analytical Theory of Heat" by Fourier about heat conduction from a high temperature to a low one without producing any mechanical work. Instead of the term "caloric," Thomson suggested "dynamics of heat."

In 1851, Thomson published a paper "On the Dynamical Theory of Heat" based on the principles of both Joule and Carnot. For the first time he introduced the idea on energy as an important property of any system of interest and stated that nothing can be lost during operation in nature, i.e., no energy can be lost. Thomson assumed that the system energy can change only by means of the interactions between the system and its surroundings if the system is closed, i.e., no material flows in or out. The interactions with the surroundings are of two kinds: due to heat and to work inputs through the boundaries of the system.

The Thomson dynamic theory of heat was very important for understanding the Joule–Carnot and Joule–Fourier theories. Thomson could now carry out an analysis of a heat engine performing the Carnot ideal reversible operation. The efficiency and work output of the Carnot heat engine have maximum values. Thomson concluded that energy can never be destroyed in a system; it can be wasted or dissipated when it might have been used as the work output in a reversible engine.

Thomson published a paper on the energy dissipation principle, where the Carnot, Joule, and Fourier theories were brought into harmony. His next important result (in 1854) was the presentation of the temperature-dependent function $F(t)$ through the absolute temperature as $F(T)$. Thomson was rewarded for his efforts on the introduction of the absolute temperature scale, namely, the modern unit of the absolute temperature was named after him as Kelvin (K).

Forty years passed from 1824, when Carnot published his memoir on the theory of heat engines, to their first invention and putting into practical use, and only afterwards did the second-generation thermodynamicists, Thomson, Rankine, and Clausius, apply his idea.

W. J. Macquorn Rankine (1820–1872) was Professor of Civil Engineering at the University of Glasgow and a colleague of Thomson. The work of the three scientists (Rankine, Clausius, and Thomson) is of great importance for thermodynamics. In my opinion, the most important of them was Rankine, since all classical books related to thermodynamics are based on the Rankine steam engine manual, diagrams, and terminology.

The leading concepts in thermodynamics are the energy, entropy, and absolute temperature. Two of them, energy and absolute temperature, were already explained, and the remaining property, entropy, was later introduced by Clausius.

According to Carnot and Clapeyron, heat was indestructible and therefore could not be converted into work in a heat engine or in any other device. After Thomson, Rudolf Clausius started to work with the Carnot–Clapeyron caloric theory. He began from the fundamental (simple, but drastic) assumption in the paper of 1850 that part of the heat input to any heat engine is converted into work as output and the rest of the heat input is simply transmitted from a higher temperature to a lower one.

In 1850, the energy concept was still not clear. In 1864, Clausius collected his papers in a book where he introduced the state function $U(V, t)$, which is of a great importance in the theory of heat. Thomson called it "mechanical energy" and later "intrinsic energy." Then Helmholtz named it "internal energy."

Clausius considered transformation/transmission of heat and realized that there will be two possible directions, "natural" and "unnatural." **The second law of thermodynamics**, as expressed by Planck, is known in modern thermodynamics as **the Planck–Kelvin statement**. According to this law, "it is impossible to construct a heat engine operating in a cyclic manner to exchange heat with only one reservoir." In other words, this law implies that it is impossible to build a 100% efficient heat engine.

It is mentioned in the paper of Clausius written in 1854 that heat can never pass itself from a colder body to a warmer one without some other changes. According to **the Clausius statement of the second law of thermodynamics**, "it is impossible to construct a device which operates on a cycle and produces no other effect than the transfer of heat from a cooler body to a hotter body." This statement has been the basis for the work of all refrigerators, heat pumps, and air conditioners.

After a long analysis, Clausius obtained the important relation for reversible and irreversible cyclic operations of a system which now is called the inequality of Clausius:

$$\oint \frac{\delta Q}{T} \le 0 \; .$$

Clausius showed further that the quantity $\dfrac{\int \delta Q}{T}$ computed for any reversible process between the reference state 0 and another state 1 is independent of the process and, consequently, is a property of the system in state 1; this property is called the entropy, and Clausius used the symbol S for a system as a whole and s per its unit mass. For reversible process

$$dS = \frac{\delta Q}{T} \; .$$

The entropy of a closed adiabatic system increases or remains constant in the limit. This is also true for an isolated system, which is a special case of a closed adiabatic system. *The principle of the entropy increase* is

$$dS \ge \frac{\delta Q}{T} \; , \quad dS_{\mathrm{is}} \ge 0 \; .$$

Josiah Willard Gibbs (1839–1903) published the works on thermodynamics based on the Clausius equations for heat and entropy:

$$\delta Q = dU + PdV \; , \quad dS = \frac{\delta Q}{T} \; .$$

From these equations, eliminating Q, he obtained

$$dU = TdS - PdV \; .$$

It follows from this equation that for a constant value of S

$$dU = -PdV \; .$$

Gibbs started from the Clausius laws according to which "the energy of the universe is constant, the entropy of the universe tends to maximum." The Gibbs papers in 1875–1878 bore the title "Principles of thermodynamics"; his book "Equilibrium of Heterogeneous Substances" covered the fundamental thermodynamic theory of gases, mixtures, surfaces, solids, phase changes, chemical reactions, fuel cells, and others. The Gibbs energy is

$$G = U + PV - TS \; .$$

From the Clausius relation for the entropy change in irreversible processes, at constant pressure P and temperature T

$$dG \le 0 \; , \quad \text{or} \quad d(U + PV - TS) \le 0 \; .$$

The third law of thermodynamics was first formulated by German chemist and physicist **Walther Nernst** (1864–1941). In his book "A Survey of Thermodynamics" (American Institute of Physics, 1994), Martin Bailyn quotes the Nernst statement of the third law as "It is impossible for any procedure to lead to the isotherm $T = 0$ in a finite number of steps." This essentially establishes a temperature of absolute zero as being unattainable by analogy with the speed of light. Theory states and experiments show that no matter how fast something is moving, it can always be made to go faster, but can never reach the speed of light. Similarly, no matter how cold a system is, it can always be made colder, but can never reach absolute zero.

Anne Rooney wrote in her book "The Story of Physics" (Arcturus, 2012): "The third law of thermodynamics requires the concept of a minimum temperature below which no temperature can ever fall — known as absolute zero." As she continued, "Robert Boyle first discussed the concept of a minimum possible temperature in 1665, in "New Experiments and Observations Touching Cold" where he referred to the idea as *primum frigidum*."

Absolute zero is believed to have been first calculated with reasonable precision in 1779 by Johann Heinrich Lambert. He based his calculation on a linear relationship between the pressure and temperature of a gas. When a gas is heated in a confined space, its pressure increases. This is because the gas temperature is a measure of the average speed of gas molecules. The hotter the gas, the faster the molecules move and the greater the pressure that they exert in their collisions with the walls of the container. It was reasonable for Lambert to assume that if the gas temperature could be brought to absolute zero, the motion of the gas molecules could be brought to a complete stop, so they could no longer exert any pressure on the walls.

The third law of thermodynamics is concerned with the limiting behavior of systems as their temperature approaches absolute zero. Most thermodynamics calculations use only entropy differences, so zero point of the entropy scale is often not important. However, we discuss the third law for purposes of completeness, since it describes the condition of zero entropy. The third law states: "The entropy of a perfect crystal is zero when the temperature of the crystal is equal to absolute zero (0 K)."

Siabal Mitra, a professor of physics at Missouri State University, provides another implication of this law: "One version of the third law states that it would require an infinite number of steps to reach absolute zero, which means you will never get there. If you could get absolute zero, it would violate the second law, because if you had a heat sink at absolute zero, then you could build a machine that was 100 percent efficient."

In theory, it would be possible to grow a perfect crystal in which all of the lattice sites are occupied by identical atoms. However, it is generally believed that it is impossible to achieve a temperature of absolute zero (although scientists have come quite close to this temperature). Therefore, all matter contains at least some entropy owing to the presence of some heat energy. Lambert calculated absolute zero to be -270^{o}C (or -454^{o}F), which was close to the modern accepted value -273.15^{o}C (-459.67^{o}F).

Because a temperature of absolute zero is physically unattainable, the third law may be restated to apply to the real world as "The entropy of a perfect crystal approaches zero as its temperature approaches absolute zero." We can extrapolate from experimental data that the entropy of a perfect crystal reaches zero at absolute zero, but we can never demonstrate this empirically.

We must also mention the contributions of Robert Mayer and Jean Baptiste Joseph Fourier in the development of thermodynamics as science. However, it was **Joseph H. Keenan** (1900–1977) who played the major role in the thermodynamics teaching for engineering. He created the MIT school of thermodynamics and published the book "Thermodynamics" (1941) that covers the fundamentals of thermodynamics with applications in mechanical and chemical engineering. He is a coauthor of "Thermodynamic Properties of Steam" (1936), a basic source of data for design in power and process machinery, which was of great importance in the steam-power industry. "Thermodynamic Properties of Air" (1945) and "Gas Tables" (1948), prepared by Keenan and Kaye, have been used extensively in design and engineering related to gas turbine, jet-propulsion machinery, and internal combustion engines. Through his writing and teaching, Keenan brought to the engineering profession the Gibbs fundamental work which for the most part had been overlooked by engineers and scientists for five decades. In 1930s, for a steady flow he adopted the Gibbs concept of thermodynamic availability that is also called exergy.

The second-law concept and the availability analysis of a power plant are of importance; the availability of a fluid increases or decreases as it passes through feed pumps, boilers, superheaters, reheaters, turbines, condensers, feed-water heaters, valves, and piping. A refrigeration cycle can be analyzed from the standpoint of the second law, and the increase in the availability in each piece of apparatus can be calculated for the use of the more effective energy resource.

Then well-known scientist **Adrian Bejan** (1948) from the Keenan MIT school clarified the use of the second-law analysis in the thermal design of energy systems and optimization. His PhD advisor Prof. J. L. Smith was Keenan's PhD student in the 1950s; Bejan earned all his degrees at MIT (PhD in 1975). He made the availability (exergy) analysis so popular under the title the second-law analysis. He showed that such an analysis can be used in all kinds of analyses of power plants, refrigerators, heat pumps, heat exchange equipment, and all types of components of energy systems. His techniques

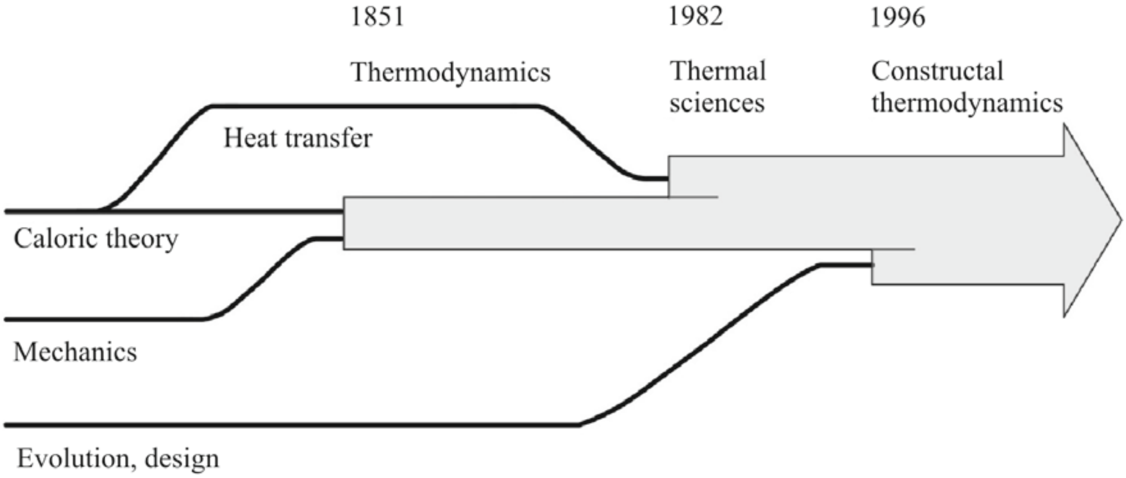

Fig. 3. Evolution of structural thermodynamics.

of analysis of exergy destruction and cost became important in thermal design and optimization. Following Keenan, Bejan made a very valuable contribution to teaching of today′s thermodynamics.

Bejan discovered *the constructal law* as a new law of physics: "For a finite-size flow system to persist in time (to live), it must evolve in such a way that it provides easier access to the imposed (global) currents that flow through it." According to this law, the changes in a configuration must occur in a particular direction in time. It states that design in nature is not static, but dynamic and evolving. In the two decades since 1996, we have seen an accelerated activity in using the constructal law in physics, biology engineering, and society. In engineering, the constructal design has triggered a technological revolution toward vascular design in many ranges, such as electronics, high-density heat exchangers, chemical engineering equipment, fuel cells, and hydraulics engineering.

The evolution and spreading of thermodynamics during the past two centuries are illustrated in Fig. 3.

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