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EVOLUTION OF THE SCIENCE OF THERMODYNAMICS: THE HISTORY

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Abstract: Until late in the 18th century, thermodynamics was seen as science of energy-Science of heat and work.During the eighteen century- or until late in the 18th century, heat was seen as a weightless fluid called "caloric".Heat will flow from high temperature to a low temperature producing useful work output conserving heat. 18th century engineers knew that machinery can be designed, and this heat flow can be used to produce useful work-HEAT ENGINE. In this study, it will be shown how science of thermodynamics evolved within almost a century, as the science of energy, absolute temperature and entropy. It is also shown that how the availability (Exergy) is introduced as the second law analysis at the school of thermodynamics at MIT and now it can be used in Constructal thermodynamics as workable, efficient solutions in analyzing energy systems and all components of all energy systems while protecting the environment.
Keywords: Caloric, heat, work, Heat engine, Absolute temperature, Energy, Availability-Exergy, Entropy.

BİLİMSEL TERMODİNAMİĞİN EVRİMİ: TARİH

Özet: 18. Yüzyılın sonuna kadar termodinamik, enerji – Isı ve iş bilimi olarak anıldı. 18. Yüzyıl boyunca – ya da 18. Yüzyılın sonuna kadar ısı, "kalorik" adı verilen ağırlıksız bir akışkan olarak görüldü. Isı, yüksek sıcaklıktan alçak sıcaklığa doğru akar, enerjisini korurken yararlı iş üretir. 18. yüzyılın mühendisleri, bir makine tasarlanabileceğini ve bu makinede ısı akışından yararlı iş üretilebileceğini biliyorlardı – ISI MAKİNESİ. Bu çalışmada, neredeyse bir yüzyıl içerisinde termodinamik biliminin bir enerji bilimi, mutlak sıcaklık ve entropi olarak nasıl evrimleştiği gösterilecektir. Ayrıca, kullanılabilirliğin (ekserji) Massachusetts Teknoloji Enstitüsü'nün (MIT) termodinamik ekolünde ikinci yasa analizleri şimdi içyapısal termodinamiği olarak nasıl ortaya konulduğu ve mühendislik termodinamiğinde enerji sistemlerinin ve enerji sistemlerinin tüm bileşenlerinin analizinde çevreyi korurken, elverişli ve verimli çözümler olarak nasıl kullanılabileceği gösterilmiştir.
Anahtar Kelimeler: Kalorik, Isı, İş, Isı Makinesi, Mutlak sıcaklık, Enerji, Kullanılabilirlik-Ekserji, Entropi.

SADI CARNOT

1796-1832, Paris-Luxembourg Palace, his father, Lazare was very influential member in the Napoleon government. He graduated from the L'Ecole Polytechnique.

The story of thermodynamics begins in 1824 in Paris, when a technical memoire was published by a young military engineer, named Sadi Carnot, and the title of the book "Reflections on the Motive Power of Fire". Actually by motive of power, he meant "work" or rate of doing work, by "fire" he meant heat.His aim was to discover the general operating principles of steam engines and other heat engines that supply work output. His work was largely ignored more than 20 years!

<u>Carnot's work was discovered 20 years later.</u>

His father Lazare Carnot was very powerful man within the government, and made important discoveries in hydraulic machinery driven by falling water, the greater the fall, the greater work output per unit of water flow input; Sadi Carnot's thinking was guided by his father's thinking: High temperature-Low temperature bodies between which heat flow rate;while driving the working part of the machine.

Steam engine invented by Arthur Wolf were used as driving machinery, ships, and Sadi Carnot was interested in this heat engine how one can get best possible performance; he aimed for the mechanical ideal, and also for ideal thermal operation.His ideal heat engine used a gaseous working substance: In today's book of thermodynamics, we see Carnot cycles on T-s and P-v diagrams, Figure 1.

Carnot insists that the forces driving an ideal heat engine be so small they can be reversed with no additional external effect and the engine can operate in the opposite direction, that is as heat engine which provides work output and can be reversed and the ideal machine requires work input and transfer heat from lower temperature to higher temperature, that is heat pump which is analogous to a pump, pumping water from low to a high level. He concluded that ideal heat engines working between two reservoirs at temperatures T1 (not absolute) and T2 with heat input Q have the same work output W, and the working fluid can be air, steam, or even a liquid independent of the working fluid.

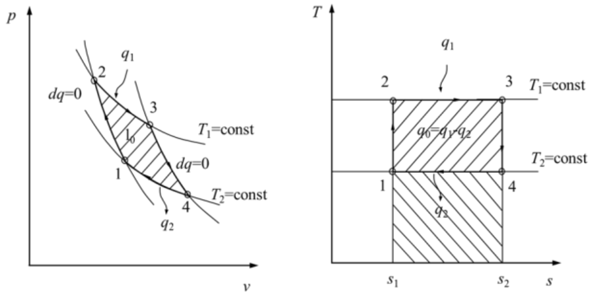

Figure 1. Carnot Cycles on P-v and T-s diagrams

The Carnot principle became an indispensable source of inspiration for all of the Carnot's successors.

AFTER CARNOT

Carnot's work was presented as a privately published memoir in 1824, one year after his father Lazare Carnot's death. The memoir was published by a leading scientific publisher, favorably reviewed and mentioned in an important journal, and then forgotten for more than twenty years!

<u>Carnot passed away in 1832 at the age of thirty six.</u>

The man who rescued Carnot's work was Emile Clapeyron, a former classmate of Carnot at the EcolePolytechnique. Clapeyron published a paper in the Journal de L'EcolePolytecnique in 1834 putting Carnot's message in the acceptable language of mathematical analysis. Carnot, was mentioning efficiency function F(t), but Clapeyron clarified how to calculate F(t).

Clapeyron's paper was translated into German and English, and for ten years or so, it was the only link between Carnot and his followers; during the 1840s and early 1850 for two second-generation thermodynamicists, a young German student at the university of Halle, Rudolf Clausius, and a recent graduate of Cambridge University, England, William Thomson (later Lord Kelvin) became interested in Carnot's work.

In different ways, Clausius, Rankine and Thomson were to extend Carnot's work into the science of heat that Thomson eventually called thermodynamics, and he defined an absolute temperature scale, and later introduced the concept of energy. With Clausius's contributions, in the Carnot's heat engine, it was cleared that heat is not only dropped in the heat engine from a high temperature, to a low temperature, but is also partially converted to work. This was a departure from Carnot's water engine analogy.

Then JOULE!

JAMES PRESCOTT JOULE (1818-1889)

Joule lived near Manchester, England, where his family operated a brewery, and he was helping to his father. Joule had no formal education, and hardly any formal training at all in science.

He did of his most important work in the early morning and evening, before and after a day at the brewery. He believed that quantitative equivalences could be found among mechanical, thermal, chemical, electrical effects. He studied such quantities connections several different ways. He investigated for example electrical effects converted to thermal, chemical, and mechanical effects and of mechanical effects converted to thermal and electrical effects.

In 1840, he demonstrated accurately that the heating produced by an electrical current in a wire is proportional to the square of current I and to the electrical resistance R, "I2R-heating law".Then, he began the measurement of the Mechanical equivalent of heat for which he is best known today. First experiments in this series were performed in 1843, when Joule was twenty-four. In Joule's famous experiments, the wheel of the induction device were driven by falling weights, mass (m), for which mechanical work is calculated in terms of "ft-lb". Heat was measured in units that fit the temperature measurements, the "British thermal unit" or Btu. At this point, let us remember that Daniel Gabriel Fahrenheit, a German physicist, engineer and glass blower has already invented the mercury-in-glass thermometer in 1714, and developed a temperature scale now named after him.

Btu, is the measure of one pound of water is raised one degree Fahrenheit (°F). He performed several cyclic processes several times. His experiments showed that work done in raising the weight is proportional to the heat delivered by the system to the calorimeter.

As results of these series of cyclic experiments(paddle-wheel) as shown in Figure 2, Joule determined the mechanical work equivalent to 1 Btu, as 896 ft-lb per Btu!

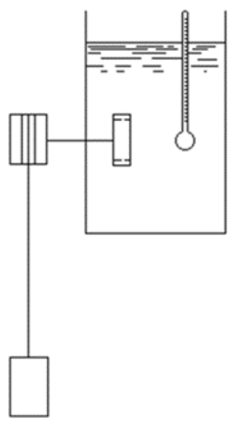

Figure 2. Joule's Paddle-Wheel experiments

Joule did thirteen experiments of this kind, then he reported an average value of 838 ft-lb per Btu which Thomson later labeled "J" to honor Joule. These important experiments were expressed later as the first law of thermodynamics for a cyclic process executed by a closed system.

$$J \oint dQ - \oint dW = 0 \quad (1)$$

If any closed system is carried through a cyclic process, then the summation of the net work delivered to the surroundings is proportional to summation of the net heat taken from the surroundings.With the paddle-wheel device and water as the calorimeter liquid, Joule obtained Joule J=773.762, J= 776.303, and 776.997 ft-lb per Btu.

Joule presented his findings from the paddle-wheel experiments in 1847 at an Oxford meeting of the British Association for the Advancement of Sciences. The communication passed without any discussions, but William Thomson was there; Faraday, George Stokes were also present.

William Thomson, at that time,was appointed as Professor of natural philosophy at Glasgow University. Thomson had some reservations about Joule's work, but he also recognized that it could not be ignored. "Joule is, I am sure, wrong in many of his ideas" but he seems to have discovered some facts of extreme importance," Thomson recalled in 1882. Joule's paper at the Oxford meeting made a great sensation!

During the three years following the Oxford meeting, Joule rose from an unknown experimentalist to a prominent position in the British scientific establishment. Recognition came first from Europe, by publishing his paddle-wheel experiments in 1847, and in 1848 Joule was elected a corresponding member of the Royal Academy of Sciences at Tulin. Only two other British scientists, Faraday and William Hersche had been honored there.In 1850, when he was thirty-one, Joule was elected as a fellow of the Royal Society.

After these eventful years, Joule made very valuable collaboration with Thomson, a theorist and experimentalists were happily united.

<u>Joule wanted to find answers, the natural laws-Nature and her laws!</u>

WILLIAM THOMSON (1824-1907)

William Thomson was a gifted problem solver as physicist, mathematician, engineer, inventor and political activist. He studied at Cambridge and published many papers on pure and applied mathematics during his undergraduate studies. Then he became Professor of natural sciences at the University of Glasgow when he was twenty-one, and elected to fellowship in the Royal Society at the age of twenty-seven.

Thomson has just graduated from Cambridge, went to Paris for about six months to meet with French mathematicians and experimentalists, and his mind was very busy with the Carnot-Joule problem! In Paris, he was searching seriously for a copy of Carnot's original memoir and he began to think about the work of Carnot, Clapeyron's paper on Carnot's method.

Previously, I have already mentioned Carnot heat engine that works like as the same way as a water wheel.

In Carnot's time heat was an indestructible uncreatable, fluid material called "caloric". By the 1840, this theory had a small but growing number of opponents; Joule and Thomson were among those opponents.

Thomson had already read the masterpiece of Fourier's Heat Theory, conduction of heat from hightemperature to a low temperature without producing any mechanical work. Instead of calling it "caloric", Thomson called "dynamic of heat", the mechanical effect of heat engine was produced directly from molecular motion.

Everything happened as a result of Joule's presentation in 1847, Oxford meeting where Joule reported his results in his famous paddle-wheel experiments. Joule convincingly approved the mechanical equivalent of heat in his various experiments. He proved that heat to work, work to heat are convertible. He claims that in a heat engine, heat was converted to work, as shown in Figure 3.

<u>In Joule's interpretation, nothing was lost in heat engine operation.</u>

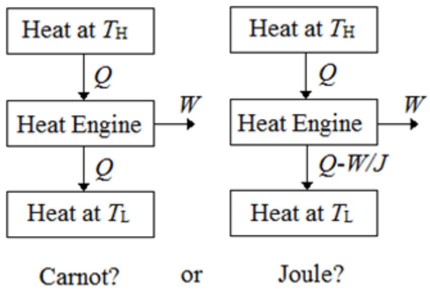

Figure 3. Carnot's and Joule's Heat Engines

In 1850-1851, Thomson realized that in a dynamical theory of heat or Joule's principle of heat and work inter-convertibility could be saved without discarding what was essential in Carnot's theory. In 1851, Thomson published a paper titled «On the Dynamical Theory of Heat», based on the principles of both Joule and Carnot. Thomson introduced for the first time the idea that energy is an important property of any system of interest. Nothing can be lost in the operation of nature, no energy can be lost.

Thomson assumed that system's energy can change only by means of interactions between system and its surroundings. If the system is closed, meaning that no material flows in or out. Interaction with the surroundings are of just two kinds, heat and work inputs to the system through boundaries of the system; if dQ and dW are small heat and work inputs to a system, then the corresponding small change in the system's energy is:

$$de = JdQ + dW \quad (2)$$

J is used to convert the heat units required for dQ to mechanical units, so it can be added to dW which is also expressed in mechanical units.

<u>Later, Helmholtz used the term (de) as the change of internal energy of the system.</u>

Thomson's Dynamic theory of Heat was his very important in understanding Joule-Carnot theories, also between theories Joule- Fourier. Thomson could now accept the analysis of a heat engine performing Carnot's ideal reversible heat engine operation. Carnot's heat engine's efficiency and work output had maximum values, nothing more could be obtained. He concluded that energy can never be destroyed in a system, it can be wasted or "dissipated when it might have been used as a work output in a reversible engine.

Thomson published a paper on the energy dissipation principle; he was happy that he brought Carnot, Joule and Fourier theories in harmony. But next important thing was to relate Carnot's temperature-dependent function F(t) to absolute temperature, F(T) in1854.

Thomson was rewarded for his efforts on the absolute temperature scale, and the modern unit of absolute temperature is named «Kelvin» K.

Two fundamental concepts, energy and absolute temperature of thermodynamics, but the remaining significance of the entropy property was introduced by Clausius.

W.J. MACQUORN RANKINE (1820-1872)

Rankine was an exceptional thermodynamicist, Prof. of Civil Engineering at the University of Glasgow and colleague of Thomson's.

These three men (Rankine, Clausius, Thomson) made the thermodynamics that empowers all of us.

In my view, Rankine is the most important of the three, because all our classical version of thermodynamics books are descendants from Rankine's steam engine manual, diagrams and terminology.

RUDOLF CLAUSIUS (1822-1888)

At least ten scientists played major roles in creating the science of thermodynamics. The leading concepts in thermodynamics are just Energy, entropy and absolute temperature.

Beginning in 1824, when Sadi Carnot published his memoir on the theory of heat engines, then, it took forty-years first to invent and put them in use. After Sadi Carnot, two second-generation thermodymicists, Thomson, Rankine and Clausius came, and took over Carnot's powerful, but neglected message.

According to Carnot and Clapeyron, heat was indestructible and therefore could not be converted to work in a heat engine or any other device. After Thomson, now Clausius started working on the Carnot-Clapeyron's caloric theory. Clausius started making the fundamental assumption in 1850 paper that part of the heat input to any heat engine is converted to work as output, the rest of heat input is simply transmitted from a higher to a lower temperature which was the one simple but drastic change made by Clausius.

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

Clausius began his transformation / transmission of heat, and realized that there will be two possible directions, one natural" and "unnatural". By then, working principles of Heat Engine that as an engine continuously operating across whose boundaries flow only heat and work became clear. The second law of thermodynamics, as expressed by Planck, is known as the Planck-Kelvin statement in modern thermodynamics books today. It is impossible to construct an engine that executes a complete cycle and produces no effect except raises a weight while it exchanges heat with a single reservoir.

In the1854 paper, Clausius wrote that heat can never pass by itself from a colder to warmer body without some other change connected at the same time which lead him to the statement of the second law of thermodynamics, which is called Clausius' statement of the 2nd Law in today's thermodynamics books: It is impossible to construct an engine that operates in a cycle and produces no effect other than the transmission of heat from a lower temperature body to a higher temperature body.

Which led to the heat pump and refrigeration machines.
After a long analysis, he could obtain the important relations for reversible and irreversible cyclic operation of a system which now is called "The Inequality of Clausius".

$$\oint \frac{dQ}{T} \leq 0 \quad (3)$$

Clausius has shown further that the $\int dQ/T$ computed for any reversible process between the reference state 0 and another state 1 is independent of the process and is, consequently, 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 or s per unit mass of the system. For an irreversible process:

$$ds = \left(\frac{dQ}{T}\right)_{rev} \tag{4}$$

and

$$s_2 - s_1 = \int_1^2 \frac{dQ}{T} \tag{5}$$

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

$$dS \geq \frac{dQ}{T} \tag{6}$$

$$dS_{isolated} \geq 0$$

JOSIAH WILLARD GIBBS (1839-1903)

Gibbs's first published work was on thermodynamics, he was strongly influenced by Clausius. Gibbs' first two papers were based on Clausius's two equations for heat,

$$dQ = dU + PdV \tag{7}$$

And entropy,

$$dS = \frac{dQ}{T} \tag{8}$$

Then from these two equations, eliminating Q, and solving for dU,

$$dU = Tds - PdV \tag{9}$$

Eq.(9) shows that internal energy is a function of S and V, U(S,V), for constant S,

$$dU = -PdV \tag{10}$$

Gibbs publishing formally in 1873-1878 on what Clausius has done. He started with Clausius's laws" the energy of universe is constant, the entropy of the universe tends to maximum. Gibbs's papers in 1875-78, were the "Principles of thermodynamics".

Gibbs's book titled Equilibrium of Heterogeneous Substances covers the fundamental thermodynamic theory of gases, mixtures, surfaces, solids, phase change, chemical reactions, fuel cells and others, with unlimited scope. In this respect, Gibbs-Dalton laws for equilibrium between the components of a mixture: The presence of a mixture of gases is the sum of pressures of the components when each occupies alone the volume of the mixture at the temperature of the mixture. The internal energy and the entropy of a mixture are respectively equal to the sums of the internal energies and entropies of the components when each occupies alone the volume of the mixture at the temperature of the mixtures. Gibbs'energy results:

$$G = U + PV - TS \tag{11}$$

From the Clausius's relations for the change of entropy for reversible and irreversible processes, and if the pressure P and temperature T are constants, then,

$$dU + d(PV) - d(TS) \leq 0$$

$$d(U + PV - TS) \leq 0$$

$$dG \leq 0$$

The equality limit of this statement applies to a reversible process or equilibrium, and

$$dG = 0$$

$$dG < 0$$

For irreversible processes at constant P and T.These relations are important especially in chemical processes and engineering applications.

Gibbs energy change G calculates the best possible electrical work obtained from an electrochemical cell (Fuel Cell) based on the reaction running reversible, as in the case of the falling heat in a heat engine.

The Gibbs energy change for chemical reaction calculates the maximum energy that is available or "free" for performing work; for this reason, Gibbs' energy is also called "free energy".

SCIENCE OF THERMODYNAMICS

We must also mention, once again the contibutionsof Robert Mayer, Walter Nerst, Fourier, for the development of Science of thermodynamics. But, the major force of thermodynamics teaching in engineering was Joseph H. Keenan at MIT. He created the MIT school of thermodynamics. Keenan's Thermodynamics book was published in 1941, and covers the fundamentals with applications in Mechanical and Chemical engineering.

JOSEPH H. KEENAN (1900-1977)

Professor Keenan is author of "Thermodynamics" (1941). He is co-author of "Thermodynamic Properties of Steam" (1936), a basic source of data for design for power and process machinery, which has been very influential in the steam-power industry.

"Thermodynamic Properties of Air" (1945) and "Gas Tables" (1948), prepared by Professor Keenan and Professor Joseph Kaye, have been used extensively in design and engineering work related to gas turbine, jet-propulsion machinery, and internal combustion engines.

Through his writing and teaching, Keenan brought to the engineering profession the fundamental work of J. Willard Gibbs in thermodynamics which for the most part, had been overlooked by engineers and scientists for five decades.In 1930's he adopted Gibbs's concept of thermodynamic availability for the steady flow, which is called Exergy outside of USA.

The Second- law concept and the availability analysis of a power-plant are important; the availability of the 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 analysed from the standpoint of the second law, the increase in availability in each piece of apparatus and irreversibilities can be calculated for the more effective energy resource use. Then, from Keenan's MIT school, the well know scientist, Adrian Bejan clarified the use of Second law analysis in the thermal design of energy systems & optimization. He is the one who made availability (exergy) analysis so popular under the title of the second law analysis.

ADRIAN BEJAN

Adrian left from communist Romania when he was 20. He earned all his degrees at MIT (BS 1971, MS 1972, PhD 1975)

Adrian Bejan is the one who made availability (exergy) analysis so popular under the title of the second law analysis in all kinds of analyses of power plants, refrigeration, heat pumps, heat exchange equipment and all kinds of components of energy systems. His techniques of analysis of exergy destruction, and cost became important in thermal design and optimization. Bejan made very valuable contribution to the teaching of today's Thermodynamics following Keenan. Adrian is a Keenan disciple since his PhD advisor Prof. J.L. Smith was Keenan's PhD student in the 1950s.

Adrian discovered the "Constructal law" as the new law of physics that accounts for design evolution which states that "for a finite-size flow system to persist in time (to live), it must evolve in such a way that it provide easier access to the imposed (global) currents that flow through it. This law commands that the changes in configuration must occur in a particular direction in time. It states that design in nature is not static, it is dynamic, evolving.

In the two decades since 1996, we have seen an accelerated activity of 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 domains such as the cooling of electronics, high density of heat exchangers, chemical engineering equipment, fuel cells, and hydraulics engineering.

The evolution and spreading of thermodynamics during the past two centuries is shown on the following Figure 4.

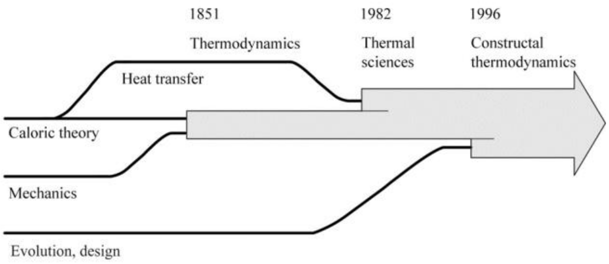

Figure 4. Evolution of the Constructal thermodynamics

Interested readers may consult with the following Refs [1-15].

REFERENCES

[1] J.H.Keenan, thermodynamics, John Wiley &Sons, 1941.

[2] M. Planck, Treatise on Thermodynamics (Translated by OGG), pp.40-47, Longmans, 1927.

[3] J.W. Gibbs, Collected Works, Vol. 1, p.51 (footnote), Longmans, 1931.

[4] H.C.Weber, Thermodynamics for Chemical Engineers, John Wiley&Sons, 1939.

[5] S.Carnot, Reflections on the Motive of Power of Fire (translated byR.Fox), Manchester University Press, 1986.

[6] J.H.Keenan, Mechanical Engineering, Vol.54, pp.195-204, 1932.

[7] A.Bejan, Advanced Engineering Thermodynamics, 2nd ed., John Wiley&Sons-1997.

[8] A. Bejan, The Physics of Life: The Evolution of Everything, St. Martin's Press, 2016.

[9] Y.A. Çengel, M.A. Boles,Thermodynamics, 4th Ed. McGraw Hill, 2002.

[10] C. Truesdell, TheTragicomical History of Thermodynamics, Springer-Verlag, 1980.

[11] D.S.L. Cardwell, A Biography of James Joule, Manchester University Press, 1989.

[12] W.H. Cropper, Great Physicists, Oxford University press, 2001.

[13] C. Smith and M. N. Wise, Energy and Empire: A Biographical Study of Lord Kelvin, Cambridge University Press, 1989.

[14] D.S.L. Cardwell, From watt to Clausius, Cornell University Press, 1971.

[15] J.G. Crowther, American Men of Science, N.Y. Norton, 1937.