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The Historical Development of Thermodynamics

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Abstract: Thermodynamics as a wide branch of physics had a long historical development from the ancient times to the 20th century. The invention of the thermometer was the first important step that made possible to formulate the first precise speculations on heat.

There were no exact theories about the nature of heat for a long time and even the majority of the scientific world in the 18th and the early 19th century viewed heat as a substance and the representatives of the Kinetic Theory were rejected and stayed in the background. The Caloric Theory successfully explained plenty of natural phenomena like gas laws and heat transfer and it was impossible to refute it until the 1850s when the Principle of Conservation of Energy was introduced (Mayer, Joule, Helmholtz).

The Second Law of Thermodynamics was discovered soon after that explanation of the tendency of thermodynamic processes and the heat loss of useful heat. The Kinetic Theory of Gases motivated the scientists to introduce the concept of entropy that was a basis to formulate the laws of thermodynamics in a perfect mathematical form and founded a new branch of physics called statistical thermodynamics.

The Third Law of Thermodynamics was discovered in the beginning of the 20th century after introducing the concept of thermodynamic potentials and the absolute temperature scale. At the same period of time the scientific issue of thermal radiation was also solved.

Keywords: history, physics, thermodynamics, heat transfer, thermal radiation

1. The invention of the thermometer [4][5][9][11][12]

The first important step to discover the principle of thermodynamics was the invention of the thermometer because precise and reliable survey results were needed. In the Ancient Times scientists wanted to measure the attributes of substances including their temperature.

Philo of Byzantium (280 BC – 220 BC) reported in his manuscript about a heat-sensing instrument. He constructed tube with a hollow sphere that was extended over a jug of water. When the sphere was placed in the sun the water began to bubble as the air expanded out of the sphere. If he put it in the shade the water rose in the tube as the air contracted in the sphere. *Hero of Alexandria* (10 AD – 70 AD) also inspected that the water level in a container rises and sinks due to the change in temperature.

In the Middle Ages scientists and physicians raised the necessity of measuring temperature. They knew that the flame has higher intensity of heat than a hot piece of iron while the quantity of heat is much lower in it but they could not clearly define the difference between temperature and quantity of heat

The Persian polymath *Avicenna* (980-1037) also recorded that he knew a mechanism to show the hotness and coldness of the air and developed an instrument in which the water level was controlled by the contraction and expansion of air but the really improvement came in Europe in the 16^{th} century.

The Italian *Galileo Galilei* (1564-1642) created the first thermometer in 1597 which was really a thermoscope because it did not have numerical scale so Galilei could find out only the relative differences between air temperature. Scientists in the 17^{th} century constructed lots of thermometers (Sagredo, Santorio, Fludd, Drebbel) but they all suffered from the disadvantage that they were also barometers. In 1654 *Ferdinando II de' Medici* (1610-1670), Grand Duke of Tuscany made a thermometer of sealed tube filled with alcohol that was only sensible to temperature and it was independent of air pressure.

The Englishman, *Robert Boyle* (1627-1691) was the first who realized the necessity of standard scales in 1662 during his experiments with that he discovered his law (Boyle's Law) that describes the relationship between the absolute pressure and volume of gas if the temperature is kept constant within a closed system.

In 1665 *Christiaan Huygens* (1629-1695) suggested to use the melting and boiling point of water as a standard scale and in 1694 *Carlo Renaldini* (1615-1698) proposed to use them as fix points with twelve equal parts between them but it was not accepted immediately because scholars were unsure that the freezing and boiling points of water are constant.

In 1724 the German physicist and glassblower *Daniel Gabriel Fahrenheit* (1686-1736) proposed a thermometer with reliable universal scale using mercury instead alcohol as the fluid within and it had three fix points. Zero was the coldest day of the winter in Danzig, the freezing point of the water was 32 degrees and the healthy human body temperature was 96 degrees that resulted 212 degrees for the boiling point of the water.

Fahrenheit's thermometer was the first standardised instrument that was suitable for scientific measurements. It was cleared that all substances have defined freezing and boiling points. Starting from this fact in 1742 the Swedish astronomer *Anders Celsius* (1701-1744) produced a thermometer with a standard scale using the melting point of water as zero and boiling point of water as 100 degrees. This scale bears his name and it is under use with Fahrenheit scale world-wide nowadays. Because of its simplicity the Celsius scale is more popular.

2. The first scientific issue: Is heat a substance or a motion? [4][5][9][11][12]

Ancient people related heat with flame and fire. The ancient Egyptians viewed it as a formation with mysterious origins. The Chinese Taoists believed that fire is one of the five principle elements like air, wood, metal and water.

Ancient Greeks generally viewed fire and heat as a substance and often connected it with life and motion. *Heraclitus* (535 BC – 475 BC) was the first who framed a theory on heat. He argued that there are three principle elements in nature – fire, water, earth – from which the fire is the central element controlling and modifying the other two. Heraclitus claimed that heat is connected with the motion because he observed that living creatures are warm and died bodies are cold. The later ancient scholars (*Empedocles, Aristotle*) believed in four principle elements (water, earth, air, fire) and they also connected the heat with life and coldness with death.

In the Middle Ages some Islamic scientists examined heat and fire and all of them connected it clearly with motion. *Abū Rayhān Bīrūnī* (973-1038) stated that the causes of heat are movement and friction. *Avicenna* and *Abd Allah Baydawi* (?-1286) also made similar discoveries that heat is generated from motion of external things and it may occur through motion-change.

Even all the scientists of the 17th century believed in the essential connection between heat and motion. The English philosopher, *Francis Bacon* (1561-1626) in his work called *Novum Organum* demonstrated that heat is a kind of motion. *Robert Boyle* and his colleague *Robert Hooke* (1635-1703) had comparable opinion that heat is nothing else but vehement motion of the elementary particles.

3. Roundabout ways: The Phlogiston and the Caloric Theory [5][9][11][12]

Now we would think that it led directly to the Kinetic Theory, but the level of the mathematical knowledge was not enough high to create satisfying answers to a lot of questions. This is why the theories on the material nature of heat became conspicuous because they were much more suitable for explaining the phenomena like melting heat, boiling heat, thermal radiation, heat transfer etc. In 1669 *Joachim Johann Becher* (1635-1682) established the Phlogiston Theory that was later developed by *Georg Ernst Stahl* (1659-1735). In his work entitled *Experimenta chymicae et physicae* (1731) proposed that heat was associated with an undetectable substance called phlogiston that was driven out of the material when it was burnt. The theory was finally refuted in 1783 by *Antoine-Laurent de Lavoisier* (1743-1794) proving the participation of oxygen in burning. He framed instead the Caloric Theory that saw heat as a weightless and invisible fluid that moves to hot bodies from the cold ones.

Herman Boerhaave (1668-1738) was the first who went to the very limits of the Caloric Theory. He pronounced that we can not make equal sign between heat, fire and light because they can manifest separately. Boerhaave supposed connection between heat and motion because rubbing together two parts of flint-stones fire came into being no matter how hot or cold they were. He tried to determine the weight of Caloricum and examined the phenomena of thermal expansion.

The concept of fire and heat became clear only in the middle of the 18th century as the Scottish physicist, *Joseph Black* (1728-1799), started his experiments at the Glasgow

University in the 1750s. He defined the difference between temperature and the quantity of heat and founded the concept of specific heat that is the measure of heat (or thermal energy) required to increase the temperature of a unit quantity of a substance by one unit.

Black's most important discovery was the observation that melting ice absorbs heat without changing temperature. From this recognition he came to a conclusion that ice needs latent heat for this modification of physical condition. It was the main substantial proof of the material nature of heat for him and in 1779 one of his students, *William Cleghorn* (1754-1783), formulated the precise definition of the Caloricum.

4. The most important results of the Caloric Theory: gas laws and heat transfer [1] [4] [5][9][11]

4.1. Gas Laws [1][9][10][11]

The reason for the long survival of the Caloric Theory was that it opened the door to obtain the gas laws and to explain the heat flow.

Based on Boyle's work *Guillaume Amontons* (1663-1705) made an accurate thermometer in 1695 and investigated the pressure and temperature of gases. He found that the pressure of gas increases by one third between the temperature of cold and boiling water. From this Amontons concluded that the reduction of temperature leads to the disappearance of pressure and with this statement he founded the theory of absolute zero of temperature.

Knowing the Caloric Theory *Jacques Alexander César Charles* (1746-1823) discovered in 1787 that at constant pressure the volume of gas increases or decreases by the same factor as its temperature. This theory was further developed by *Joseph Louis Gay-Lussac* (1778-1750) and in 1802 he published his law that the pressure of a gas of fixed volume is directly proportional to its temperature.

Then only one step was needed when in 1834 *Benoît Paul Émile Clapeyron* (1799-1864) formulated the Combined Gas Law and stated that the ratio between the pressure-volume product and the temperature of a gas remains constant.

Clapeyron could not calculate the value of this constant without the knowledge of Avogadro's Law and the absolute zero of temperature, but when these things were discovered and also accepted a decade later, the French chemist *Henri Victor Regnault* (1810-1878) created the Ideal Gas Law

$$pV = \frac{m}{M} R_0 T$$

where p is the absolute pressure of gas, V is volume, m is the mass, M is the molar mass, R_0 is the ideal gas constant and T is the absolute temperature.

4.2. The theory of heat transfer [3][5][9][10][11]

Even in 1686 *Edmund Halley* (1656-1742) identified the fact that warm air rises and realized that solar heating is the cause of atmospheric motions.

The first publication about heat transmission was written by *Isaac Newton* (1643-1727) in 1701 and stated that the rate of heat loss of a body is proportional to the difference in temperatures between the body and its surroundings. This law was not enough precise and it was further developed after the foundation of the laws of fluid mechanics. The first attempt to prove this law was made by *Pierre-Louis Dulong* (1785-1838) and *Alexis Thérèse Petit* (1791-1820) in 1817 and pointed that Newton's Law is correct only by low differences of temperature.

In the early 18th century it was not easy to see that all materials had determined conductivity of heat but when the new science of electricity appeared it became apparent that some materials were good conductors and others were effective insulators. In 1785 *Jan Ingen-Housz* (1730-1799) raised an idea that based on their electrical properties some materials might be good thermal conductors or thermal insulator too.

In 1777 *Carl Wilhelm Scheele* (1742-1786) distinguished the three forms of heat transfer from each other – the thermal radiation, thermal conduction and thermal convection – and lots of experiments began in the late 18th century about them. In 1804 *John Leslie* (1766-1832) observed that the cooling effect of stream is increasing with its speed. In the same year he carried out his famous experiments with the Leslie cube (see later). He was the first who artificially froze water into ice in 1810.

The most important result of the Caloric Theory is associated with the name of the French mathematician, *Jean Baptiste Joseph Fourier* (1768-1830). In 1807 he formulated his empirical law of heat conduction based on his observations. It states that the rate of heat flow through two surfaces at right angles of a homogenous solid in a unit of time is directly proportional to thermal conductivity (heat transfer coefficient, λ) and to the temperature difference along the path of the heat flow and inversely proportional to the distance between the ends of the crossed surfaces:

$$q = \lambda \frac{\Delta T}{\Delta x}$$

In this formula q is the heat flux, λ is the heat transfer coefficient, ΔT is the temperature difference between the ends and Δx is the difference between the ends.

Fourier's Law was not accepted for 15 years and it was finally published in 1822 in his monograph entitled *Théorie analytique de la chaleur* (The Analytic Theory of Heat). In this work Fourier summarized his most important discoveries and formulated own theory in a correct mathematical form by working out the differential form of thermal conduction with the help of Fourier series.

The decisive step in the application of Fourier's Law and the concept of heat transfer coefficient was taken by *Ernst Karl Wilhelm Nusselt* (1882-1957) when his paper called *Das Grundgesetz des Wärmeübergangs* (The Basic Law of Heat Transfer) was published in 1915.

5. The first attempts of the Kinetic Theory [4][9][11]

In spite of the rapid successes and propagation of the Caloric Theory there were a few scientists who took a stand for the Kinetic Theory of heat. In 1716 *Jakob Hermann* (1678-1733) pointed out that the atmospheric pressure is proportional to the air density and to the square of the average velocity of moving particles in atmosphere. *Leonhard Paul Euler* (1707-1783) even computed the value of this average velocity as 477 m/s.

In 1738 *Daniel Bernoulli* (1700-1782) published his most important work called *Hydrodynamique* (Hydrodynamics). Based on the relation of Boyle's Law showed that as temperature changes the pressure will change proportionally to the square of the particle velocities.

In 1745 the Russian chemist *Mikhail Vasilyevich Lomonosov* (1711-1765) also wrote a relevant work against Caloric Theory under the title of *Размышления о причине теплоты и холода* (Reflections on the Reason of Heat and Cold). He reported that heat is generated by motion because when we rub our hands together or strike the iron intensively they become warmer. He explained that heat is nothing else but the high-speed velocity of motion of invisible material particles. In his later works he tried to put into words the Principle of Conservation of Energy and diagnosed that however much matter is added to any body, as much is taken away from another.

In the 18th century works of these scientists about the Kinetic Theory created little stir throughout the world because of the huge popularity of the Caloric Theory. In addition there were lingual difficulties too, because Lomonosov published his works in Russian and they were not attractive in Western Europe.

Caloric Theory had only two weak points – the friction heat and the weight of the Caloricum – and a few practical researchers tried to take advantage of this situation. The cannon manufacturer *Benjamin Thomson, Count Rumford* (1753-1814) realized that the most suitable moments to take the weight of Caloricum when the ice is melting because at this moment ice absorbs a lot of heat without changing temperature. He took absolutely accurate and precise measurements with his apparatus and finally declared that even if Caloricum had weight it is immensely small.

In 1798 Rumford made a study about the frictional heat that was generated through boring the cannons. He immersed a cannon barrel in water and showed that the water could be boiled by the frictional heat generated by the boring tool. Rumford demonstrated through the use of friction that it was possible to convert work to heat and this heat seemed to be inexhaustible. As a result of these experiments Rumford suggested that heat is a form of motion.

The connection between heat and friction was also analysed in 1799 by *Humphrey Davy* (1778-1829). In his experiment he rubbed two pieces of insulated ice together and showed that melting heat could be originated only from mechanical work.

Rumford and Davy were very close to refute the Caloric Theory but the advocates of it could easily explain the results of their experiments supposing the weightlessness of Caloricum.

6. The devolution of the Caloric Theory and the recruitment of the Kinetic Theory [2][4][9][11]

The overthrow of the Caloric Theory became possible after the birth and verification of the Principle of Conservation of Energy. Although the foundations of this theory are findable in the work of Thales of Miletus and lots of others the first mathematical formula was created by *Gottfried Wilhelm Leibniz* (1646-1716) who noticed that in many mechanical systems a determinate quantity of vis viva (living force) is conserved.

Instead the name of vis viva *Thomas Young* (1773-1829) suggested to use the expression of energy in 1802 but he still used Leibniz's formula (mv^2) to calculate the quantity of it. Only in 1829 *Gaspard-Gustave de Coriolis* (1792-1843) recalibrated it to an appropriate formula of $\frac{1}{2}mv^2$ and named it as kinetic energy.

It was easy to understand the connection between mechanical work and kinetic energy but the verification of the mechanical equivalent of heat was much more difficult. The encouragement was brought by the steam engine that was already invented in the 17th century but it was improved by *James Watt* (1736-1819) only in 1769. The main problem with these machines was that they were slow and converted less than 2% of the invested fuel into useful work. It was immediate to enlarge the useful effect of steam engines that was urged by Watt.

About the first experiments and measurement on the enlargement of the useful effect was published in 1776 by the Scottish engineer *John Smeaton* (1724-1792) in which he supported the vis viva theory. Decades later *William Hyde Wollaston* (1766-1828) and *Peter Ewart* (1767-1842) also confirmed Smeaton's publication but they were attacked on the plea that they are in conflict with Newton's law on impulse.

An important step was presented in 1824 by the French engineer, *Nicolas Leonard Sadi Carnot* (1796-1832) who published his work under the title of *Réflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance* (Reflexions on the Motive Power of Fire). On the analogy of the hydropower engine he designed a hypothetical engine (Carnot heat engine) that transfers energy from a warm region to a cool region of space and, in the process, converting some of that energy to mechanical work. This engine operates on a thermodynamic cycle called Carnot cycle that consists of four steps: 1. Reversible isothermal expansion of the gas at a hot temperature T_H (isothermal heat addition). 2. Isentropic (reversible adiabatic) expansion of the gas (isentropic work output). 3. Reversible isothermal compression of the gas at a cold temperature T_C (isothermal heat rejection). 4. Isentropic compression of the gas (isentropic work input). After the fourth step the gas returns to the initial state.

Based on the Caloric Theory Carnot viewed heat as a substance and computed the efficiency of the Carnot heat engine with the following relationship:

$$\eta = \frac{Q(T_1 - T_2)}{Q} = \frac{T_1 - T_2}{T_1}$$

where η is the efficiency, Q is the heat put into the system, T_1 is the absolute temperature of the hot reservoir and T_2 is the absolute temperature of the cold reservoir.

Although he got seemly correct value for the efficiency the analogy that he used was perfectly incorrect. There is not as much heat in the warm region as in the cold region because the heat changes into mechanical work. On the other hand the recognition that the useful effect of the engine depends only on the temperature difference and it is independent of the working substance was perfect.

In his later memorandums before his early death there are plenty of indications to the Principle of Conservation of Energy and to the vitality of the Kinetic Theory.

7. The First Law of Thermodynamics – The Principle of Conservation of Energy [1][2][9][11][12]

The German surgeon *Julius Robert von Mayer* (1814-1878) started a study on the physical side of the symptoms of life during his journey in Dutch East India in 1840 and noticed that the venous blood of the sailors in the tropics is much darker than in cold climates. He concluded that the chemical processes of the body get their sources of energy for oxidation from the nature.

Arriving home he wrote a scientific paper in 1841 under the name of *Über die quantitative und qualitative Bestimmung der Kräfte* (On the Quantitative and Qualitative Determination of Forces). It was ignored by the physicists because of its strange argumentation that were based on the principle of causa aequat effectum so he could publish it next year in a chemical journal under the title of *Bemerkungen über die Kräfte der unbelebten Natur* (Remarks on the Forces of Inorganic Nature). This fundamental paper contained the first adequate formulation about the Law of Conservation of Energy that although work and heat are different forms of energy, they can be transformed into one another. He also specified theoretically the numerical value of the mechanical equivalent of heat as 365mkp (3580J) which is a little bit far from the real value but the order of size and the deduction was correct. Mayer also gave suggestions how to transform experimentally kinetic energy into heat.

Contemporaneously *James Prescott Joule* (1818-1889) made experiments and measurements to estimate the mechanical equivalent of heat and in 1843 he announced his results in a scientific meeting in Cork but there was only meagre attendance. In 1845 Joule wrote a paper *On the Existence of an Equivalment Relation Between Heat and the Ordinary Forms of Mechanical Power* and sent it to the British Association meeting in Cambridge. He reported about his best-known experiment using a falling weight to spin a paddle-wheel in an insulated barrel of water that increased the water temperature. Firstly he estimated the mechanical equivalent of heat as 424mkp (4158J) that was later refined by him as 427mkp (4187J).

The Law of Conservation of Energy was outlined in the works of Mayer and Joule but the modern form of it was formulated by the German physician *Ludwig Ferdinand von Helmholtz* (1821-1894). Studying the muscle metabolism he observed that no energy is lost in the muscle movement. In 1847 he based his book *Über die Erhaltung der Kraft* (On the Conservation of Energy) on a rule that all form of energy (mechanic, heat, light, magnetism) are equivalent. His theorem was hardly disputed and the Law of Conservation of Energy could be gone out of mind if did not raise up the interest of *William Thomson, Lord Kelvin* (1824-1907) who recognized the significance of Helmholtz's paper. He experimented in order to bloster Joule's results and in 1848 he published his article *On the Absolute Thermometric Scale*. He suggested the introduction of an absolute temperature scale about which Amontons had speculated in 1695. Based on the Celsius scale Kelvin determined the absolute zero temperature in -273°C under which the kinetic energy of material particles is as low as possible.

8. The Second Law of Thermodynamics and the Kinetic Theory of Gases[1][2][4][5][9][11][12]

In the middle of the 19th century it was trivial that the Law of Conservation of Energy in not enough to explain the natural phenomenon because – as Carnot stated formerly – there is a determined tendency of the thermodynamic processes and the heat can spontaneously flow only from hot to cold materials. This is why the Second Law of Thermodynamics was needed and this necessity was recognized by *Rudolf Julius Emanuel Clausius* (1822-1888).

In 1850 he wrote his famous paper *Über die bewegende Kraft der Wärme* (On the Moving Force of Heat and the Laws of Heat) in which he stated the basic idea of the second law that heat generally cannot flow spontaneously from cold to hot bodies. If it could happen it would be possible to transform the 100% of heat into mechanical energy.

Another formulation of the second law was written down in 1851 by Lord Kelvin in his work entitled *On the Dynamical Theory of Heat* that it is impossible to convert heat completely into work in a cyclic process.

These negative sentences as the law of thermodynamics sounded very strange for the physicists so a new idea was needed to formulate a more adequate definition. It is going to be the idea of entropy a decade later.

At the same time the work of Bernoulli was rediscovered by *John Herapath* (1790-1868) in 1816 and submitted a paper to the Royal Society but it was rejected because its conclusions were seemed to be erroneous.

After the studying of Bernoulli's and Herapath's work *John James Waterston* (1811-1883) wrote a publication in 1843 under the title of *Thoughts on the Mental Functions*. He correctly derived the consequence that the gas pressure is generated by the high-speed motion of the material particles and countable with multiplying the number of molecules per unit volume, the molecular mass, and the molecular mean-squared velocity.

However it contained the elementary form of the Kinetic Theory of Gases this paper was rejected by the Royal Society because of its modern intonation and he could publish a short abstract of it. In 1848 Joule made calculations in order to compute the speed of the hydrogen molecule but his article in 1851 did not arouse the interest so together with Waterston's work it had only a little influence on the next generation.

The real breakthrough came after the article of *August Karl Krönig* (1822-1879) in 1856. It was based on Waterston's work and its simple gas-kinetic model gave plenty of motivations and ideas for the other researchers. In 1857 Clausius wrote a paper under the title of *Über die Art der Bewegung, welche wir Wärme nennen* (On the Kind of Motion which we call Heat) in which he stated that the internal energy of gases equals with the kinetic energy of the atoms or molecules of gases He developed a much more complex but sophisticated theory than Kröning that included not only the translational but also the rotational and vibrational molecular motions.

This article motivated the Scottish physicist, *James Clerk Maxwell* (1831-1879) to give up the theorem that in a given amount of gas the molecules have the same speed and formulated the Maxwell Distribution of Molecular Velocities with which he founded a new branch of physics called statistical thermodynamics. He published his formula in 1860 in his work called *Illustrations of the Dynamical Theory of Gases* that described the particle speeds of gases at a determinate temperature and showed the statistical distribution of it. Maxwell worked out the equipartition theorem which means that in thermal equilibrium the total kinetic energy of a system is shared equally (in average) among all of its various forms, so the average kinetic energy in the translational motion of a molecule should equal the average kinetic energy in its rotational motion. After universalizing this law he also stated that the internal energy is equally shared between the degrees of freedom and it depends only on the temperature of the system.

9. Entropy, Statistical Thermodynamics and the Third Law of Thermodynamics [1][2][7][8][9]

Joule and Kelvin also speculated that there was an inevitable loss of useful heat in all thermodynamic processes and observed that natural processes are tended from an organized to a disorganized state. In addition in the 1850s it was necessary to find a correct mathematical description for the Second Law of Thermodynamics because the former definitions were not as accurate as needed.

This is why coined Clausius the concept of entropy in 1865 which means how organized or disorganized a system is. With the help of entropy we can explain the tendency of processes because the most likely event happens in the nature. It was also possible to formulate mathematically why flows spontaneously heat from hot into cold bodies. Because decreasing of temperature results the increasing of entropy.

The young Austrian physicist *Ludwig Eduard Boltzmann* (1844-1906) started to deal with the Kinetic Theory of gases in 1866. His work was promoted by Maxwell's book called *Theory of Heat* in 1871 and confirmed that the thermodynamic systems is tended towards the thermal equilibrium because this is the most likely state.

Developing Maxwell's equipartition theory and the distribution of molecular velocities he calculated the value of kinetic energy to each degree of freedom with the formula of:

$$\frac{1}{2}kT$$

where T is the absolute temperature and k is the Boltzmann's constant and equals to $1{,}38065\times10^{-23}$ J/K. With the help of entropy Boltzmann redefined the Second Law of Thermodynamics in 1877. He introduced the concept of thermodynamics probability as the number of microstates corresponding to the current macrostate and formulated the connection between entropy and molecular motion showing that the logarithm of thermodynamic probability (W) is directly proportional with the entropy (S).

$$S = k * \ln W$$

Before the Third Law of Thermodynamics the last important step was taken by the American physicist and chemist *Josiah Willard Gibbs* (1839-1903) by introducing the concept of the thermodynamic potentials and free energy in 1876 in his monograph called *On the Equilibrium of Heterogeneous Substances*. Thermodynamic potentials could be formulated with the help of the state parameters like volume (V), pressure (p), temperature (T) and internal energy (U) and they make easier to calculate some characteristics of the system (heat capacity, reaction heat). These potentials are free energy (F), enthalpy (H) and free enthalpy (Gibbs energy, G) and they measure the useful work of a closed thermodynamic system at constant temperature and volume (free energy), or at constant pressure (enthalpy) or at constant pressure and temperature (Gibbs energy).

Studying the high-temperature reaction of gases *Walther Hermann Nernst* (1864-1941) analyzed these kinds of thermodynamic potentials in 1889. He was deeply influenced by the thermodynamic researches of *Max Karl Ernst Ludwig Planck* (1858-1947) and the birth of quantum mechanics in 1900 and started to examine the change in specific heat of different materials. In 1906 he published his theorem with which he established the Third Law of Thermodynamics. This law describes the behaviour of a thermodynamic system as the temperature decreases to the absolute zero. Nernst stated that the entropy of a system at a temperature of absolute zero becomes zero in the case of perfect crystalline substances. He also laid down that it is impossible to reduce the temperature of any system to the absolute zero in the finite number of steps.

$$\lim_{T \to 0} \Delta S = 0$$

In this formula T is the absolute temperature and S is the entropy of the system.

10. Thermal radiation [1][3][4][5][6][9][11][12]

It was an important scientific issue from the beginnings of the thermodynamics to solve the problem of thermal radiation. Scientists in the Middle Ages observed that a heated piece of iron radiates heat and light at the same time but the forms of heat transfer were distinguished only in 1777 by Scheele as convection, conduction and radiation.

The Swiss physicist *Pierre Prévost* (1751-1839) showed it first in 1791 that all bodies radiate heat no matter how hot or cold they are and discovered in 1809 that the radiated heat depends only on the temperature of the radiating body and it is independent from the temperature of the surroundings.

In 1804 *John Leslie* (1766-1832) experimented with his famous apparatus called Leslie cube in order to monitor the intensity of radiant heat. He filled a cubical vessel with boiling water and composed one side with highly polished metal and two sides with dull metal. One side of the cube was painted black. During his experiments he detected the greatest radiation from the black side and irrelevant from the polished side.

Using an optical bench that was set up with theropiles, shields and heat and light sources the Italian physicist *Macedonio Melloni* (1798-1854) examined carefully the black body radiation and in 1831 he showed that radiant heat could be reflected, refracted and polarized as light.

The Prussian physicist, *Gustav Robert Kirchhoff* (1824-1887) was interested in black-body radiation too and in 1859 he noticed a simple but important connection between the emission and absorption of radiating bodies. Kirchhoff's Law of the Thermal Radiation states that in a unit of time the emission of a radiating body or a surface at given temperature and frequency equals its absorption, so the ratio of the emission and absorption is independent from the material parameters of the radiating body.

The further development was promoted by Maxwell's conclusion in 1862 that there is a clear connection between light, electromagnetic and thermal radiation. *John Tyndall* (1820-1893) also made experiments about thermal radiation in the 1860s and loaded with errors measured that the emission of black-body at 1473K is 11,7 times higher than at a temperature of 798K. His measurements were analyzed by the Slovenian physicist, *Jožef Štefan* (1835-1893) in 1879 and realized a connection between Tyndall's results. He constructed a law that the total energy (E) radiated per unit surface area of a black body in unit of time is directly proportional to the fourth power of the black body's absolute temperature (T):

$$E = \sigma T^4$$

Using the laws of thermodynamics Boltzmann also recognized the same connection in 1884 therefore this law was named Štefan-Boltzmann Law. The σ constant in the formula (Štefan-Boltzmann constant) was determined as $5{,}672 \times 10^{-8} W/m^2K^4$.

The solution of the radiant heat problem got near when in 1893 *Wilhelm Karl Werner Wien* (1864-1928) noticed an empirical formula between the temperature (T) of the body and the peak wavelength (λ_{max}) emitted by it:

$$\lambda_{\max} T = 2{,}8978 * 10^{-3}\, mK$$

He also ascertained that hotter bodies emit most of their radiation at shorter and colder bodies at longer wavelengths. Based on Maxwell's Law of Speed Distribution he created a formula to describe the intensity of black body radiation in 1896.

At the same time *Lord Rayleigh* (1842-1919) and *James Hopwood Jeans* (1877-1946) tried to introduce another kind of formula to describe spectral radiance of electromagnetic radiation that was later known as Rayleigh-Jeans Law.

Plenty of scientific researchers (Lummer, Pringsheim, Rubens, Kurlbaum) wanted to measure the intensity of thermal radiation in a huge scale of wavelengths and found out that Wien's Law is applicable only at short and Rayleigh-Jeans Law only at long wavelengths.

Finally the German physicist *Max Karl Ernst Ludwig Planck* (1858-1947) solved the problem and created a perfect formula that describes the black body radiation at all wavelengths as a function of temperature and wavelength

$$E = \frac{c^2}{h\lambda^5} \frac{1}{e^{\frac{ch}{k\lambda T}} - 1}$$

where c is the speed of light, h is Planck's constant, λ is the wavelength, k is Boltzmann's constant and T is the temperature of the black body.

To construct this relationship Planck had to postulate that energy could be emitted only in quantized form. This was presented by him on 14th December 1900 in Berlin and this date is declared as the birth of Quantum Physics.

Planck also gave a very simple formula to describe the energy quantum (energy of the photon) with the product of the frequency of its associated electromagnetic wave (ν) and the Planck constant (h=6,626×10^{-34} Js):

$$E = h\nu$$

On the basis of Planck's quantum theory *Albert Einstein* (1879-1955) could come forward in 1905 with the idea of the quantization of light. In his article entitled *Über einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt* (On a Heuristic Point of View Concerning the Production and Transformation of Light) Einstein stated that light consists of localized particles (quanta). This theory was first rejected and it became fully accepted only in 1919. In 1906 Einstein also solved with the help of the quantum theory the dilemma why exists a huge difference between the theoretically and measured specific heat of solids.

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