A Companion to Physics of the XIXth century - part 2

Slide 3 shows the time table of the most important discoveries in the physics of heat in the period 1600-1900. Slide 4 contains a more detailed summary of events.

At the turn of the XIXth century the view that heat is a substance - caloric - than can be passed from one body to another, was firmly established. The strict mathematical theory of heat was constructed mainly by the French scientists Jean-Baptiste Fourier, Pierre Simon Laplace, and Siméon Poisson. Slide 5 presents some mathematical formulae of that theory. The students less versed in mathematics may skip the formulae presented there, but only note that the caloric theory had the **single** fundamental equation which expressed the amount of caloric as a function of pressure and temperature. This was different from the present theory (thermodynamics) in which we have TWO fundamental equations: one which expresses the conservation of energy, and the second one which describes the direction of the flow of energy (e.g. the equation for the internal energy U and the equation for the entropy S).

Slides 6 and 7 pertain to the Poisson's theory, Slides 8 and 9 - to the Fourier's theory of heat transport.

Heat machines had been constructed since the beginning of the XVIIIth century by trial and error, without any theoretical fundament. The breakthrough came in 1824. In that year the French military engineer Sadi Carnot published a short booklet *Reflexions sur la puissance motrice du feu et sur les machines propres a développer cette puissance* (*Reflections on the motive power of heat and on engines suitable for developing this power*). Carnot assumed that the production of motive power, that is, work, occurs as the result of the transfer of caloric from a hotter to a colder body. Caloric was assumed to be conserved in that process, similarly to water which produces power in a water-wheel (Slides 10-11). Short excerpts from Carnot's brochure are presented in Slides 12-15. Carnot's fundamental conclusion was that the amount of work produced by a heat engine depends only on the difference of temperatures of the bodies between which the transfer of caloric occurs.

The first graphic representation of the Carnot's cycle was published ten years later by Clapeyron (Slide 16). The students of physics know well that Carnot's theorem remains valid in the modern theory which has no reference to caloric.

Slides 17-32 contain material concerning the discovery of the conservation of energy and the establishment of the two laws of thermodynamics.

The discovery of conservation of energy had been „hanging in the air" since about 1830. Many scientists wrote on that subject but their statements were largely vague and not supported by experimental evidence (Slides 18-19). It is usually agreed that the discovery of the conservation of energy had been made independently by Mayer, Joule and Helmholtz (Slide 17).

Julius Robert Mayer was a German physician. His paper *Bemerkungen über die Kräfte der unbelebten Natur* (*Remarks on the forces of non-living matter*) was published in 1842 in „Annalen der Chemie und Pharmacie", which physicists rarely read. Moreover, Mayer's style was quite confusing (see Slides 20 and 21) except for the last page (Slide 22) in which the author gave a clear statement of the equivalence of heat and mechanical energy and quoted the first estimate of the mechanical equivalent of heat. In his later paper Mayer clearly stated that „in all physical and chemical processes a given force remains constant" (Slides 23 and 24). Notice that at that time the term „force" was used instead of „energy" which was introduced later.

James Prescott Joule from Manchester was an experimenter. He earned his living by running the family brewery and could afford to organize his private laboratory in which he performed various experiments. Slide 25 shows his installation to measure heat generated in water from the friction of a paddle wheel which was rotated by the fall-down of the weights. Joule also rotated the armature of an electric motor in the field of an electromagnet in a water bath and measured heat produced from mechanical energy. He made several measurements of the mechanical equivalent of heat.

Herman Helmholtz was both physicist and physician. In his paper *Über die Erhaltung der Kraft* (*On the conservation of force*) published in 1847 he had discussed and elucidated the conservation of energy to its full extent (Slide 26).

In June 1847 Joule met William Thomson during the meeting of the British Association for the Advancement of Science (BAAS) in Oxford. Thomson at that time firmly believed in Carnot's theory with indestructible caloric, so that he took Joule's ideas to be wrong. Soon, however, he became convinced by Joule and converted to the dynamical theory of heat. Unknown to him the German physicist Rudolf Clausius had been also working on the problem and in April 1850 published the famous paper *On the moving force of heat* (Slide 28) in which he reconciled the ideas of Carnot and Joule. Thomson quickly followed with his paper (Slide 29). The changes in terminology are summarized in Slide 30. Scottish physicist William J. Macquorn Rankine expressed conservation of energy by summing up all its known forms (Slide 31).

Clausius had clear priority in establishing the second law of thermodynamics (1850). Thomson derived it independently and stated differently (1851). It is however easy to show that the formulations of Clausius and Thomson are equivalent (Slide 32). Clausius argued that the second law of thermodynamics could be expressed by „equivalence value", the quantity measuring the tendency of heat to pass from warmer to colder bodies

Slide 33 gives a summary of the most important steps in establishing the dynamical theory of heat and its links with thermodynamics. The main founders of the statistical physics are presented in Slide 34. In 1865 Clausius introduced entropy S in place of „equivalence value" and by using this concept presented a very elegant and concise formulation of the two laws of thermodynamics (Slide 35).

By the early 1870s the Austrian physicist Ludwig Boltzmann adopted the view that the second law of thermodynamics was a statistical theorem. In a paper published in 1872 he gave general proof of the uniqueness of Maxwell's distirubution law. He demonstrated that whatever the initial state of a gas, Maxwell's velocity distribution would describe its equilibrium state. In 1877 Boltzmann published very important paper on the connection between the second law of thermodynamics and the theory of probability. He derived fundamental equation $S = \mathrm{k} \log W$, which connected entropy S with thermodynamic probability W. After Boltzmann's death his formula had been inscribed on his tombstone in the cemetary in Vienna (Slide 36).

Friedrich Wilhelm Ostwald was opposed to the use of atomistic concepts in chemistry, and he rejected all associated concepts, the kinetic theory of gases, and the programme of mechanical explanation in physics. He claimed that scientists should consider only measurable quantities, such as e.g. energy, temperature, specific heat etc., while all hypothetical entities, such as invisible atoms or molecules, shouldn't have any place in science. Ostwald's approach, called „energetics", gained support of Ernest Mach and some other physicists. Boltzmann protested against violent attacks on his theory (Slide 37).

Slides 38 and 39 give a summary of efforts to liquify gases. As early as in 1789 Antoine Lavoisier wrote in his *Traité elémentaire de Chimie:*

„If the Earth were suddenly transported into a very cold region, the water which at present composes our seas, rivers, and springs, and probably the greater number of the fluids we are acquainted with, would be converted into solid mountains and hard rocks. (...) the air, or at least some part of aeriform fluids which now compose the mass of our atmosphere, would doubtless lose its elasticity for want of a sufficient temperature to retain it in that state: it would return to the liquid state of existence, and new liquids would be formed, of whose properties we cannot, at present, form the most distant idea."

Michael Faraday succeded in liquifying many gases except for a few „permanent", such as hydrogen H_2, nitrogen N_2, oxygen O_2, carbon monoxide CO, nitric oxide NO, and methane CH_4. These gases remained aeriform even at – 110^{o} C, the lowest temperature obtained by Faraday. In 1861 Thomas Andrews discovered the existence of the „critical point", above which gases could not be liquified. Further efforts went therefore into lowering the temperature as much as possible. In 1877 Louis Cailletet in France and Raoul Pictet in Switzerland independently succeeded in obtaining momentary mist in the vessel after rapid expansion of air it contained. The mist lasted only small fraction of the second, so that no study of its properties was possible. This was the ***dynamic*** liquefaction of air.

In 1883 ***static*** liquefaction of oxygen, nitrogen and carbon monoxide was achieved by Karol Olszewski and Zygmunt Wróblewski at the Jagellonian University in Cracow. Polish scientists could study properties of these gases in the liquid form. Later, in 1894, Olszewski succeeded in liquifying argon, one of the newly discovered inert gases. The last gas to be liquified was helium. During further cryogenic studies Kamerlingh-Onnes in Leiden accidentally discovered superconductivity, the phenomenon which remained unexplained for the next sixty years. In 1927 Willem Keesom from Leiden and Mieczysław Wolfke from Warsaw Polytechnic discovered a new form of helium: helium II proved to be the quantum liquid having the property of superfluidity.

Slides 40-65. Maxwell's synthesis.

The Scottish physicist James Clerk Maxwell was one of the greatest scientists in history (Slide 41). It is worth remembering that his first name was James, and Clerk Maxwell - the double family name. It happened so because in the XVIIIth century one of his ancestors George Clerk married Miss Dorothea Maxwell and added her family name to his. Nowadays many misinformed people think that Clerk is the second name of Maxwell. Indeed, his double family name is almost always shortened to Maxwell.

After studies at Edinburgh and Cambridge Maxwell became professor of physics at the university of Aberdeen, and then moved to King's College in London. In his youth he was interested in the kinetic theory of matter and in his paper *Illustrations of the dynamical theory of gases* presented derivation of the energy and velocity distributions of gas particles, known now as Maxwell's distrubutions.

Maxwell's main interest was in electromagnetic phenomena. He first gave the mathematical form to Faraday's intuitive notion of the field and field lines. His first studies involved a mechanical model of the „magnetic medium" (Slides 42-45). At the end of 1864 he submitted for publication his most important paper *A dynamical theory of the electromagnetic field*, in which he presented the new theory of electromagnetism. Slides 46-55 contain important excerpts from that paper. Maxwell studied a continuous magnetic medium and made use of the well known equations of the mechanics of such a medium. He did not neglect the numerical coincidence between the velocity of light c and the ratio of electrostatic and electromagnetic units v as measured by Weber and also by himself. After detailed exploration of that fact he concluded that light may be an electromagnetic disturbance (Slide 55). This brilliant conclusion was verified in 1887 by Heinrich Hertz.

In 1873 Maxwell published a voluminous textbook *Treatise on electricity and magnetism* (Slides 56-63). He still carefully avoided hypotheses concerning the nature of the electric current and the carriers of electricity (Slides 58-59). In 1873 the data on numerical values of c and v were still scarce (Slide 62). In the third edition of the *Treatise* (1890) there were many more data confirming Maxwell's ideas (Slide 63).

Maxwell did not use vector calculus and worked with his equations for the components. Hence there were originally twenty „Maxwell's equations" (Slides 53-54).

Maxwell's equations in the form presently used have been first written down by Oliver Heaviside (Slides 64-65).

Slides 66-70 contain excerpts from the *Autobiography* of Albert Einstein who learned Maxwell's theory in his student times. The great Dutch theorist Hendrik Lorentz greatly modified Maxwell's theory as described in Slides 71-74.

Slides 75 and 76 contain an amusing fragment on the properties of hypothetical luminiferous ether taken from the physics textbook published in 1884.

Maxwell's electromagnetic theory was confirmed by the brilliant discovery of electromagnetic waves by the German physicist Heinrich Hertz (1887). The Italian engineer Guglielmo Marconi soon applied that discovery for long-range intercontinental communication. It had a profound impact on our civilization.

Hertz experimented with a small dipole antenna and spark-gap receiver. In Slides 78 and 79 we have his original drawings of the experimental equipment and his visualization of the formation and propagation of an electromagnetic wave.

As a side note we may see the original illustration of the first public demonstration of the Foucault's pendulum in Paris (Slide 80). It provided evident proof for Earth's rotation.

Discovery of the periodic system of elements (slides 81-84).

In 1815 English physician William Prout attempted to show that all atomic weigths of known elements are multiples of that of hydrogen. It raised the question whether the elements were simple or instead compounded of smaller, more fundamental parts. However, when more precise measurements by Berzelius showed that the atomic weights were not simple integers, the Prout's thesis was put aside. Other chemists tried to order known elements in groups of similar properties. The German chemist Döbereiner noticed a regular increment in the atomic weights of certain groups of three analogous elements. A young English chemist John Newlands remarked that if the elements were arranged in ascending atomic weights, every eighth element seemed to have similar properties; he called it „the law of octaves".

Russian chemist Dmitri Mendeleev was the first to propose ordering known chemical elements in columns and rows according to their atomic weights and chemical properties. His short paper was published in 1869 (Slide 83). A few months later, in 1870, German chemist Julius Lothar Meyer proposed similar periodic system. Mendeleev's proposal was more successful because the author left gaps in his table of elements and boldly suggested the existence and properties of hitherto unknown elements, which were soon discovered and filled those gaps.

The discovery of inert gases and radioactive elements expanded the Mendeleev system.