Journal of Thermal Analysis and Calorimetry, Vol. 88 (2007) 3, 763–768

FROM CALORIC TO STATHMOGRAPH AND POLAROGRAPHY

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Present contribution briefly describes some historical features, which are focused back to the history of the Middle European learning as promoted by the foundation of the Charles University in Prague 1348. Physics and its neighboring areas are mentioned discussing some crucial scientific contributions and stressing out some prominent scholars, such as Tycho de Brahe, Johannes Kepler, Tadeáš Hájek, Marcus Marci, Jan A. Commenius (caloric), Prokop Diviš, Bernard Bolzano, Christian Doppler, Ernst Mach, Albert Einstein, Václav Šimerka, František Záviška, Čeněk Strouhal, Reinhold Fürst or Stanislav Škramovský (statmograph) and Jaroslav Heyrovský (polarography), the latter being already the representative of modern age.

Keywords: *alchemy, caloric, Charles university, Commenius, Heyrovsky, history of physics, Middle Europe, Skramovsky*

Historical Prague and its famous Charles University

One of the most important moments in the history of old Bohemia was the foundation of Charles University in Prague, as the first European university north of the Alps, by Emperor Charles the IV. One of its first achievements was the introduction of medieval kinematics, which was brought to Prague by Johannes de Holandria, an Oxfordian from Merton College, who in the year 1368 provided the so-called Merton' theorem of uniform acceleration to public and detailed this approach during his stay in Prague. Later Czech astronomer Jan Šindel (1375–1456) was studying the planetary motion and his astronomical tables were greatly appreciated by Tycho de Brahe while staying in Prague at the end of the 16th century. Šindel had also a share in designing the advanced astrolabe in the famous Prague's astronomical clock.

Little renown is Ioannes Marcus Marci (Jan Marek Marků 1595–1667) who probably helped to reveal the fundamental properties of the spectral colors that emerge when light passes through glass prism, was already aware of their monochromatic properties, i.e., any succeeding refraction or reflection did not change colors. He also studied the color change in rays when spectral colors are mixed and in the field of spectral dispersion of light he was actually a predecessor of Isac Newton. He wrote for that time very advanced books. e.g. [1], which possibly foreshadowed some laws. Besides the refraction of light he conducted the first-ever systematic study of the impact of bodies, he discovered the difference between elastic and inelastic impacts intuitively moving his thoughts within the reach of the conservation laws. Marci,

Fig. 1 From left: Charles University in Prague (founded by Emperor Charles IV. 1348 and some of their exceptional members and associates, astronomer Kepler Johannes (1571–1630), rector and mathematician Marcus Marci Ioannes (from Kronland, 1595–1667) and famous professor of mathematics and practical geometry Doppler Christian (1803–1853)

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1388–6150/$20.00
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Springer, Dordrecht, The Netherlands

however, was strongly convinced that white light was the simplest element (‘quinta essentia’), which, interestingly, was close to the subsequent concept of ‘elementary waves’ propounded about fifty years later by Huyghens in the wave theory of light. There, however, is incomplete information concerning Marci`s educational activities. He was the rector of the famous Charles University and, perhaps, introduced a word first specialization called ‘chimiatrie’, which was conceivably taught as an unusual subject with regards the traditional university disciplines: major ‘artes liberales’ and minor ‘artes mechanicae’ (i.e., learning common crafts such as warfare, navigation, business, agriculture, hunting, medicine or veterinary) but not in ‘artes incertae’ (that was a part of the habitually rejected ‘equivocal arts’ associated with occultism, which traditionally involved alchemy).

Some medivial alchemists and the introduction of caloric

When Rudolph the II (1552–1612) became the Emperor of the Holy Roman Empire and the King of Bohemia, he provided in Prague court a vital support to alchemists, astronomers and physicists. Among the most outstanding scientists were Tycho de Brahe (1546–1601) and Johannes Kepler (1571–1630) whose astronomical observations and calculations were published in the well-known Rudolphine tables. After the death of Tycho de Brahe, Johannes Kepler replaced his position of a royal mathematician in Prague in the year 1601. Using Tycho de Brahe’s data, Kepler determined elliptic orbit of Venus. In his 1609 treatise ‘Astronomia Nova’ Kepler published his two first laws, controlling the motion of planets and according to which the orbit of a planet/comet about the Sun is an ellipse with the Sun’s center of mass at one focus.

Foremost Czech physician and astronomer, Chef Medical Supervisor of the Kingdom of Bohemia at the court of Rudolph the II, was Thaddaeus Hagecius ab Hagek (Tadeáš Hájek z Hájků, 1525–1600) known as an author of several astronomical tractates and books on geodesy, botanics and medicine particularly acknowledged for the first concise book on the beer-making, ‘De cerevisia’ (1585). He essentially helped the flourishing period of alchemy and played a significant role in persuading Rudolph the II to invite Tycho de Brahe to come to Prague.

Special attention should be paid to the Czech thinker and Bohemian educator, latter refugee Jan Amos Comenius (Komenský 1592–1670). In his Physicae Synopsis, which he finished in 1629 (published first in Leipzig in 1633), he showed the importance of hotness and coldness in all natural processes. Heat (or better fire) is considered as the cause of all motions of things. The expansion of substances and the increasing the space they occupy is caused by their dilution with heat. By the influence of cold the substance gains in density and shrinks: the condensation of vapor to liquid water is given as an example. Comenius also determined, though very inaccurately, the volume increase in the gas phase caused by the evaporation of a unit volume of liquid water. In Amsterdam in 1659 he published a treatise on the principles of heat and cold [2], which was probably inspired by the works of the Italian philosopher Bernardino Telesius. The third chapter of Comenius’ book was devoted to the description of the influence of temperature changes on the properties of substances. The aim and principles of thermal analysis were literally given in the first paragraph of this chapter: citing the English translation [3] ‘In order to observe clearly the effects of heat and cold, we must take a visible object and observe its changes occurring during its heating and subsequent cooling so that the effects of heat and cold become apparent to our senses.’ In the following 19 paragraphs of this chapter Comenius gave a rather systematic description (and also a partially

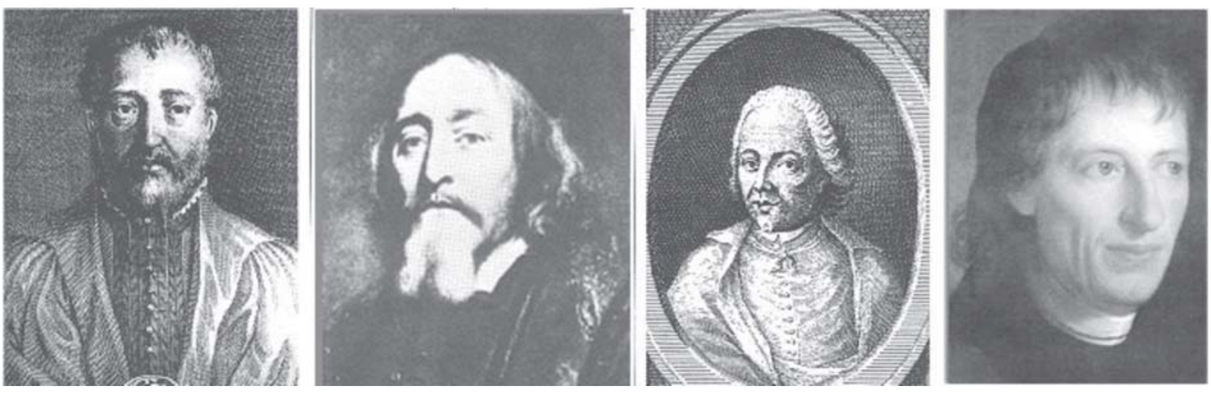

Fig. 2 From left: Hájek Tadeáš (from Hájků, 1526–1600), Komenský Jan Amos (Comenius, 1592–1670), Prokop Diviš (1696–1765) and Bolzano Bernard (1781–1848)

correct interpretation) of the effects of continuous heating and cooling of water and air, and also stressed the reversibility of processes such as, for example, evaporation and condensation, etc., anticipating somehow the concept of latent heat. Comenius concludes this chapter as follows: 'All shows therefore that both heat and cold are a motion, which had to be proved.' In the following chapter Comenius described and almost correctly explained the function of a thermoscope ('vitrum caldarium') and introduced his own qualitative scale with three degrees of heat above and three degrees of cold below the ambient temperature.

It is difficult to trace and thus hard to say if it was possible (though likely) to disseminate the idea of caloric from Amsterdam (when Comenius mostly lived and also died) to Scotland where a century later a new substance, or better a matter of fire, likewise called caloric (caloricum), was thoroughly introduced. It was assumed, e.g., that caloric creeps between the constituent parts of a substance causing its expansion. Although caloric differed from foregoing concept of phlogiston (because it could be later measured with an apparatus called a calorimeter) it is not clear who was the first using such an instrument. If we follow the studies of Mackenzie and Brush [4, 5] and Thenard [6] they assigned it to Wilcke. It, however, contradicts to the opinion presented in the study by McKie and Heathcode [7] who consider it just a legend and assume that the priority of familiarity of ice calorimeter belongs to Laplace who was most likely the acknowledged inventor and first true user of this instrument (likely as early as in 1782). In fact, Lavoisier and Laplace entitled the first chapter of their famous 'Mémoire sur la Chaleur' (Paris 1783) as 'Presentation of a new means for measuring heat' whereas the report of calorimetric employment by Black seemed to first appear almost a century later in the Jamin's Course of Physics (Mallet–Bachelier, Paris 1868).

Caloric was seen as an imponderable element with its own properties. Unfortunately, the great propagator, Joseph Black (and his student Irvine), published almost nothing in their own lifetimes [8] and their attitudes were mostly reconstructed from contemporary comments and essays published after their deaths. Black supposed that heat was absorbed by a body during melting or vaporization, simply because at the melting- or boiling- points sudden changes took place in the ability of the body to accumulate heat (~1761). Irvine's account that the relative quantities of heat contained in equal weights of different substances at any given temperature (i.e., their 'absolute heats') were proportional to their 'capacities' at that temperature and it is worth noting that the term 'capacity' was used by both Black and later also Irvine to indicate specific heats [8]. Black also introduced the term 'latent heat' which meant the absorption of heat as the consequence of the change of state.

Black's elegant explanation of latent heat to the young Watts became the source of the invention of the businesslike steam engine as well as the inspiration for the first research in theory related to the novel domain of thermochemistry, which searched for general laws that linked heat, with changes of state. Rumford presented qualitative arguments for such a fluid theory of heat with which he succeeded to evaluate the mechanical equivalent of heat. This theory, however, was not accepted until the later approval by Mayer and, in particular, by Joule, who also applied Rumford's theory to the transformation of electrical work. The use of customary units called 'calories' was coined by Clément, who was giving in 1824 the following definitions: a 'small calorie' allowed to increase by one degree the temperature of 1 g of water, whereas a 'large calorie' allowed to melt 1 g of ice. The word 'calorie' was then introduced into the vocabulary of academic physicists and chemists (Favre and Silbermann [9]) in 1845. The characterization of one kilocalorie as 427 kilogram-meters was launched by Mayer in the year 1845. The caloric-like description of heat as a fluid has survived, nevertheless, until today being a convenient tool for easy mathematical description of heat flows [3, 10–14]. Recently we tried to refresh the concept of caloric in the view of entropy and its connection to information [15].

Worth noting is the theory of Prokop Diviš (Divisch 1696–1765), which belongs to early pioneering times. Accordingly, 'Light of the First Day of Creation' is regarded to be identical with electricity, which is an inherent quality of all things, permeating the whole Universe and manifesting itself by electric and thermal phenomena [16]. Such an idea is, surprisingly, in an apparent agreement with the modern idea of electromagnetic zero-point background radiation [17].

Important role played the Prague Jesuit College of Clementinum and its famous library and observatory (opened in the 1720s) where about 1780 Antonin Strnad (1747–1799) laid the foundation to the oldest known series of systematic metrological observations. Worth noting are physicists and mathematicians Josef Stepling (1716–1778) and Jan Tesánek (1728–1788) who published many original studies and initiated publishing of Prague edition of Newton's 'Principia' supplemented with his own commentaries, in that time best edition reasoned with better mathematical background.

Renaissance of Prague physics

The first half of the 19th Century mathematical and physical studies in Prague became again on a par with

Fig. 3 From left: Václav Šimerka (1819–1887), Friedrich Reinitzer (1857–1927), Ernest Mach (1838–1916), Albert Einstein (1879–1955)

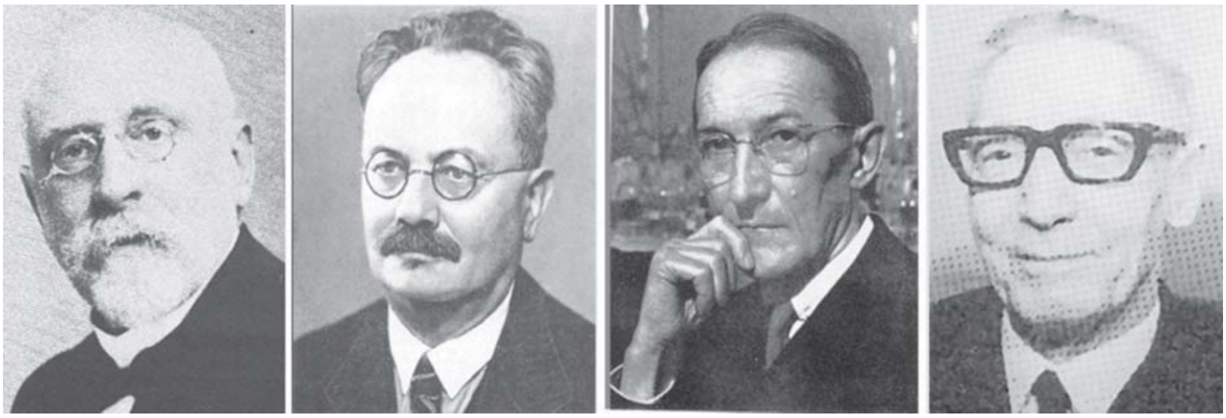

Fig. 4 From left: Čeněk Strouhal (1850–1922), František Záviška (1879–1945), Jaroslav Heyrovský (1890–1967), Stanislav Škramovský (1901–1983)

the world science. Important role paid some scientists such as František J. Gestner (1756–1832) who is also known as a pioneer of the railway transport in Europe. Excellent achievements are duly associated with the name of Bernard Bolzano (1781–1848) particularly in mathematical logic and analysis and with his friend Christian Doppler (1803–1853) who came to Prague from Vienna in 1829. His famous paper was inspired by astronomical phenomenon: the components of many binary stars differ from each other in color. Though, according to present knowledge, the observed color difference is due to the difference of surface temperatures and not to the difference in radial velocities, the principle itself is correct, being verified, e.g., in acoustics and optics. In 1867 arrived to Prague Ernest Mach (1838–1916) and spent there nearly 30 years. He is known for his discussion of Newton's Principia and critique of conceptual monstrosity of absolute space in his book 'The Science of Mechanics' (1883). Mach encouraged and inspired one of his students (later professor of theoretical physics) Jan Koláček (1851–1913) to study some of his hypothesis later approving that the Mach's theory correctly describes the dispersion of light, dichroism and circular birefringence. The Mach successor at Prague German University was Ernst Lecher (1856–1926) who is well known for his research on electromagnetic waves (i.e. Lecher wires). Mach also analyzed conceptual basis of calorimetry from more general, almost philosophical, point of views [18]. His influence on the further development of physics was tremendous and he established a mathematically specialized school – a great deal of his attention devoted to optics and acoustics. One of his personal scientific contacts was Czech famous Jan E. Purkyně (1787–1869) internationally known for discoveries in physiology. Another young assistant of Mach was Čeněk Strouhal (1850–1922), later first Czech professor appointed for experimental physics. His studies in acoustic are well known and the Strouhal's number concerning friction tones (oscillation) is named after him. He wrote and exceptional book on heat called 'Thermics' [19].

Czech priest (and, unfortunately, rather unknown mathematician) Václav Šimerka (1819–1887) introduced quantitative evaluation in psychology (logarithmic connotation of feelings) providing early basis for the theory of information [20]. Czech-born Friedrich Reinitzer (1857–1927) is famous as the discoverer of cholesterol (including its metamorphosis and stoichiometry formulae $C_{27}H_{46}O$) and is also known for his pioneering work in the field of liquid crystals (latter widespread by O. Lehmann). Bohumil Kučera (1874–1921) examined effect of electrical polarization on surface tension in the interface of two liquids prompting the idea of a new technique latter known as the drop-weight method, which provided physical basis for a new, today widely utilized, analytical method called polarography [21] as introduced by Jaroslav Heyrovský (1890–1967), which was awarded by Nobel price in 1959 [22].

An original development of weight measurements is connected with the name Stanislav Škramovský (1901–1983), who, at the Charles University, investigated thermal decomposition of complex oxalates which led him in 1932 to his own construction of an apparatus named 'stathmograph' (from Greek 'stathmos'=mass, weight) [23] that made it possible to measure mass changes. Independently, in the same time Duval used for his way of weight measurements the Latin-based term 'thermogravimetry' that later became generally accepted in thermal analysis. As the principle scheme of the stathmograph instrument is not generally known, it is perhaps worth mentioning to describe the arrangement. Škramovský placed a weighted sample into the drying oven on a dish suspended on a long filament passing through a hole in its upper wall (forming the balance case) and hooked to the left arm of an analytical balance. A mirror attached to the beam was reflecting the image of a light slit into a slowly rotating drum lined with photosensitive paper. The unwanted vibration was reduced by an attached glass rod immersed into paraffin oil and temperature was registered automatically by means of a mercury thermometer provided by platinum contacts distributed along the whole length of capillary.

A most prominent personality, which spent fruitful time in Prague was Albert Einstein (1879–1955) [24], a German physicist, originator of theories of relativity, laws of motion and rest, simultaneity and interrelation of mass and energy, quantum theory of photoelectric effect, theory of specific heats, Brownian motion, etc. (see the book 'Builders of the Universe' 1932). In 1911 he obtained his first professorship at theoretical physics at the German University of Prague where he closely cooperated with his friend professor of mathematics, Georg Pick (1859–1942). While in Prague he published 11 papers, most extensive being the survey of the theory of specific heats and very important were studies related with his favorite problem – the interaction of radiation with matter and effort to construct a relativistic theory of gravitation [25].

Worth noting is the so-called Planck-Einstein transformation formula for temperature which reads $T=T_0\sqrt{[1-(v/c)^2]}$ [25] and is possibly related to the previous dissertation work by K. von Mosengeil, posthumously published in Ann. Physik 22 (1907) 867. It means that the temperature of a body observed from the system moving with a relative velocity, v, is lower than the temperature in rest system. Basing on this idea in the article published in Ann. Physik 26 (1908) 1, Planck assumed that the First and Second Law of thermodynamics keep their form in all inertial frames. In the year 1953, however, Einstein wrote a letter to M. von Laue in which he doubts the correctness of this formula and rather speculated about a formula used inverse (temperature as observed in moving system is higher). This statement, which was later proved by H. Ott [26], thus reads as $T=T_0\sqrt{[1-(v/c)^2]}$. In both these cases information about the temperature is regarded to be mediated by the coherent electromagnetic radiation. Interestingly, in the case, where temperature is considered to be essentially local property and the thermometer reading is transferred to moving system, e.g., by means of digital coding, the temperature, in the contrast to both above formulae, must be considered as ralativistically invariant.

Another distinguished, but unjustly not very appreciated, savant born in Prague was Reinhold Fürth (1893–1979) who devoted his scientific life to the research into the fundamentals of statistical physics [27]. Besides an extensive work concerning Brownian motion and noise phenomena he is also author of stochastic interpretation of quantum mechanics [28]. Accordingly to this theory, the Schrödinger equation is nothing but the classical diffusion equation with complex diffusion constant $\sim j\hbar/2m$. This statement became later a corner–stone of so-called stochastic electrodynamics, which provides an alternative to quantum mechanics [29].

One of the outstanding teachers, who earned great merit for introducing modern theoretical physics and thermodynamics to the curriculum of Charles University, was Frantisek Záviška (1879–1945). One of his textbooks was the first monograph on relativity published in Czech and he is an author of excellent books on thermodynamics [30]. He also concerned waveguides and independently deduced relevant theory early before the microwave technique became important. Other notable physicist was Augustin Žáček (1886–1961) who studied damped electromagnetic oscillations in vacuum electronic systems. His extended studies culminated at 1924 in the discovery of the principle of magnetron, later becoming the basis of radar systems.

The historical development and use of the methods of thermal analysis in the territory of former Czechoslovakia is linked with the names Otto Kallauner (1886–1972) and Jospeh Matějka (1892–1960) who introduced thermal analysis as the novel technique during the period of the so-called 'rational analysis' of ceramic raw materials [31]. Much credit for further development of modern thermal analysis is attributed with Rudolph Barta (1897–1985) who stimulated his coworkers (Vladimír Šatava) and his students (Jaroslav Šesták) at the Institute of Chemical Technology in Prague (the latter mentioned names became also initiators of the foundation of the International Confederation for Thermal Analysis in the year 1965 [32]).

Some other details were published elsewhere [31–34].

Acknowledgements

This study was supported by the grant No. A100100639 of the Grant Agency of the Academy of Sciences of Czech Republic and the Institutional FZU research plan No. AVOZ10100521 and the UWB project MSMT No. 4977751303.

References

1 M. Marci, 'De proportione motu', Prague 1639.
2 J. A. Comenius, 'Disquisitiones de Caloris et Frigoris Natura', Amsterdam 1659.
3 J. Šesták, 'Heat, Thermal Analysis and Society', Nucleus, Hradec Králové 2004.
4 R. C. Mackenzie, 'History of Thermal Analysis', special issue of Thermochim. Acta, 73 (1984).
5 S. G. Brush, 'The Kind of Motion we call Heat'. Vol. I & II , North Holand, Amsterdam 1976.
6 L.Thenard, 'Treatise of Chemistry' 6^{th} edition, Crochard, Paris 1836.
7 D. McKie and N. H. V. Heathcote, 'The Discovery of Specific and Latent Heats', Arnold, London 1935.
8 R. Fox, 'The Caloric Theory of Gases: from Lavoisier to Regnault', Claredon Press, Oxford 1971.
9 P. Favre and J. Silbermann, C. R. Acad. Sci., 20 (1845) 1567.
10 R. Clausius, 'Mechanische Wärmetheorie', Vieweg u. Sohn, Braunschweig 1876.
11 J. M. Socquet, 'Essai sur le calorique', Paris 1801.
12 P. Kelland, 'Theory of Heat', Cambridge 1837.
13 R. B. Lindsay, 'Energy: historical development of the concept', Dowden, Stroudburg 1975.
14 J. J. Mareš, J. Therm. Anal. Cal., 60 (2000) 1081.
15 J. J. Mareš and J. Šesták, J. Therm. Anal. Cal., 82 (2005) 681.
16 P. Divisch, 'Längst verlangte Theorie von der meteorologischen Electricite, Magiam Naturalem benahmet', J. H. P. Schramm, Tübingen 1765.
17 M. Sparnaay, 'Historical Background of the Casimir Effect' in 'Physics in the Making' (A. Sarlemijn, M. Sparnaay, Eds), Elsevier, Amsterdam 1989.
18 E. Mach, 'Die Principien der Wärmelehre', Leipzig 1896.
19 Č. Strouhal, 'Thermika' (Thermics), JČMF, Praha 1908 (in Czech).
20 P. V. Šimerka, 'Síla přesvědčení: pokus v duchovní mechanice' (Strength of conviction, an attempt to mental mechanics), Časopis pro pěstování matemat. fyziky, 11 (1882) 75 (in Czech); A. Pánek, 'Život a působení Šimerky' (Šimerka's life and actuation), Časopis pro pěstování matemat. fyziky, 17 (1888) 253 as well as J. Fiala in 'Jubilejni Almanach JCSNF', Praha 1987, p. 97.
21 J. Heyrovsky, 'Poralographie', Springer, Vienna 1941.
22 J. Janta and J. Niederle (Eds), 'Physics and Prague', Academie, Prague 2005.
23 S. Škramovský, Chemické Listy, 26 (1932) 521 (in Czech).
24 J. Bičák, Čes. Čas. Fyz., A29 (1979) 222 (in Czech).
25 A. Einstein, Jhb. Radioact. Electron, 4 (1907) 411.
26 H. Ott, Z. Phys., 175 (1963) 70.
27 J. J. Mareš, J. Šesták, J. Stávek, H. Ševčíková, J. Krištofik and P. Hubík, Physica, E29 (2005) 145.
28 R. Fürth, Z. Phys., 81 (1933) 143.
29 J. J. Mareš, J. Stávek and J. Šesták, J. Chem. Phys., 121 (2004) 1499.
30 F. Záviška, 'Termodynamika' (Thermodynamics), JČMF, Praha 1943 (in Czech).
31 I. Proks, 'Evaluation of the Knowledge of Phase Equilibria' first chapter in the book 'Kinetic Phase Diagrams' (Z. Chvoj, J. Šesták, A. Tříska, Eds), Elsevier, Amsterdam 1991.
32 J. Šesták, 'Some historical aspects of thermal analysis: origin of Termanal and ICTA' in the proceedings of Termanal 2005, p. 3 (Eds E. Klein, E. Smrčková, P. Šimon).
33 P. Cardillo, J. Therm. Anal. Cal., 72 (2002) 7.
34 J. Šesták, 'Science of heat and Thermophysical Studies: a generalized approach to thermal analysis', Elsevier, Amsterdam 2005.

DOI: 10.1007/s10973-006-8210-1