



Editorial

Making impact in thermal sciences: Overview of highly cited papers published in Thermochimica Acta

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ABSTRACT

Thermochimica Acta has been serving the thermal science community for 40 years and has now published its 500th volume. The editors provide a brief overview of the highly cited papers published by the journal. Analysis of the topics of the highly cited papers suggests that Thermochimica Acta possesses major strength in the areas of instrumentation, materials, and kinetics.

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1. Introduction

Thermochimica Acta has been serving the thermal science community for 40 years and has now issued its 500th volume. It is an opportune time to evaluate the major strengths of our journal and the impact it has been making in the field of thermal sciences. We can do this by looking at the Thermochimica Acta papers that have been highly cited since the journal inception in 1970. The numbers of citations are readily available through Scopus[®],¹ an Elsevier abstract and citation database of peer-reviewed literature [1]. We have looked at the papers that generate largest numbers of citations in the three categories: (1) the total number of citations since publication; (2) the average number of annual citations since publication; and (3) the average number of annual citations of the papers published since 2005. The papers having more than 100 total citations or more than 10 annual citations have been conditionally viewed as making the long term impact. On the other hand, the papers having more than 5 annual citations since 2005 have been used to identify today's hot topics. A brief overview of the resulting papers suggests that they can be combined roughly in three general topics: instrumentation, materials, and kinetics.

2. Instrumentation

As stated by the first editor of Thermochimica Acta, Wendlandt, in his editorial to the first issue of the journal "The subject matter of Thermochimica Acta is primarily the applications of calorimetric and thermoanalytical techniques to research problems. . ." [2]. However, since the very beginning the development of new and improved calorimetric and thermoanalytical techniques has been as important a topic as their applications. The number of publications in the area of instrumentation peaked in the 1990th with

the hot discussions about temperature modulated differential scanning calorimetry (TMDSC) and related techniques. A mathematical description of TMDSC was published by Wunderlich in his 1994 paper [3] (321 total, 20 annual citations) that so far has collected the largest total number of citations among all Thermochimica Acta papers. The controversy was heated by a 1994 paper by Reading [4] (218 total, 14 annual citations) and two 1995 papers by Schawe [5] (156 total, 10 annual citations) and [6] (129 total, 9 annual citations). Beside regular papers Thermochimica Acta has published a number of topical special issues. The 1997 special issue "Temperature Modulated Calorimetry" [7] (818 total, 63 annual citations) is presently the most cited special issue of the journal. Later on, more than 150 papers making use of TMDSC were published in Thermochimica Acta. The most cited out of this group is a 1995 paper by Van Assche [8] (101 total, 7 annual citations) about isothermal cure of a thermosetting system.

In calorimetry and thermal analysis, calibrations are essential for obtaining reliable data. Several approaches to instrument calibration as well as recommendations for calibration standards have been published over the past 40 years. The activities of the ICTAC working group "thermochemistry" were summarized in a 1999 paper [9] (253 total, 23 annual citations) on reference materials for calorimetry and differential thermal analysis. A working group of the German Society for Thermal Analysis (GEFTA) published in the early 1990th a series of papers about temperature and caloric calibration of differential scanning calorimeters (DSC), e.g. [10] (101 total, 6 annual citations).

In addition to the aforementioned topics, new approaches to calorimetry, thermal analysis, and thermodynamics have been widely presented in Thermochimica Acta. In 1980, Townsend and Tou published a paper on "Thermal hazard evaluation by an accelerating rate calorimeter" [11] (144 total, 5 annual citations). The technique of transformation rate controlled thermal analysis was discussed by Rouquerol in his 1989 paper [12] (117 total, 6 annual citations). Beside the "classical" calorimetric and thermoanalytical techniques new approaches were presented as well. Landry [13] (30 total, 6 annual citations) described experimental considerations

¹ Please note that abstract records in Scopus cover references from 1996 onward, while abstract records go back to as far as 1966. This might have implications for the number of citations to articles published before 1996.

for thermoporometry measurements by means of DSC. Lupascu et al. [14] (30 total, 6 annual citations) reported calorimetric experiments on nanometer thin polymer films. Minakov et al. [15] (21 total, 5 annual citations) made use of chip based calorimeters for ultra-fast scanning measurement. Keshavarz [16] (29 total, 6 annual citations) proposed a simplified procedure for determining heats of detonation. Zeitler et al. [17] (25 total, 5 annual citations) attracted readers of *Thermochimica Acta* with a paper about terahertz spectroscopy of carbamazepine. Schartel et al. [18] (15 total, 5 annual citations) presented “pyrolysis combustion flow calorimeter” as a tool to assess flame retarded materials.

In recent years several new topics have attracted a great deal of interest. These include: determination of enthalpies of sublimation [19] (72 total, 12 annual citations) and [20] (11 total, 6 annual citations), thermal properties of phase change materials [21] (23 total, 8 annual citations) and nanofluids [22] (13 total, 6 annual citations), nanocomposites [23] (15 total, 5 annual citations), and ionic liquids, e.g. [24] (40 total, 8 annual citations) and [25] (26 total, 5 annual citations). Furthermore, thermodynamic properties of materials have been of a considerable interest to the readers of *Thermochimica Acta*. In 1977 Jacob and Fitzner published a paper about thermodynamics of ternary alloys [26] (130 total, 4 annual citations). A thermodynamic model of binary solvent was published by Acree Jr. [27] (123 total, 7 annual citations) in 1992. Johari and Andersson discussed vibrational and relaxational properties of crystalline and amorphous ices in their 2007 paper [28] (15 total, 5 annual citations).

3. Materials

A large number of high impact papers published in *Thermochimica Acta* deals with the study of composite materials. Xie et al. [29] (107 total, 12 annual citations) studied organically modified montmorillonite nanocomposites, showing an outstanding combination of stiffness, strength and weight. Since many of these materials are used as heat and fire barriers, the combined use of thermal analysis, infrared, and mass spectrometry techniques provides useful information about the thermal stability and the degradation products. To improve the thermal stability of similar systems, Awad et al. [30] (85 total, 14 annual citations) used XRD, TGA and thermal desorption mass spectroscopy to study alkyl-imidazolium-treated montmorillonite clays, and found them to have better thermal stability than the alkyl-ammonium analogues. A detailed study of the factors influencing the thermal stability of polymer/montmorillonite nanocomposites and the role played by different polymeric matrixes has been reported by Leszczyska et al. in two recent review papers [31,32] (46 and 29 total, 15 and 10 annual citations, respectively). Modification of montmorillonite with an oligomeric surfactant and blending it with polyethylene and polypropylene was used also to improve the fire resistant properties of these polymers that demonstrated a reduction of 40% in peak heat release with only 5% inorganic clay loading [33] (31 total, 6 annual citations). Montmorillonite functionalised with a zwitterionic surfactant was incorporated in poly(methyl methacrylate), PMMA, by emulsion polymerization [34] (29 total, 7 annual citations), and showed a glass transition temperature 18 °C higher than for virgin PMMA, whereas an increase of only 10 °C was found for *in situ* polymerization. Thermal degradation of commercial organoclays has been also studied [35] (17 total, 6 annual citations); their decomposition pattern, onset of the decomposition and composition of evolved gases depend on degradation of both tallow residue and unexchanged surfactant. Other composites studied were alumina and zirconia-reinforced silicon rubber [36] (25 total, 5 annual citations), to be used as elastomeric thermal pads, which showed increased thermal stability of the silicone

rubber. Compared to pristine polyaniline (PANI) its zirconia composites have also demonstrated improved thermal stability due to the interaction between PANI and ZrO₂ that restricts the mobility of PANI chains and shields the degradation of PANI [37] (21 total, 5 annual citations). Finally, oxidative reaction of cellulose with sodium methaperiodate and UV light treatment is reported [38] (30 total, 6 annual citations) to initiate a grafting process that helps to improve the thermal stability of textiles as shown by TGA.

Fina et al. [39] (36 total, 9 annual citations) have explored the mechanism of the thermal degradation of polyhedral oligomeric silsesquioxanes cages, differing in attached groups (hydrogen, methyl, isobutyl, octyl, phenyl, and vinyl). Chrissafis et al. [40] (25 total, 6 annual citations) have shown that the molecular weight of aliphatic polyesters synthesized from succinic acid and ethylene glycol is strongly related to the thermal stability of the initial oligomers. TGA runs have demonstrated that the samples with different molecular weights are characterized by different thermal stability, related to their intrinsic viscosity, whereas kinetic analysis has revealed that the thermal degradation is more complex for polyesters with low molecular weight than that of those with high molecular weights.

Thermal properties of hydrophilic polymers are determined by their interaction with water that has been shown [41] (109 total, 9 annual citations) to take place via several different mechanisms. The thermal behaviour of chitosan blends has been studied by Pawlak and Mucha whose two papers deal with the degradation kinetics [42] (98 total, 14 annual citations) and the macromolecular dynamics [43] (31 total, 6 annual citations) of these systems. The effect of the chemical structure of poly(ethylene succinate) and poly(butylene succinate) on the kinetics and mechanisms of their thermal decomposition has been studied by DSC, TGA and ¹H NMR [44] (28 total, 6 annual citations).

The thermal decomposition of B–N–H compounds (viz., NH₃BH₃ and (H₂BNH₂)_x) has been examined by Wolf et al. [45] (107 total, 11 annual citations) who used DSC and TGA-FTIR techniques to demonstrate that the process occurs exothermally and accompanied by a release of 2.2 mol H₂/mol BH₃NH₃ [46] (96 total, 12 annual citations). Milling and/or doping (with hexachloroplatinate) have been found [47] (26 total, 7 annual citations) to affect the kinetic parameters of the decomposition of BH₃NH₃. Polymeric aminoborazine, (H₂BNH₂)_x, can be isolated below 100 °C during the thermal decomposition of solid borazane [48] (42 total, 8 annual citations). The product undergoes the thermal decomposition at 100–230 °C, releasing an additional mole of H₂ per mole of H₂BNH₂ unit.

Thermal decomposition of ammonium perchlorate has been thoroughly reviewed by Boldyrev [49] (29 total, 7 annual citations). As reported by Wang et al. [50] (42 total, 8 annual citations) NiO nanoparticles catalyze the reaction, decreasing the decomposition temperature and increasing about three times the heat of decomposition. The nanoparticles demonstrate better catalytic efficiency than regular particles.

Nanocrystalline boehmite obtained by hydrolysis of aluminum sec-butoxide has been treated thermally to prepare alumina whose surface properties are found [51] (28 total, 6 annual citations) to mostly depend on the acid concentration used for peptization during the synthesis. One of the factors determining the activity of heterogeneous catalysts is the size and shape of their pores, usually determined from nitrogen adsorption isotherms by the Barrett–Joyner–Halenda method. Brun et al. have proposed [52] (208 total, 6 annual citations) an alternative procedure, the so-called thermoporometry, which makes use of microcalorimetry. Microcalorimetry has also been utilized to monitor bimolecular dehydration of methanol to dimethyl ether in the presence of heterogeneous catalysts that have also been characterized in terms of the surface acidity and coke formation [53] (29 total, 6 annual citations).

Thermal properties of ionic liquids (IL) have received much attention. DSC and TGA-SDTA have been used to study several imidazolium salts [54] (226 total, 23 annual citations), indicating that the thermal decomposition can be endothermic as well as exothermic for inorganic and organic anions, respectively. Thermochemical properties of IL determine their use as heat-transfer fluids and large-scale solar energy collectors [55] (83 total, 17 annual citations). Thermal decomposition takes place above $\sim 230^\circ\text{C}$ [56] (27 total, 7 annual citations), although it has been claimed [57] (65 total, 11 annual citations) that experimental conditions during laboratory measurements of thermal stability can overrate the range of thermal stability.

The presence of water in pharmaceutical hydrates influences the intermolecular interactions and crystalline disorder, as concluded from the application of isothermal microcalorimetry and other techniques [58] (138 total, 9 annual citations). Microcalorimetry and solution calorimetry have been used by Giron [59] (197 total, 13 annual citations) to determine thermodynamic data, to produce modifications and to distinguish between polymorphs, solvates and impurities. Extraction of metal cations from aqueous solutions by silica surfaces grafted with N-containing anchoring units was followed by calorimetry, and the thermodynamic parameters of the process were determined [60] (32 total, 6 annual citations). Thermal conductivity measurements on nanofluids (nanometer-sized particles dispersed in a base fluid) show that the volume fraction of nanoparticles affects both conductivity and stability of these new engineering materials [61] (22 total, 7 annual citations). DSC studies of the melting behaviour of aluminum nanoparticles covered with an oxide passivation layer has revealed a relationship between particle size and melting response as well as the role played by the oxide shell [62] (19 total, 6 annual citations). The aggregation behavior and thermodynamic parameters of pure cationic surfactants (quaternary salts) in water have been measured by different methods [63], including differential conductivity measurements used for obtaining precise values of the critical micelle concentration.

4. Kinetics

Kinetics has been a major topic of our journal since its inception. As a matter of fact, the first issue of *Thermochimica Acta* published in 1970 contained 13 research papers of which 3 were devoted to kinetics. Of the early kinetics papers, two publications have made a major impact. It is a 1971 paper by Sestak and Berggren [64] (270 total, 7 annual citations) and a 1976 paper by Sourour and Kamal [65] (190 total, 6 annual citations). Both papers have proposed generalized kinetic models. The Sestak-Berggren model has dealt with the kinetics of solid-state reactions, whereas the Sourour-Kamal model has dealt with kinetics of epoxy curing. A significant impact (109 total, 5 annual citations) has been made by a 1986 paper of Madhusudanan et al. [66]. It is devoted to improving the accuracy of approximations to the temperature integral. Back then the issue was of critical importance because neither personal computers nor user-friendly software for numerical integration were as readily available as they are today. The problem of the temperature integral approximations has been critically reviewed in the significant paper (127 total, 10 annual citations) by the pioneer of thermal analysis kinetics Flynn [67]. In this 1997 paper, he has concluded that “in this age of vast computational capabilities, there is no valid reason not to use precise values for the temperature integral when calculating kinetics parameters”. Indeed, modern methods of kinetic computations make use of accurate numerical integration.

A major impact (270 total, 25 annual citations) on the field of the thermal analysis kinetics has been made by a 1999 paper of Vyazovkin and Wight [68], who have compared two computational

approaches to kinetic evaluations: an approach that uses fitting reaction models to single heating rate data and an isoconversional approach that eliminates the model-fitting step by using multiple heating rate data. The paper has demonstrated the fundamental flaws of the popular single-heating rate methods and has played a critical role in promoting isoconversional methods that were used far more rarely. This paper has so far gained the largest number of average annual citations among all *Thermochimica Acta* papers. An important paper (125 total, 18 annual citations) by Starink [69] has comprehensively compared the accuracy of various isoconversional methods and provided a guidance on their practical use. Although isoconversional methods allow the activation energy to be evaluated without determining the reaction model, the latter can be established by using several computational procedures. One of the most popular procedures has been described in the influential paper (171 total, 10 annual citations) by Malek [70]. The kinetic approach developed by Malek has been successfully adjusted to kinetic analysis of crystallizations in amorphous materials [71]. The 2000 paper by Malek [71] has made a significant impact on the field as indicated by 114 total and 11 annual citations.

Among highly cited (220 total, 22 annual citations) is a paper that summarizes the results of the ICTAC kinetics project [72] as well as the papers of several individual participants of the project: Vyazovkin [73] (180 total, 18 annual citations), Maciejewski [74] (128 total, 13 annual citations), and Burnham [75] (105 total, 11 annual citations). The most important message of these publications is that reliable kinetic computations should use multiple data sets obtained at different temperature programs, whereas the methods based on a single heating rate data set must be avoided.

There have been a number of hot kinetic papers published since 2005. A paper by Papageorgiou et al. [76] devoted to the crystallization kinetics of polypropylene – SiO_2 composites has been cited 68 times at an average rate of 14 citations per year. Another hot paper (23 total, 6 annual citations) is that by Cheng et al. [77] deals with crystallization kinetics of Bi_2O_3 – B_2O_3 glasses. A significant impact (21 total, 5 annual citations) is being made by a paper by Pineau et al. [78] who report the results of a comprehensive kinetic study of reduction of iron oxides by H_2 .

Among the hot papers a notable impact is being made by several papers devoted almost entirely to the applications of isoconversional kinetic analysis. A paper by Khawam and Flanagan [79] (35 total, 7 annual citations) explores the nature of the variation in the activation energy as a function of the conversion. A work by Saha et al. [80] (25 total, 6 annual citations) deals with isoconversional analysis of isothermal and non-isothermal decomposition polyethylene terephthalate samples. Isoconversional kinetic analysis of stoichiometric and off-stoichiometric epoxy-amine cures has been reported by Sbirrazzuoli et al. [81] whose paper has been cited 22 times at an average rate of 6 annual citations. A study by Jankovic et al. [82] (16 total, 5 annual citations) demonstrated advantages of isoconversional analysis as applied to the kinetics of non-isothermal dehydration of equilibrium swollen poly(acrylic acid) hydrogel.

5. Summary and outlook

Thermochimica Acta has been a source of highly cited papers especially in the areas of instrumentation, materials and kinetics. Its ISI impact factor has been growing continuously and has recently reached 1.659. The increase in impact is largely due to the journal's emphasis on publishing papers that have a strong scholarly motivation and report results of high relevance and significance. Regrettably, not all manuscripts submitted match these criteria, and the current rejection rate is 53%. According to the latest Journal Citation Reports® [83], only 8% of cites generated by Ther-

Thermochimica Acta have been “self-cites”, i.e., originated from papers published in our journal. The impact factor without self-cites is 1.518. This particular structure of the impact factor suggests that *Thermochimica Acta* makes significant scholarly impact beyond the tightly knit thermal analysis community. For comparison, the *Journal of Thermal Analysis and Calorimetry*, whose most recent impact factor is 1.630, has generated 61% of self-cites so that its impact factor without self-cites is 0.625 [83].

The success of our journal arises from the joint effort of the authors, who submit high quality papers, the reviewers, who provide the authors with valuable critiques, the editorial board, who advises the editors on the journal strategies, the editors, who control the journal scope and handle evaluation of the manuscripts, and, last but not least, the publishers, who take care of timely publishing and efficient dissemination of information. Undoubtedly, all the parties have been working together successfully making important contributions to the development of *Thermochimica Acta* in terms of the impact, quality, and time to publication, which currently averages at 4.9 months. We look forward to this trend to continue through the years to come.

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