Chapter 5
Epilogue

Since no one knows the future, who can tell someone else what is to come?

Ecclesiastes 8:7

To conclude the book I would like to share some thoughts on the present status of the isoconversional kinetics and its future progress and challenges. Without a doubt, isoconversional methods currently present the major computational technique for exploring the kinetics of thermally stimulated processes. It should be noted that isoconversional methods started making a significant impact only about a decade ago. A descriptive picture can be obtained by comparing the numbers of citations to the three most popular isoconversional methods [1–4] with the three most popular single-heating rate methods [5–7]. The numbers shown in Fig. 5.1a indicate that the community started to prefer the isoconversional methods to the single-heating-rate ones only past 2004. Apparently, the change was inspired by the results of the International Confederation of Thermal Analysis and Calorimetry (ICTAC) 2000 Kinetic Project that officially recognized the deficiency of the single-heating-rate kinetic analyses [8–11].

The data also indicate (Fig. 5.1a) that the gap between the isoconversional and single-heating-rate methods is growing, although not fast enough. For example, when considering the six aforementioned highly popular methods, the citations to the single-heating-rate methods presently appear to be about one third of the total number of the citations (Fig. 5.1b). The actual fraction may be somewhat smaller because there are a number of newer isoconversional methods not included in the estimate. Nonetheless, it is quite unsettling to realize that 20–30 % of kinetic results reported in the current literature are still produced by single-heating-rate methods which are known to be flawed computationally and incapable of producing reliable kinetic data. While not exactly a problem of the isoconversional kinetics, the thermal analysis community at large definitely faces a challenge to convince the remaining devotees of the single-heating-rate methods to abandon their atavistic ways.

It is no secret that nowadays most of the isoconversional kinetics computations are conducted by the integral methods. Analysis of the literature citations to the integral isoconversional methods reveals another curious detail. The majority of workers prefer to use computationally outdated methods of Ozawa [2] and Flynn

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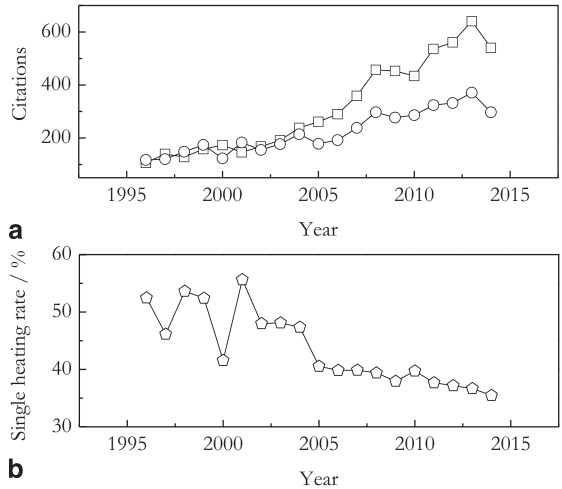


Fig. 5.1 **a** Number of citations to the three most popular single heating rate methods [5–7] (*circles*) and three most popular isoconversional methods [1–4] (*squares*) **b** Fraction of citations to the single heating rate methods [5–7]. Here and in Figures 5.2 and 5.3 the citations are found by using the Scopus database. For 2014, the citations represent first ten month of the year

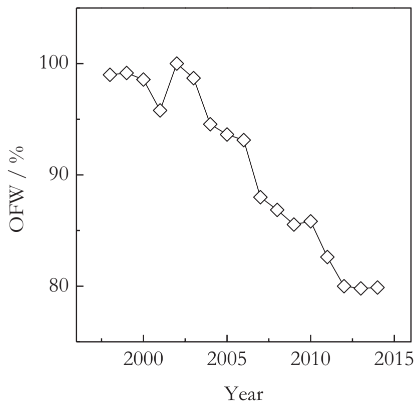
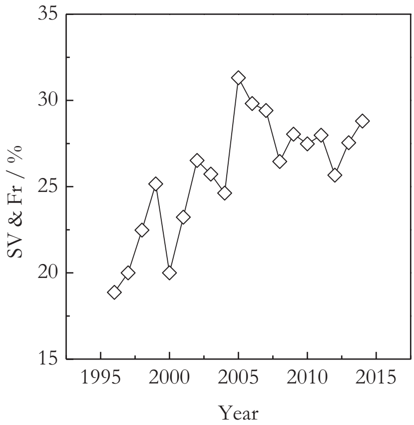


Fig. 5.2 Fraction of citations to the methods of Ozawa and Flynn and Wall (*OFW*)

and Wall [3, 4] to significantly more accurate methods discussed in Sect. 2.1.2. It is even more surprising that these crude methods are preferred to the methods of Starink [12] and of Kissinger–Akahira–Sunose [13] that are just as simple computationally but yield markedly more accurate results. Analysis of the citation data for these four methods is shown in Fig. 5.2. It is seen that among these four methods the fraction of Ozawa and Flynn–Wall methods steadily decreases but still remains at remarkably high 80 %. The need for broader use of the more accurate methods was strenuously emphasized in the ICTAC 2011 recommendations [14]. Certainly, further efforts are required to promote modern integral methods.

Closely related is the problem of promoting the isoconversional methods that can properly account for variation in the activation energy and are applicable to arbitrary

Fig. 5.3 Fraction of citations to the methods of Friedman (*Fr*) and Vyazovkin (*SV*)



temperature programs, including cooling. This is accomplishable by employing the good old method of Friedman as well as flexible integral methods (Sect. 2.1.2). Again, we can estimate the use of such methods by analyzing the literature citations. Of the flexible integral methods, so far only the Vyazovkin method [15] has generated significant number of citations. The fraction of citations to the Vyazovkin and Friedman methods among the total number of citations to these two methods and the four rigid integral methods (Ozawa, Flynn–Wall, Kissinger–Akahira–Sunose, and Starink) is still less than one third (Fig. 5.3). Although in many situations the use of the Friedman and flexible integral methods may not be necessary, it is important to continue reiterating the message of the ICTAC 2011 recommendations [14] that in certain cases it is mandatory. Such cases include the situations when data collected on cooling as well as when the sample temperature deviates significantly from the program temperature.

However important, the problems associated with computations only partially determine the progress of the isoconversional kinetics. For the most part, the progress has been and will be defined by searching and finding the links between the variation of the effective activation energy and the process mechanism. In this book, I have given many examples of how such links can be established for a variety of physical and chemical processes. In the area of chemical processes, such links have been explored successfully for years. On the other hand, the isoconversional kinetics of physical processes (phase transitions) is yet largely unchartered territory. That is why much of my effort in this book has been focused on this particular topic. Although this field is full of theoretical and experimental challenges, I believe that in the future, the kinetic exploration of physical processes will provide the biggest contribution to the progress of the isoconversional kinetics.

References

1. Friedman HL (1964) Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic. J Polym Sci Part C 6:183–195
2. Ozawa T (1965) A new method of analyzing thermogravimetric data. Bull Chem Soc Jpn 38:1881–1886
3. Flynn JH, Wall LA (1966) A quick, direct method for the determination of activation energy from thermogravimetric data. J Polym Sci B, Polym Lett 4:323–328
4. Flynn JH, Wall LA (1966) General treatment of the thermogravimetry of polymers. J Res Nat Bur Stand Part A 70:487–523
5. Freeman ES, Carroll B (1958) The application of thermoanalytical techniques to reaction kinetics. J Phys Chem 62:394–397
6. Horowitz HH, Metzger G (1963) A new analysis of thermogravimetric traces. Anal Chem 35:1464–1468
7. Coats AW, Redfern JP (1964) Kinetic parameters from thermogravimetric data. Nature 201:68–69
8. Brown ME, Maciejewski M, Vyazovkin S, Nomen R, Sempere J, Burnham A, Opfermann J, Strey R, Anderson HL, Kemmler A, Keuleers R, Janssens J, Desseyn HO, Li CR, Tang TB, Roduit B, Malek J, Mitsuhashi T (2000) Computational aspects of kinetic analysis. Part A: the ICTAC kinetics project-data, methods and results. Thermochim Acta 355:125–143
9. Maciejewski M (2000) Computational aspects of kinetic analysis. Part B: the ICTAC kinetics project—the decomposition kinetics of calcium carbonate revisited, or some tips on survival in the kinetic minefield. Thermochim Acta 355:145–154
10. Vyazovkin S (2000) Computational aspects of kinetic analysis. Part C: the ICTAC kinetics project—the light at the end of the tunnel? Thermochim Acta 355:155–163
11. Burnham AK (2000) Computational aspects of kinetic analysis. Part D: the ICTAC kinetics project—multi-thermal–history model-fitting methods and their relation to isoconversional methods. Thermochim Acta 355:165–170
12. Starink MJ (2003) The determination of activation energy from linear heating rate experiments: a comparison of the accuracy of isoconversion methods. Thermochim Acta 404:163–176
13. Akahira T, Sunose T (1971) Method of determining activation deterioration constant of electrical insulating materials. Res Report Chiba Inst Technol (Sci Technol) 16:22–31
14. Vyazovkin S, Burnham AK, Criado JM, Pérez-Maqueda LA, Popescu C, Sbirrazzuoli N (2011) ICTAC kinetics committee recommendations for performing kinetic computations on thermal analysis data. Thermochim Acta 520:1–19
15. Vyazovkin S (2001) Modification of the integral isoconversional method to account for variation in the activation energy. J Comput Chem 22:178–183