Thermochimica Acta, 203 (1992) xix–xxiv
Elsevier Science Publishers B.V., Amsterdam

Foreword to the collection of papers dedicated to J.H. Flynn and some philosophical thoughts regarding non-isothermal kinetics

Jaroslav Šesták and Věra Šesták'ová

Institute of Physics of the Czech Academy of Sciences, V stráni 3, 15000 Prague 5 (Czech and Slovak Federal Rep.)

(Received 18 November 1991)

Our friendship with Joseph H. Flynn and his family dates back to August 1968 when, during the course of the 3rd ICTA at Worcester, Czechoslovakia was invaded by Soviet troops. Joe's generous offer for Jaroslav to spend several days in his lovely home full of children in Bethesda helped to overcome Jaroslav's depression and anxiety about whether he would ever be able to return home. In spite of the fact that Věra later faced a secure future after she obtained her MS degree at the University of Missouri at Rolla, we ventured after two years in the USA to go back to Prague as we felt a personal responsibility for the survival under the communist dictatorship of our part of science (which was somehow indistinguishable from our old national cultural tradition). In December 1989, the Flynns' message was the first letter from abroad congratulating us on the victory of our "velvet revolution" which restored the country's tradition of pre-war democracy, the very reason for our return in the early seventies.

In between, we kept close contact on both scientific and personal bases during which we profited much from their moral support and Joe's superior ideas and articles, starting as early as his invention of the sectional method of kinetic evaluation [1] and the first review ever published on non-isothermal kinetics [2]. This was followed by articles such as an improvement of DSC theory [3,4] and up to his latest contribution to the general understanding of kinetics [5]. What is more, despite his being a serious scientist, he has a sense of humor which we very much appreciated, as exemplified by the inclusion of cartoons in his lectures on polymer relaxations, showing eggs aging, as well as a deep philosophical understanding of science as a useful part of human activity. His gentle and modest personality is well known to all members of the thermoanalytical family where we are not alone in enjoying his sincere friendship. At the age at which others retire he undertook the undesirable role of coordinating the rather heterogeneous interests and goals of thermal analysis kinetics, and he succeeded in establishing a valuable working party [6,7] which has already produced useful ideas and instructions, thus accomplishing his life's work of developing the modern understanding of non-isothermal kinetics.

During the past twenty years we felt the deep political isolation of our home country, entirely surrounded by an iron fence placed there unfortunately by our countrymen. However, the model of a giant "brain" precisely calibrating production to social need did not lead to economic salvation nor succeed as a general information (rather "propaganda") source. On the contrary a widespread diffusion of radios, underground literature and, later, small computers, videos and satellites, became responsible for progress, which made it practically impossible for the authorities to control the flow of information, especially political. Fortunately such an increasing flow of knowledge received from abroad, despite all the restrictions, made the fence obsolete. In the same way, however, we may put a fence around the laws of nature that we are trying to elucidate. Feeling freed by having now dismantled one fence, we must not diminish all that was done earlier, but neither can we get rid of all bad habits instantaneously, especially because we do not know precisely what is irreplaceable and what must be changed to survive, and often the ethical side is opposed to the economic one. Similarly we have adopted our scientific theories and experimentations, again fenced within our world of scientific countrymen, often saying that everything outside the fence is regarded as irrelevant and that everything inside is considered relevant. Breaking down the fence without regard to both previous knowledge and continuity will be meaningless and shortsighted.

Without repeating our previous thoughts [8,9] let us look at our world of kinetics and the frequent attempts to condemn most previous kinetic data without providing any new ideas and goals. We certainly are not going to get it right because of a change in our basic assumptions, dividing our theory into relevant and irrelevant. Most of them are, in fact, pleasant mystifications. It is the nature of science to give us only an approximation of what goes on inside the fence, and whether we treat kinetics on the basis of a tricky form of an exponential, or whether one sets out some other concepts, is a part of practical science in which we are always decoding a part of nature which is not complete. We simply cannot get away from our finiteness (such as function plasticity or parameter interrelations), although such a decoding can certainly lead to good laws. However, it never provides us with a conceptual picture of the nature of kinetics. One can admit that a change in the conceptual picture in the scientific world is a normal sign of progress because we have to extend the boundaries of the relevant future even further in our well-established kinetics. However, we do not yet know a better form in which to express a thermally activated process even on the basis of distribution statistics and/or probability attempts. Moreover when dropping into a deeper philosophy, none of our explanations can be true in the sense that there is no ultimate truth accessible, for the simple reason that we always have to make a certain compromise in the study of reaction kinetics in order to carry out an experiment or to develop a theory. We say isothermal or linear non-isothermal, but we speak about the thermal behavior of the surroundings and not about the entire reaction. We again have to decide what is relevant and irrelevant, being aware that any such decision we make is a conventional simplification enabling us to enjoy an imaginative and creative piece of guesswork.

Kinetics itself is not only a suitable formalizable system requiring certain assumptions, but it also exhibits the simplification that some parts lose full connectivity. In any strictly formal mathematical way, no kinetic theory embraces all questions that can be asked. In addition, if no longer distinguishing between reality and fiction (artifacts), we can equally prove and/or reject everything. Our often mechanistic approach is not a universal solution but a mere strategy for a better understanding. The determination of certain numerical values, whatever we call them, is only our best attempt to compare them with each other, although sometimes they are found to be irrelevant. Single-valued (centered) data produced by the thermoanalytical instruments we use are not relevant enough to obtain the multiple information necessary for structural kinetics study. Although often preferred, direct morphological observations are even worse owing to complications with sample preparation (such as reaction freeze-in uncertainty due to quenching or its distortion by surface polishing) and negligible (spot) representation. Therefore, we were pleased to receive here those articles which somehow tried to correlate these numerical values (still maintaining the conventional term of activation energy) obtained by various (even non-standard) techniques with respect to some physical-chemical aspects of solid state processes. Although still questioned, the importance of such activation energies as a certain representation of thermoanalytical measurements, has been shown to be indispensable. Most critical problems associated with dynamic kinetic measurements, however, have a general significance in many applied kinetic problems, including an impact on traditional equilibrium thermodynamics in the evaluation of metastable and kinetic phase diagrams [10] as a part of modern materials science [11]. It is to be remembered that kinetic studies were the bases for better understanding of technological processes yielding progressive materials such as hardened steels or toughened oxide ceramics [11].

Therefore, we were happy to welcome contributions from a variety of scientists in their specializations to document the utility of kinetics, not only in the different fields of science but also to show that it is widespread over all the continents. The subjects published extended from theoretical treatises to applications concerned not only with progressive preparative methods (such as alloy precipitations or superconductor formation) but also with the behavior of biological samples. One can easily recognize most of the distinguished names from the kinetics literature, as well as some "rising stars", all of them honoring the creative work of Joseph H. Flynn. One still finds contradictory and unsolved approaches so typical in the recent development of thermal analysis kinetics; these we included intentionally without broad restrictions and with minor review and editorial changes, in order to allow the reader to see what current kinetics is and what is still needed. In addition, it may be instructive to trace how much scientific naivety is still contained in some of the present kinetic communications.

Jaroslav, however, did not resist the temptation to add some of his very personal remarks. Having an invitation to read a plenary lecture at the ESTAC 5 (Nice 1991), he tried his best to take advantage of including updated ideas in cooperation with some top kineticists (the Rouquerols, Criado, Málek) in order to present an improved view of current non-isothermal kinetics [12]. Listening to the other lectures on this topic, Jaroslav got the feeling that he could easily repeat his 20 year-old lecture at the ICTA 3 in Davos, 1971 [13] or one of his fights against scepticism (involved mainly in spreading the negative side of non-isothermal kinetics) by formulating a dozen of the most pertinent questions and answers [8]. As the program chairman of the ICTA 8 in Bratislava 1985 [14], Jaroslav insisted upon the inclusion of non-isothermal kinetics among the specialized workshops [6] which, thanks to Joseph H. Flynn, later developed into regular working meetings. At the thermoanalytical conferences, however, approaches to thermal analysis kinetics emerge which have very little or no relation to overall thermoanalytical studies. They seem to the authors to be showing us "TA students" how kinetics is or can be complicated, instructing us in the texbook cases of elementary reactions (Boldyreva, ESTAC 5 Nice 1991 [15]) or showing known (but yet unsolvable) difficulties with gradients in solids (Jesenák, ICTA 8 Bratislava 1985 [16]). Furthermore, it became popular to emphasize irrationality whenever it could be found (Maciejewski, ESTAC 4 Jena 1987 and ESTAC 5 Nice 1991 [17]), already fashionable in the early seventies [18,19], and often repeating the already classical treatise on thermal analysis kinetics by Garn [20]; his book from 1964 can still be recommended to those who may trouble themselves to find it in the library, as are other classic papers [21].

This, however, is far from the actual need of solving the most marginal and yet most discussed problems of non-isothermal kinetics. Just to mention a few, these include the meaning of the isothermal and non-isothermal derivatives in the derivative equation (initiated by MacCallum and Tanner [22]), habitually repeated and misunderstood; the unrestricted use of kinetics models derived under strictly isothermal conditions (their non-isothermal form having been proved valid independently by Henderson [23], DeBruijn et al. [24] and Šesták [25]); or arithmetic manipulations involved in the temperature integration of the Arrhenius rate constant (first published as early as 1928 by Akahira [26]). The troublesome integration was also substituted by an approximation in the first non-isothermal evaluation method ever published [27] which recently celebrated its 40th anniversary [28]. Quite a few articles tackling this problem have yielded a simple evaluation method of plotting a model relation logarithm against reciprocal temperature (independently reported by Zsako [29], MacCallum and Tanner [30] and Šatava [31]), in which they in fact neglected the integration, nicely hidden behind ingenious mathematics involved in the approximation of the exponential integral ($p(x)$ function). This resembled the much earlier but rejected approach by Reich and Levi [32] who assumed that the exponential was a temperature constant, even in non-isothermal kinetics. There is another very recent problem hidden in the arbitrary use of advanced statistical algorithms for solving inappropriate cases; a certain primitiveness of kinetic evaluations can be found in even very expensive software accessories of very sophisticated all-computerized thermoanalytical instruments. It was my original wish to present here a comparison of all the available kinetic programs, asking the manufacturers to cooperate. However, I could not offer the same opportunity to all of them and so I leave this idea, as well as many other useful topics not included or even mentioned, for later processing.

So we have many things still left to analyze as vital goals of our future kinetic collections and kinetic meetings, hopefully to be mainly realized through the strong leadership of the ICTA Committee Chairman, Joseph H. Flynn. In this context we must appreciate even more Joe's realistic viewpoint of science and his firm attempts to give non-isothermal kinetics better standards and a better reputation. So let us wish him in his seventies all the best of health and humor and also a fortunate hand in steering our thermoanalytical kinetic family to a better understanding of kinetics and of our human relationships with one another.

REFERENCES

1 J.H. Flynn and L.A. Wall, Polym. Lett., 4 (1966) 323; 5 (1967) 191.
2 J.H. Flynn and L.A. Wall, J. Res. Nat. Bur. Stand., 70A (1966) 487.
3 C.H. Guttman and J.H. Flynn, Anal. Chem., 45 (1973) 408.
4 J.H. Flynn, Thermochim. Acta, 8 (1974) 69.
5 J.H. Flynn, J. Therm. Anal., 34 (1988) 365; 36 (1990) 1579.
6 J.H. Flynn, M. Brown and J. Šesták, Thermochim. Acta, 110 (1987) 101.
7 J.H. Flynn, M. Brown, E. Segal and J. Šesták, Thermochim. Acta, 148 (1989) 45.
8 J. Šesták, J. Therm. Anal., 16 (1979) 503.
9 J. Šesták, J. Therm. Anal., 33 (1988) 1263; ICTA Newsletter 22 (1988) 20.
10 J. Šesták and Z. Chvoj, J. Therm. Anal., 32 (1987) 1645.
11 Z. Chvoj, J. Šesták and A. Tříska, Kinetic Phase Diagrams, Elsevier, Amsterdam, 1991.
12 J. Málek, J. Šesták, F. Rouquerol, J. Rouquerol, J.M. Criado and A. Ortega, J. Therm. Anal., 38 (1992) 71.
13 J. Šesták, in Thermal Analysis, Vol. 1, Birkhauser, Basel, 1972, p. 3.

14 V. Balek and J. Šesták, special issue of Thermochim. Acta, 110 Thermal Analysis Highlights, Elsevier, 1987.
15 E. Boldyreva, J. Therm. Anal., 38 (1992) 89.
16 V. Jesenák, Thermochim. Acta, 92 (1985) 39.
17 M. Maciejewski, J. Therm. Anal., 33 (1988) 1269; 38 (1992) 51.
18 P.D. Garn, CRC Crit. Rev. Anal. Chem., 1972, p. 65.
19 B.S. Girgis, Trans. Br. Ceram. Soc., 72 (1972) 177.
20 P.D. Garn, Thermoanalytical Methods of Investigation, Academic Press, New York, 1964.
21 R.L. Reed, L. Webster and B.S. Gottfried, Ind. Eng. Chem. Fundam., 4 (1965) 38.
22 J.R. MacCallum and J. Tanner, Nature 225 (1970) 427.
23 W.D. Henderson, J. Therm. Anal., 15 (1979) 325; J. Non-Cryst. Solids, 30 (1979) 301.
24 T.W.J. DeBruijn, W.A. DeJoung and P.J. Van Der Berg, Thermochim. Acta, 45 (1981) 315.
25 J. Šesták, Thermal Analysis, ESTAC 2, Aberdeen, Heyden, London, 1981, p. 115.
26 T. Akahira, Sci. Pap. Inst. Phys. Chem. Res. Tokyo, 3 (1929) 181.
27 D.W. Van Krevelen, C. Van Heerden and F.J. Hutjens, Fuel, 30 (1951) 253.
28 J.M. Criado, J. Málek and J. Šesták, Thermochim. Acta, 175 (1991) 229.
29 M. Zsako, J. Phys. Chem., 72 (1968) 2406.
30 J.R. MacCallum and J. Tanner, Eur. Polym. J., 6 (1970) 1033.
31 V. Šatava, Thermochim. Acta, 2 (1971) 423.
32 L. Reich and D. Levi, Makromol. Chem., 66 (1963) 102.