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Early papers by Takeo Ozawa and their continuing relevance[1]

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Abstract

Eight of the early scientific papers of Takeo Ozawa are listed and their citations in journals are discussed. Some of them are cited with greater and greater frequency as the years go by. They and others of his early works still merit further attention by the scientific community. Their important features are summarized and their relevancy to present day thermal analysis, theory and application is evaluated.

Keywords: Differential scanning calorimetry; Differential thermal analysis; Diffusion; Kinetics; Non-isothermal crystallization; Polymer degradation; Takeo Ozawa; Thermal analysis; Thermogravimetry

1. Introduction

The acid test for a truly significant scientific paper is its continuing referral by the scientific community over the decades following its publication. A number of the early papers of Takeo Ozawa fit this category. Some of his early papers [1–8] are listed in Table 1. Their significance to present day thermal analysis kinetics will be the focus of this contribution.

A typical scientific paper may be cited a few times during the first ten years of its existence (often mainly by its author) and then it may disappear from the cited literature. As stated above, several of Ozawa's papers are in the process of becoming "timeless": interest in them is not abating, but, to the contrary, continues to rise even twenty or thirty years after their publication. (Unfortunately it appears that many authors just cite them without rereading them: it would be well for them to return their attention to these original papers as they would surely gain fresh insights into the fundamentals of thermoanalytical theory and techniques.) Also, as can be seen in Table 1, several of his early papers appear to have not yet received the notice by the scientific

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[1] Dedicated to Takeo Ozawa on the Occasion of his 65th Birthday.

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Table 1
Number of citations of some of the early papers by Takeo Ozawa (from Citation Index, 1965–1994)[a]

	Number of citations per five-year Period							
	[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]
1965–1969	8	7	n/a	n/a	n/a	n/a	n/a	n/a
1970–1974	34	4	9	5	n/a	n/a	n/a	n/a
1975–1979	46	2	23	11	8	12	4	3
1980–1984	74	5	60	23	2	10	4	13
1985–1989	107	8	95	41	4	16	9	19
1990–1994	169	4	149	73	3	20	12	14

[a] See References.

community that they merit. A short critical discussion of the significance of all of these papers follows.

In the 1960s and early 1970s, Ozawa was applying nonisothermal kinetics analysis to model functions for diffusion, random scission of polymers, crystallization kinetics, etc. Thus he was, quite properly, not merely trying to determine empirical kinetics parameters but also to establish reaction mechanisms. This, of course, was at a time when many workers in the field of thermal analysis were fully satisfied to misapply "first-order reaction rate kinetics" models to any and all thermal analysis reactions that they encountered.

Unfortunately, as far as the development of Thermal Analysis Kinetics is concerned, Ozawa had to refocus his talents for many years toward fuel cell development and other areas of science. However, recent literature indicates that in "retirement" he will be able to return to his "first love" and that thermal analysis kinetics will again be enriched by his special insights. (For examples of these more recent publications, see the Ozawa bibliography in this volume.)

Here we will briefly review the salient features and suggest some untapped potentials of eight of his papers in the period 1965–1976.

2. "A New Method of Analyzing Thermogravimetric Data" [1] (1965)

It is seen in Table 1 that this paper has become the most frequently cited of all of Ozawa's papers. This author can claim to be the first to point out its significance. When

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[1] The four pioneering papers for the Isoconversional Kinetics Analysis Methods were by Henry L. Freidman [10], Takeo Ozawa [1], Joseph H. Flynn [9], and Charles D. Doyle [11]. They were published in the years 1964–1966. Freidman was the first to propose an Isoconversional Method. His Differential Technique was presented at the Symposia, "Thermal Analysis of High Polymers", in 1963 and published in 1964. Ozawa's paper, the first published Integral Technique, was submitted February 23, 1965 and published November 1965 by the Bulletin of the Chemical Society of Japan. Flynn's paper, proposing a technique almost identical to Ozawa's, was submitted to Journal of Polymer Science, Polymer Letters, before December 1, 1965 and published in the following year. Doyle published the basic integral equation "to be used at two different heating rates" (equation 4–131, page 183) in his massive (and seldom cited) paper and review article, "Quantitative Calculations in Thermogravimetric Analysis", published in 1966.

I discovered in the 1966 Chemical Abstracts that a paper by Ozawa in the Bulletin of the Chemical Society of Japan [1] had, to a large extent, rendered redundant a paper of mine that had been accepted by the Journal of Polymer Science Letters [9], my first feelings were ones of shock and disappointment[1]. These initial feelings changed to admiration when I read his paper and retrieved my review article (published in the 1966 Journal of Research of the National Bureau of Standards [12]) from the NBS Editorial Review Board and inserted an addition which began, "In an excellent and important paper, recently to come to our attention, Ozawa develops ---" (Eq. (1) below) "... He sets up appropriate theoretical master-curves ... ", and ended "... This appears to be one of the best and most generally applicable methods yet developed."

In addition to presenting the now widely accepted isoconversional method based upon the equation

$$-\log(\beta)_1 - 0.457(E/RT_1) = -\log(\beta)_2 - 0.457(E/RT_2) \tag{1}$$

where β is the heating rate, E the activation energy, R the gas constant, and T the absolute temperature, this paper proposed other important advances in nonisothermal kinetics.

For example, he applied the random main chain scission kinetics equations of Simha and Wall [13] to the nonisothermal degradation of nylon 6. The kinetics for this reaction are "autocatalytic" for weight loss experiments since most of the fragments formed in the beginning are too large to evaporate and only later, when small volatile fragments are being produced more abundantly, does the rate peak through a maximum. By applying the random scission degradation kinetics formula, the best fit for the value of L, the smallest fragment which will not volatilize, was determined. This was accomplished by utilizing the concept of reduced time and coalescing the curves at different heating rates into a single master curve by application of a "shift factor" along the temperature coordinate. Master curves were produced from which the fit of the experimental data to the proposed mechanism could be tested and, most importantly, all of the kinetics parameters (the energy of activation, the preexponential factor, and even, in this case, the value of L) could be determined.

Thus, in 1965, when most thermal analysts were fitting data with first-order or, at best, nth-order kinetics, Ozawa recognized the importance of using realistic formulations for the rate function and testing their applicability over wide temperature and conversion ranges. His methods of analysis developed in this paper are applicable to any form of reaction kinetics whose temperature dependence can be fitted by a single set of Arrhenius parameters.

Modifications of these techniques have reached their culmination in some of the recent sophisticated computer programs of Vyazovkin which are reviewed in ref. [14].

3. "A New Method of Quantitative Differential Thermal Analysis" [2] (1966)

This paper, with only thirty citations between 1966 and 1994, would not seem to have received the attention that it deserves. However, like many of Ozawa's papers, it contains so much more than just what is indicated by the title. One can hope that it has been read much more frequently than these few citations suggest. It pioneered a new instrumental design for what was later to become classified as Heat Flux Differential Scanning Calorimetry (DSC). This instrument was never marketed commercially so there has been little reason to cite this paper on this account. Over and above the description of and experimental verifications for a new quantitative DTA instrument, it also includes a rigorous and comprehensive theoretical analysis of these types of instruments based on Carslaw and Jaeger's [15] heat conduction equations. In this theoretical development, the necessary role of temperature gradients and the important concepts of sensitivity and response time of the system are developed and evaluated. The limitations of DTA are discussed as well as its unique advantages over classical calorimetry when they are applied to the field of high temperature and pressure calorimetry.

This paper should be read by all those interested in the theory, design and interpretation of modern Differential Scanning Calorimetry.

4. "Kinetic Analysis of Derivative Curves in Thermal Analysis" [3] (1970)

This paper is presently approaching paper [1] for frequency of citations with 149 recorded between 1990 and 1994 (see Table 1). In it, the concepts in Ref. [1] are expanded and new methods are developed and applied to derivative thermal analysis curves. These two methods of kinetics analysis can be applied to the following general kinetics equation

$$\mathrm{d}x/\mathrm{d}t = A\,(-E/RT)\,g(x) \tag{2}$$

where t is the time and A is the frequency factor, and $g(x)$ can be the analytical expression for any general type of reaction. Of course, Eq. (2) limits the application to cases which can be described by a single set of Arrhenius parameters.

Both methods utilize the reduced time concept developed in Ref. [1]. The reduced time θ is defined as

$$\theta = [E/\beta R]\,p(E/RT) \tag{3}$$

where

$$p(y) = -\int_0^y [\exp(-y)/y^2]\,\mathrm{d}y \tag{4}$$

The first method utilizes a linear relation between peak temperature and heating rate, and requires only values for the rate and heating rate to obtain the activation energy. The second method requires values for the conversion, as well as the rate of conversion, as functions of temperature. The preexponential factor A is determined from the shift factor, and the proposed form of $g(x)$ is deduced from comparison of the shape of the ln $\mathrm{d}C/\mathrm{d}A\theta$ vs. ln $A\theta$ curves with master curves for model processes.

The method can be applied to complex processes such as diffusion, randomly initiated degradation of polymers, etc., as long as the temperature dependence can be represented by a single set of Arrhenius parameters. If superposition of the curves at differing heating rates cannot be attained, then this is evidence that the reaction does not proceed by a simple mechanism, that is, two or more processes with differing Arrhenius parameters are involved.

It is unfortunate that some investigators who purport to apply these methods to thermal analysis kinetics data apparently do not adhere to Ozawa's rigorous criteria which include adherence to the superposition principle. As he points out, the crux of the technique depends upon, firstly, the precise superposibility of the reduced time plots for the curves obtained at differing heating rates and, secondly, upon the identification of $g(x)$ from comparison of the experimental curves with theoretical master curves for model reaction mechanisms.

The methods developed in this paper continue to be among the few really satisfactory ones available for analyzing thermal analysis kinetics data.

5. "Kinetics of Non-isothermal Crystallization" [4] (1971)

This paper appears to have been "discovered" by polymer scientists and others during the past ten years (73 citations between 1990 and 1994) and now is beginning to receive the attention that it deserves. It applies the theory of nucleation and growth in crystallization kinetics to nonisothermal systems.

The Avrami nucleation equations are developed for constant and multiple heating rate cases for both cooling and heating, to obtain

$$\log\{-\ln[1-C(T)]\} = \log X(T) - n\log(\beta) \tag{5}$$

where $C(T)$ is the conversion, $X(T)$ is the cooling (or heating) function derived from the extended Avrami equation for nucleation and growth, and n is the Avrami constant.

The method is illustrated by analysis of data from the crystallization of poly(ethylene terephthalate). The values of n are determined from the shift factor obtained by Ozawa's method of forming the master curves from the isoconversional plots. He points out that n depends upon not only the number of dimensions of crystalline growth, but also other factors such as the fold length of the polymer chains, the crystallization temperature and secondary crystallization. The effect of secondary crystallization is observed from deviations when attempting the superposition of the $\log\{-\ln[1-C(T)]\}$ vs. heating rate curves at differing heating rates.

This paper now serves as a model for the interpretation of dynamic crystallization studies.

6. "Non-isothermal Kinetics of Diffusion and its Application to Thermal Analysis" [5] (1973)

It has become fashionable in the past decade to attempt to fit $g(\alpha)$, the function of conversion, with various "diffusional" functions. However, from the number of citations, seventeen, this paper definitely appears to have not received the attention that it deserves. In it, Ozawa rigorously extends the classic diffusion equations [16] to nonisothermal conditions and applies his multiple heating rate and reduced time techniques of kinetics analysis described in Sections 2 and 4 above, and he illustrates their use by applying these methods to the volatilization of toluene from an epoxy resin.

In this paper, solutions for the diffusion equation for the nonisothermal case are developed to obtain equations for D/a^2, where D is the diffusion constant and a is the distance term (for a sphere, cylinder or plates). Examples are given to demonstrate how to confirm whether these resulting equations apply by utilizing plots of $\ln \mathrm{d}C/\mathrm{d}\theta$ vs. C, C vs. θ, and $\mathrm{d}C/\mathrm{d}\theta$ vs. θ, where θ is the reduced time as described previously. As in the above papers, the reduced time plots test the applicability of the diffusion equations to the experimental data; the Arrhenius parameters and also, in this case, the average radii, are obtained from their slopes and shift factors. For the diffusion of toluene in the epoxy resin, the superimposed plots of $\log D/a^2$ vs. $1/T$ indicated that the two plate specimens followed Arrhenius behavior while the rates for the powdered specimens followed some other type of temperature dependence.

Present day investigators should take a new look at these applications of Ozawa's reduced time method as it is applied to diffusional processes. It permits one to make a critical assessment of the applicability of the diffusion mechanism and to determine all the parameters for the diffusion process.

7. "Critical Investigation of Methods for Kinetic Analysis of Thermoanalytical Data" [6] (1975)

This paper demonstrates the inability of the methods of Freeman and Carroll [17], Coats and Redfern [18] and Sharp and Wentworth [19] to give correct Arrhenius parameters for constant heating rate experiments for which kinetics do not follow first-or nth-order reactions. Such large errors in activation energy often result in spite of the "good fit" of experimental data at a single heating rate to an nth-order equation. Although these flaws in "reaction order" kinetics methods were previously stated and demonstrated in lengthy review articles by this author [12, 20] as well as by Ozawa in his previous papers, it appeared that they were not sufficiently emphasized and that precautions presented in these early papers were widely ignored.

Therefore, in this paper, Ozawa shows, step by step, how these then popular (and still widely used!) methods will give deceptive straight line plots for kinetics data that do not follow nth-order kinetics. He generates data for a first-order reaction, a second-order reaction, two cases of random scission in main chains of polymers (autocatalytic reaction), and a system of two parallel competitive reactions, and applies the above methods of kinetics analysis to them. Thereby he clearly demonstrates how these methods give grossly incorrect values for the activation energy and how the differing heating rate method will test the assumptions made in setting up the kinetics equations and yield correct values for the kinetics parameters.

Unfortunately, in spite of Ozawa's efforts in this paper, thermal analysis literature still contains cases where his carefully documented precautions about the dangers of the use of these simplistic methods are ignored. (It is amazing how referees will still tolerate the use of these methods in papers where the assumed form of the conversion function has not been established by isothermal experiment.) Fortunately, these cases are found much less frequently now as more and more thermal analysts are paying attention to the establishing of reaction mechanism rather than simply calculating "values for E and ln A".

8. "Some Demonstrations of the Effect of the Heating Rate on Thermoanalytical Curves" [7] (1976)

There are other "early" publications in the thermal analysis literature which discuss the effect of heating rate on the thermoanalytical curves for "simple and complex" reaction systems, for example, Refs. [12, 21, 22]. However, in this paper, Ozawa applies his special insights into nonisothermal kinetics to give an instructive and still relevant discussion of the advantages of using heating rate variation to identify and elucidate the complications of "independent" and "competitive" reaction kinetics.

In it, he illustrates how, for either two parallel competitive reaction systems or two independent reaction systems, their derivative peaks may separate upon change in heating rate. Both the advantages and disadvantages of multiple heating rate methods are compared with those of isothermal methods when they are applied to these multiple step reactions.

This is one of the pioneering papers on the use of variation of the heating rate to interpret reaction kinetics involving two or more reactions with differing Arrhenius parameters. It should be read by all those who are engaged in thermal analysis kinetics.

9. "A Modified Method for Kinetic Analysis of Thermoanalytical Data" [8] (1976)

In this paper, which is cited with moderate frequency, Ozawa improves his master curve method of kinetics analysis by developing a technique in which linear relations are utilized to elucidate the mechanism and the preexponential factor. Plots of $-\ln(1-x)$ or $-\ln(1-C)$ against reduced time θ result in a straight line if the correct kinetics equation is used. It is, of course, a great advantage to assess fit to a linear relationship rather than a curved one when determining the kinetics model and calculating precise values for kinetics parameters such as the preexponential factor.

Ozawa illustrates this technique by applying it to the decomposition of polycaprolactam. Linear plots of $-\ln(1-x)$ vs. θ substantiated that the kinetics were consistent with a random scission mechanism.

This paper renders his method of kinetics analysis more simple to interpret. These techniques should be included by all those who use his "reduced time" method of kinetics analysis.

10. Conclusions

In his early papers, discussed above, Ozawa developed theory and techniques which antedated, by over several decades, the more sophisticated treatments of present day thermal analysis kinetics. He not only developed correct and stringent guidelines to follow in order to select correct analytical functions for the reaction rate dependence but also set up precise procedures to obtain kinetics parameters from them.

Ozawa, in his papers, illustrated how thermal analysis kinetics could be used to augment isothermal studies, not substituted for them. Thus he rigorously developed nonisothermal methods for determining kinetics parameters for one-, two-and three-dimensional diffusion, random (autocatalytic) polymer degradation, crystallization (Avrami nucleation), and various reaction order kinetics. He emphasized that these mechanisms were to be applied to reactions which could be identified by isothermal (or equivalent reduced time) plots to follow their particular form of the kinetics equation. (The present day vogue is to force-fit nonisothermal data to one or several equations from a canonical ensemble of $f(\alpha)$ equations.) Then, once the kinetics was established, his nonisothermal techniques could be used to test these kinetics functions over various temperatures, conversions and heating rates to expose any deviations or other complexities in the reaction mechanism.

It has taken many years for the thermal analysis community in general to accept the importance of isoconversional kinetics analysis and thus advance the sophistication of their treatment of thermal analysis kinetics to the point it is today. Those engaged in thermal analysis kinetics studies can still learn much from the detail of the early work of Ozawa which have been but briefly discussed in this paper.

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