The Status and Progress of Thermal Analysis Kinetics

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Abstract. Thermal analysis kinetics has been applied rapidly in recent decades. Thermal analysis technology is widely used in various fields under the commercialization of analyser. In this paper, the thermal analysis dynamics equation, the application development of thermal analysis technology and the development of data processing method are introduced in this paper, and the research of thermal analysis dynamics is described. And the prospect of the research direction is also put forward.

1. Introduction
Thermal analysis methods can be traced back to 1920s, but the establishment and development of a systematic method, as a system method, is mainly in the 50s [1]. With the requirement of material thermal stability, life assessment and physical-chemical reaction analysis, the wide application of computer technology, the growing maturity and efficiency of thermal analysis technology and instruments, the thermal analysis dynamics has a great developed rapidly in the last few decades. Thermo analysis technology has been widely used in the fields of petroleum, chemical, inorganic, organic building materials, rubber, plastics, metallurgy, medicine, food, biochemistry, polymer synthesis, food, energy, architecture, and biogeochemistry and so on, and has formed an independent subject [2]. In this paper, the dynamic equation of thermal analysis, mechanism function, the development and application of thermal analysis technology and the research of data processing method are described and introduced, and the development of thermal analysis dynamics is put forward.

2. Kinetic equation of thermal analysis
The thermal decomposition of solid materials can be generally expressed as follows: A (s) \( \rightarrow \) B (s) + C (g), the kinetic equation of homogeneous reaction under isothermal condition is as follows:

\[
\frac{dc}{dt} = k(T) f(e)
\]

C is the concentration of product, and t is time, \( f(e) \) is rate constant, \( k(T) \) is reaction mechanism function.

But in fact, the research object is usually the heterogeneous reaction under the non-isothermal condition. The kinetic equation of the thermal analysis is divided into the first class dynamic equation and the second class dynamic equation. The difference between the two types is whether the
differential equation introduces $T_0$, and the integral temperature integral of the first kind of dynamic equation has no analytical solution. The expression is shown in Table 1.

| Table 1. Two class dynamic equations |
|-------------------------------------|
| **Differential equation** | **Class I dynamic equation** | $\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha)$ |
| **Integral formula** | **Class II dynamic equation** | $\frac{d\alpha}{dT} = \frac{A}{\beta} \int_0^1 \left[1 + \frac{E}{RT} \left(\frac{T_0}{T}\right)\right] \exp\left(-\frac{E}{RT}\right) f(\alpha)$ |

$f(\alpha), G(\alpha)$ is reaction mechanism function. $\alpha$ is the percentage of transformation, and $\beta$ is the heating rate.

2.1. Mechanism function
Kinetic mechanism function of reaction $f(\alpha)$ is a function relation between the reaction rate (k) and the conversion rate of the solid matter ($\alpha$), which directly determines the shape of the TA curve. And the dynamic mechanism function is based on the assumption that the reactant particles have a regular geometric shape and the reaction activity of each phase [3]. However, the thermal decomposition of solid material in the actual test will also be influenced by many factors such as the size of the reactant particles, the chemical composition of the reactants, and the geometry of the reactants. This series of complex reaction conditions and reaction environment leads to the kinetic mechanism function of thermal analysis in some cases can describe the reaction process basically. In some cases, the ideal model is not consistent with the actual TA curve, or a reaction process can be described by several mechanism functions. Therefore, researchers have been working on improving the accuracy of the mechanism function. Šesták introduced a "adjustment function" $a(\alpha)$ to represent the real dynamic mechanism function $h(\alpha), h(\alpha) = f(\alpha)a(\alpha)$, on the original ideal mechanism function $f(\alpha)$. After that, the kinetic mechanism function called S-B (m, n), $h(\alpha) = \alpha^m(1-\alpha)^n$, is obtained through Gorbatchev simplification., Among them, m and n are called dynamic mode exponents, which determine the TA curve making the shape [4].

2.2. Dynamic parameters
In the non-isothermal heterogeneous reaction, the Arrehenius equation of isothermal homogeneous reaction is also applied directly.

$$k = A \exp\left(-\frac{E_\alpha}{RT}\right), \quad \ln k = -\frac{E_\alpha}{RT} + \text{const}$$

A linear relationship is between $\ln k$ and $1/T$. The slope is $-E_\alpha/R$, and the intercept is $\ln A$.

The purpose of dynamics research is to solve $E, A$ and $f(\alpha)$, namely the so-called "three factors of dynamics". $E$ is energy of activation, and $A$ refers to the former factor. The pre finger factor $A$ is a constant which is independent of reaction temperature and reactant concentration, which is determined by the nature of the reaction only. As long as the K value measured by the experiment, then $\ln k$ is plotted with $1/T$, and the E value can be obtained.
3. Research progress of thermal analysis technology

As a scientific experimental method, the core of thermal analysis is to study the change rate and temperature of physical and chemical changes, as well as the energy and quality changes involved in the heat or cooling of materials [5]. The International Association for thermal analysis (ICTA) defines the thermal analysis technology as follows: thermal analysis is a kind of technology to measure the relationship between physical properties and temperature of a substance under the control of the temperature of a program [6]. Programmed temperature control means heating or cooling according to some rule, usually is linear heating or cooling.

3.1. Classification of thermal analysis techniques

The thermal analysis method is one of the instrument technology methods. It is an important tool in the field of heterogeneous system to determine the macro average properties of the sample varying with temperature, which belongs to the category of characterization technology. The following is the classification of thermal analysis technology by ICTA. Thermogravimetry, differential thermal analysis and differential scanning calorimetry are the most widely used. See Table 2 for details.

| Physical property | Abbreviation | Full name |
|-------------------|--------------|-----------|
| 1 Quality         | TG           | Thermogravimetry |
|                   |              | Isobaric Mass-change Determination |
|                   | EGD          | Evolved Gas Detection |
|                   | EGA          | Evolved Gas Analysis |
|                   |              | Emanation Thermal Analysis |
|                   |              | Thermoparticulate Analysis |
| 2 Temperature     | DTA          | Differential Thermal Analysis |
|                   |              | Heating Curve Determination |
|                   | DSC          | Differential Scanning Calorimetry |
| 3 Enthalpy        |              | Thermodilatometry |
| 4 Size            | TMA          | Thermomechanical Analysis |
| 5 Mechanical properties | DMA   | Dynamic Mechanical Analysis |
| 6 Acoustic characteristics |          | Thermoelectricity |

Thermogravimetry is the most widely used method of measuring the change of mass and temperature (or time) under program control [7]. The one is static thermogravimetry, which is divided into isobaric and isothermal mass change measurement, and the other is non-isothermal (or dynamic) thermogravimetric method. Differential thermal analysis is a method of measuring the relationship between temperature difference and temperature (or time) of a sample and a reference material under a programmed temperature to identify the physical and chemical properties of the material, such as composition structure and thermal effect of conversion temperature [8]. Differential scanning calorimetry (DSC) is a method of heating or cooling the sample and the reference material at a certain rate of heating or cooling in the same temperature environment, and recording the relationship between the required energy difference and time or temperature when the temperature difference is equal to 0. Combined thermal analysis technology is the latest development field, one is the combination of thermal analysis technology, such as TG-DTA, TG-DTG and DSC-TG, and the other is the combination of thermal analysis and other analytical techniques, such as mass spectrometry, Fourier infrared spectroscopy, gas chromatography and diffraction analysis, commonly used in TG-MS, TG-DTA/DSC-MS, and TG. -FTIR-MS and so on.
3.2. Application of thermal analysis technology

Thermal analysis technology has been widely used in many fields, such as energetic materials, polymer materials, inorganic materials, drugs, environmental analysis and metallurgy, and has gradually formed an independent subject. Zhan Tang and other [9] use the DSC method to test the HMX of the single explosive. The measured thermal decomposition data are safe and reliable. The obtained thermal decomposition parameters and mechanism functions provide the basis for the safety application and evaluation of HMX. In the field of polymer materials, thermogravimetry, differential thermal analysis and thermomechanical method are the most widely used. It provides a test method and scientific basis for the analysis and research of properties, structures, production and preparation in the field of material science. Thermal analysis technology has been widely and deeply applied in both pharmaceutical and pharmacological research, especially in quantitative analysis of drug components, determination of drug purity, pharmacokinetics and thermal stability.

4. Research on data processing method

Solid phase reaction kinetics has always been the core of thermal analysis kinetics. Its main task is to determine the mechanism of solid phase reaction and related kinetic parameters. At present, there are many corresponding data processing methods, which are divided into integral method and differential method from mathematical processing. It is divided into single scan rate method and multiple scan rate method from operation mode [10]. The single scanning rate method is a method for analyzing the points on the same TA curve at the same scanning rate, which is called the mechanism function method. This method takes the mechanism function \( f(\alpha) \) or \( G(\alpha) \) into the linear equation which combines the integral and the differential expression. The best linear relation is the most almost entire mechanism function. The slope and intercept of the straight line are the activation energy \( E \) and the pre exponential factor \( A \). But the actual research proves that the reliability of the selected mechanism function can not be guaranteed, and the dynamic parameters of the same reaction process are different under different conditions. Multiple scanning rate method is a dynamic analysis of several TA curves measured at different heating rates. Iso-conversional method is the most commonly used. The main method is: for the same reaction of the same substance and experiment at different heating rates, a set of curves about \( \alpha \) and \( T \) can be obtained, and the data is placed under the same conversion rate \( \alpha \). It can avoid the mechanism function. To obtain reliable kinetic parameters, it is also called non mechanism function method. Table 3 is the common integral methods and differential methods.

| Table 3. The common integral method and differential method |
|-------------------------------------------------------------|
| **Integral method**                                         | **Differential method** |
| Phadnis Broido                                             | Exothermic rate method |
| Doyle Improved Coats-Redfern                                | Feature point analysis |
| Ozawa Coats-Redfern                                        | Kissinger Freeman-Carroll |
| Flynn-Wall-Ozawa (FWO)                                     | Newkirk Vachuska-Voboril |
| Rongzu Hu Hongxu Gao Haifa Zhang                            | Friedman Friedman-Ozawa |
|                                                             | Achar-Brindley-Sharp Kissinger-Akahira-Sunose |
|                                                             | (ABS) (KAS) |

The isoconversion method has KAS, Ozawa, FR, Friedman, Kissinger and FWO. The earliest isoconversional methods, such as Ozawa, KAS and Kissinger, need to introduce temperature approximate integral, which will produce certain error. The variant FWO method, developed on the basis of the equal conversion method by Popescu, which is developed on the basis of the equal conversion method, can determine the most probable mechanism function without introducing any approximation to the temperature integral and considering the specific form of the rate constant [11]. With the continuous development of data processing methods, a series of methods such as advanced iso-conversional method, Vyazovkin model-free kinetic analysis, double step method and neural network method have
been developed continuously, and the application in a certain field is very good. The scholars at home and abroad have done a detailed explanation, due to the limitation of space. Not to say one by one.

5. Expectation
In the aspect of dynamic equations, a new more reasonable non isothermal rate formula is sought to replace the original Arrhenius formula in order to ensure more consistent with the actual reaction. In the data processing, In the aspect of data processing, one is to improve the traditional integral method and differential method by using nonlinear fitting or iterative method, another is seeking new ways. In the thermal analysis technology, the combination of thermal analysis technology and the combined use of gas chromatography, mass spectrometry, x ray diffraction and other detection methods have become a trend. The results of thermal analysis are more in line with the actual situation of complex reactions, and reduce the impact of experimental conditions and data processing on the final results.

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