



2014

# THEORETICAL STUDY OF THERMAL ANALYSIS KINETICS

Yunqing Han

*University of Kentucky*, [hyqingus@gmail.com](mailto:hyqingus@gmail.com)

**[Click here to let us know how access to this document benefits you.](#)**

---

## Recommended Citation

Han, Yunqing, "THEORETICAL STUDY OF THERMAL ANALYSIS KINETICS" (2014). *Theses and Dissertations--Mechanical Engineering*. 35.

[https://uknowledge.uky.edu/me\\_etds/35](https://uknowledge.uky.edu/me_etds/35)

This Doctoral Dissertation is brought to you for free and open access by the Mechanical Engineering at UKnowledge. It has been accepted for inclusion in Theses and Dissertations--Mechanical Engineering by an authorized administrator of UKnowledge. For more information, please contact [UKnowledge@lsv.uky.edu](mailto:UKnowledge@lsv.uky.edu).

**STUDENT AGREEMENT:**

I represent that my thesis or dissertation and abstract are my original work. Proper attribution has been given to all outside sources. I understand that I am solely responsible for obtaining any needed copyright permissions. I have obtained needed written permission statement(s) from the owner(s) of each third-party copyrighted matter to be included in my work, allowing electronic distribution (if such use is not permitted by the fair use doctrine) which will be submitted to UKnowledge as Additional File.

I hereby grant to The University of Kentucky and its agents the irrevocable, non-exclusive, and royalty-free license to archive and make accessible my work in whole or in part in all forms of media, now or hereafter known. I agree that the document mentioned above may be made available immediately for worldwide access unless an embargo applies.

I retain all other ownership rights to the copyright of my work. I also retain the right to use in future works (such as articles or books) all or part of my work. I understand that I am free to register the copyright to my work.

**REVIEW, APPROVAL AND ACCEPTANCE**

The document mentioned above has been reviewed and accepted by the student's advisor, on behalf of the advisory committee, and by the Director of Graduate Studies (DGS), on behalf of the program; we verify that this is the final, approved version of the student's thesis including all changes required by the advisory committee. The undersigned agree to abide by the statements above.

Yunqing Han, Student

Dr. Kozo Saito, Major Professor

Dr. James M McDonald, Director of Graduate Studies

---

THEORETICAL STUDY OF THERMAL ANALYSIS KINETICS

---

Dissertation

---

A dissertation submitted in partial fulfillment of the  
requirements for the degree of Doctor of Philosophy in the  
College of Engineering  
at the University of Kentucky

By  
Yunqing Han  
Lexington, Kentucky  
Director: Dr. Saito, Professor of Mechanical Engineering  
Lexington, Kentucky  
2014  
Copyright © Yunqing Han 2014

## ABSTRACT OF DISSERTATION

### THEORETICAL STUDY OF THERMAL ANALYSIS KINETICS

In the past decades, a great variety of model fitting and model free (isoconversional) methods have been developed for extracting kinetic parameters for solid state reactions from thermally stimulated experimental data (TGA, DSC, DTA etc.). However, these methods have met with significant controversies about their methodologies. Firstly, model-fitting methods have been strongly criticized because almost any reaction mechanism can be used to fit the experimental data satisfactorily with drastic variations of the kinetic parameters, and no good criterion exists to tell which mechanism is the best choice. Secondly, previous model free methods originated from the isoconversional principle, which is often called the basic assumption; previous studies comparing the accuracy of model free methods have not paid attention to the influence of the principle on model free methods and, therefore, their conclusions are problematic.

This work gives, firstly, a critical study of previous methods for evaluating kinetic parameters of solid state reactions and a critical analysis of the isoconversional principle of model free methods. Then an analysis is given of the invariant kinetic parameters method and recommends an incremental version of it. Based on the incremental method and model free method, a comprehensive method is proposed that predicts the degree of the dependences of activation energy on heating programs, and obtains reliable kinetic parameters. In addition, this work also compares the accuracy of previous methods and gives recommendations to apply them to kinetic studies.

**KEYWORDS:** Thermal Analysis Kinetics, Model Fitting method, Model Free Method, Comprehensive Method, Activation Energy

Yunqing Han

---

Student's Signature

05-08-2014

---

Date

Approval Page

STUDY ON METHODOLOGY OF  
THERMAL ANALYSIS  
KINETICS

By

Yunqing Han

Dr. Kozo Saito

---

Director of Dissertation

Dr. James McDonough

---

Director of Graduate Studies

05-08-2014

---

**To my mother, Fang Li**

Your support, encouragement, and endless dedication have sustained me throughout my life.

## ACKNOWLEDGMENTS

I would like to especially express my sincere gratitude to my advisor Dr. Kozo Saito for his guidance in both academic progress and attitude toward life. I am also thankful to my co-advisor Dr. Tianxiang Li for his support and helpful discussions. I am also grateful to Dr. John Stencil for his patience and instructive comments while reviewing my work. I am thankful for the encouragement provided by both Dr. Nelson Akafuah and Dr. Ahmad Salaimah during the preparation of this dissertation. And I am also greatly thankful to the external examiner Dr. Peter Hislop, and the entire dissertation committee: Dr. Dusan Sekulic, Dr. Tate Tsang, Dr. David Herrin, Dr. José Graña-Otero for their invaluable discussions.

I also would like to thank to Ms. Brittany Adam, Mr. Justin English, Mr. Matthew Lane, Mr. Nicholas Cprek, Mr. Jeremy Fugate, Ms. Madison Donoho, Ms. Kendall Kruszewski, Mr. Greg Brotzge, Mr. Brent Hale, Mrs. Rebecca Hale, Mr. Philip Duff, Ms. Emily Woods and Ms. Corrie Mckee, for their company, friendship, and especially the time they dedicated in correcting my pronunciations. Without their help, the tremendous improvement in my English efficiency would not have been possible. They also made my stay at the University of Kentucky enjoyable and made the three years fly by; I will fondly look back on those memories.

I also would like to thank my friends especially, Shaoqian Wang, Yulong Yao, Qiao Liang, Hao Zhang for their friendship and encouragement. I would also like to thank my roommate Jian Zhang, who has greatly broadened my vision to living philosophy and motivated my ambitious to personal success.

Specially, I also would like to thank the warmhearted, sincere, and conscientious lady, Ms. Claire A. Adams. There are questions, such as the meaning of death and life, and what on earth is love, that always confused me and they never seem to have standard answers. As a person who wants but does not have a religion at this time, it seems every person could be a teacher, and I do not know where my final spiritual destination is. However, her existence has shown me how peaceful

and joyful it is to be a person of devout faith and it is worthy to calm down and listen to my heart,  
not just to make a life.

Lastly, my appreciation goes to Robert Frost, who wrote my favorite English poem:

#### The Road not Taken

Two roads diverged in a yellow wood  
and sorry I could not travel both  
And be one traveller, long I stood  
and looked down one as far as I could  
to where it bent in the undergrowth;  
Then took the other, as just as fair,  
and having perhaps the better claim  
because it was grassy and wanted wear;  
though as for that, the passing there  
had worn them really about the same,  
And both that morning equally lay  
in leaves no feet had trodden black.  
Oh, I kept the first for another day!  
Yet knowing how way leads on to way,  
I doubted if I should ever come back.  
I shall be telling this with a sigh  
Somewhere ages and ages hence:  
Two roads diverged in a wood, and I --  
I took the one less travelled by,  
and that has made all the difference



## TABLE OF CONTENTS

ACKNOWLEDGMENTS .....	iii
LIST OF FIGURES .....	vii
LIST OF TABLES.....	ix
<b>CHAPTER 1: Introduction</b> .....	1
1.1 Kinetics of Thermally Stimulated Solid Reactions.....	1
1.2 Kinetic Triplets and Equations.....	3
1.3 Outline of Dissertation .....	7
<b>CHAPTER 2: PREVIOUS METHODS AND COMPARISONS</b> .....	9
2.1 General Equation and Temperature Integral .....	9
2.2 Model Fitting Methods .....	10
2.3 Invariant Kinetic Parameters Method .....	15
2.4 Model Free Method.....	16
2.4.1 Isoconversional Principle.....	16
2.4.2 Differential Isoconversional Methods.....	17
2.4.3 Regular Integral Methods.....	18
2.4.3.1 Ozawa-Flynn-Wall Method .....	18
2.4.3.2 Vyazovkin Method.....	19
2.4.3.3 Li-Tang Method .....	20
2.4.3.4 Kissinger-Akahira-Sunose Method.....	21
2.4.4 Advanced Integral Methods .....	22
2.4.4.1 Advanced Vyazovkin Method .....	22
2.4.4.2 Advanced Li-Tang Method.....	23
2.4.5 Modulated Thermogravimetry Methods .....	24
<b>CHAPTER 3: MODIFICATION OF REGULAR LI-TANG METHOD AND ORTEGA METHOD</b> .....	25
3.1 Advanced Li-Tang Method.....	26
3.1.1 Methodology of Advanced Li-Tang Method .....	26
3.1.2 Numerical Applications .....	29
3.1.3 Experimental Example.....	32
3.2 Modified Ortega Method .....	33
3.2.1 Methodology of Modified Ortega Method.....	33
3.2.2 Results and Discussion .....	37

3.2.2.1	Simulation without Noise.....	37
3.2.2.2	Simulation with Noise.....	39
3.2.2.3	Experimental Application .....	40
3.3	Conclusions.....	41
<b>CHAPTER 4: COMPREHENSIVE METHOD BASED ON MODEL-FREE AND IKP METHODS TO EVALUATE KINETIC PARAMETERS.....</b>		<b>43</b>
4.1	Critical Analysis of Model Free Methods.....	44
4.2	Analysis of IKP Method .....	46
4.3	Proposition of a Comprehensive Method.....	47
4.4	Simulation Validations.....	54
4.5	Experimental Validation .....	59
4.6	Conclusion .....	61
<b>CHAPTER 5: ACCURACY OF ISOCONVERSIONAL METHODS WITH A CONSIDERATION OF BASIC ASSUMPTION.....</b>		<b>63</b>
5.1	Previous Comments about Isoconversional Methods .....	63
5.2	Error Sources of Isoconversional Methods.....	64
5.3	Simulations and Analysis.....	67
5.3.1	Parallel Independent Reaction .....	67
5.3.2	Parallel Competitive Reaction .....	72
5.4	Conclusion .....	75
<b>CHAPTER 6: Conclusion .....</b>		<b>77</b>
<b>References .....</b>		<b>79</b>
<b>Vita.....</b>		<b>91</b>

LIST OF FIGURES

Figure 1.1 Schematic of TG and DSC plots.....2

Figure 3.1  $E_{\alpha}$  dependencies evaluated for the simulated process by Li-Tang method with different lower limit of the integral,  $\alpha_1$ , as well as by OFW, AIC, FR and the new method ..... 30

Figure 3.2  $E_{\alpha}$  dependencies evaluated for the  $\text{SrCO}_3$  decomposition by the new method, FR method and AIC method..... 31

Figure 3.3  $E_{\alpha}$  dependencies obtained for the  $\text{SrCO}_3$  decomposition by the new method and Li-Tang method with different lower integral limit,  $\alpha_1$ , and by OFW method..... 32

Figure 3.4 Dependence of  $E_{\alpha}$  on the value  $\alpha$  evaluated by FR, AIC, OFW, the original Ortega method, and the modified Ortega method with  $\Delta\alpha=0.04$ ..... 36

Figure 3.5 Dependence of  $E_{\alpha}$  on the value  $\alpha$  for the simulated single step reaction FR, AIC, and the original Ortega method with  $\Delta\alpha =0.01$ , and the modified Ortega method with  $\Delta\alpha =0.04$ ..... 38

Figure 3.6 Dependence of  $E_{\alpha}$  on the value  $\alpha$  obtained for the experiments of  $\text{SrCO}_3$  decomposition by AIC, the modified Ortega method, and the original Ortega method, all with  $\Delta\alpha =0.04$ ..... 39

Figure 3.7 Dependence of  $E_{\alpha}$  on the value  $\alpha$  obtained for the experiments of  $\text{SrCO}_3$  decomposition by AIC, FR and Ortega method all with  $\Delta\alpha=0.04$ ..... 40

Figure 4.1 The dependences of E and  $\ln A$  on  $\alpha$  of a single step reaction determined by IIKP method ..... 46

Figure 4.2 Schematic of IIKP principle for complex reactions..... 48

Figure 4.3 Flow chart of comprehensive method..... 50

Figure 4.4	Values of activation energy determined by FR and IIKP methods for simulation test S1.....	41
Figure 4.5	Values of activation energy determined by FR and IIKP methods for simulation test S2.....	52
Figure 4.6	Values of activation energy determined by FR and IIKP methods for simulation test S3.....	52
Figure 4.7	Values of activation energy determined by FR and IIKP methods for simulation test S4.....	53
Figure 4.8	Values of activation energy determined by FR and IIKP methods for simulation test S5.....	53
Figure 4.9	Values of activation energy determined by FR and IIKP methods for simulation test S6.....	54
Figure 4.10	Values of activation energy determined by FR and IIKP methods for simulation test S7.....	56
Figure 4.11	Values of activation energy obtained by different methods for experiment data ...	60
Figure 4.12	Values of selected activation energy determined by comprehensive method.....	60
Figure 5.1	Simulation results obtained from test T1, (beta1-3 are true values for different $\beta_i$ : it also applies all Figures) .....	66
Figure 5.2	Simulation results obtained from test T2 .....	67
Figure 5.3	Simulation results obtained from test T3 .....	68
Figure 5.4	Simulation results obtained from test T4 .....	69
Figure 5.5	Simulation results obtained from test T5 .....	70
Figure 5.6	Simulation results obtained from test T6 .....	71
Figure 5.7	Simulation results obtained from test T7 .....	72
Figure 5.8	Simulation results obtained from test T8 .....	73
Figure 5.9	Simulation results obtained from test T9 .....	74

## LIST OF TABLES

Table 1.1	Expressions of functions of the most common reaction mechanisms.....	5
Table 4.1	The values of $E_{inv}$ and $A_{inv}$ obtained by IIKP method .....	57

## **CHAPTER 1: INTRODUCTION**

### *1.1 Kinetics of Thermally Stimulated Solid Reactions*

Thermal activation is, probably, the most common means to stimulate solid state reactions, although the applications of photo activation, magnetic field, pressure, and electrochemical potentials are also possible. By activating by external heating or cooling stimuli, the structure, phase state, and chemical properties of solids are changeable; thermal analysis techniques measure the physical and chemical changes of solids as a function of temperature in controlled thermal conditions. Thermal analysis techniques have been employed since the early 20th century and are increasingly important as an analytical tool in the fields of chemistry, physics, materials, geology, metallurgy, medicine, and combustion.

The development of thermal analytical instruments and thermal analysis methods have provided a useful tool to obtain the kinetic parameters of solid state reactions with a small amount of solid sample. The most common and widely used thermal analysis techniques are Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). TGA is a method commonly used to measure selected characteristics of materials' mass changes due to decomposition, oxidation, or loss of volatiles (e.g., moisture and combustibles) and to record information digitally as a function of increasing temperature and/or of time (Fig. 1.1). Most typical TGA applications are studies of reaction kinetics and degradation mechanisms, materials characterization by analysis of characteristic decomposition patterns, and determination of organic or inorganic contents in samples. DSC is a thermoanalytical technique that measures the difference in the amount of heat needed to increase the temperature of a sample and a reference as a function of temperature. The fundamental mechanism underlying this technique is that, more or less, the reactions will be exothermic or endothermic, and heat will need to flow to or from the sample and reference to keep them at the same temperature when the sample experiences a physical transformation. For instance, a phase transition from solid to liquid absorbs heat; when a solid sample melts, it will

take more heat to increase its temperature at the same rate as the reference, and DSC is able to measure the amount of heat absorbed or released during the reaction (Fig. 1.1). DSC is also applied to observe more subtle physical changes (e.g., glass transitions and polymer curing). A similar technique is differential thermal analysis (DTA) in which heat flows to the reference and the sample and is kept the same rather than the temperature. Hence, DSC and DTA provide similar information. Solid state kinetic data obtained by TGA and DSC are of an increasing practical interest because a growing number of technologically important processes like thermal energetic materials and crystalline solids, thermal oxidation and pyrolysis of fuels and polymers, crystallization of glasses and polymers, and the solidification of metallic alloys are fruitfully studied using these techniques [1].

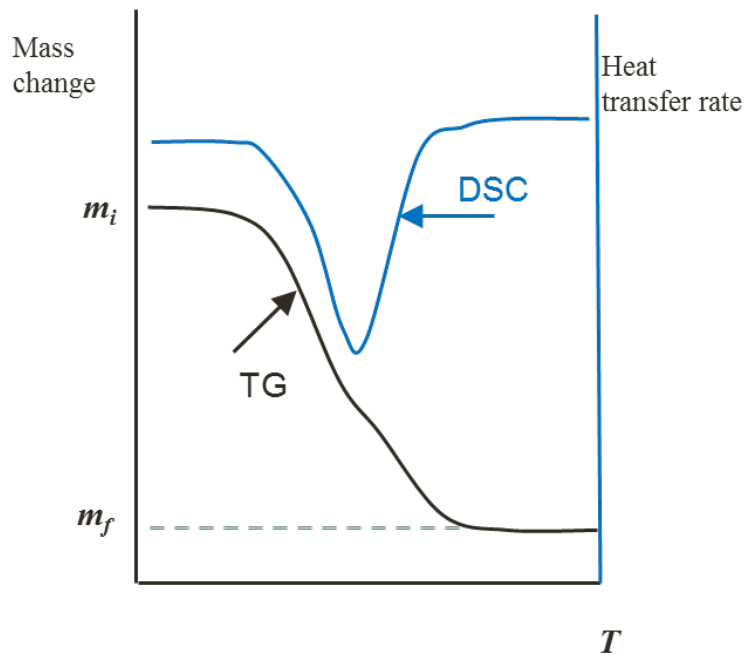


Figure 1.1 Schematic of TG and DSC plots

Thermal Analysis Kinetics (TAK) seeks to quantitatively analyze the relationships between temperature and physical properties (e.g., the mass change as a function of time) measured by the thermal analysis techniques. The development of TAK is based on chemical thermodynamics,

chemical kinetics and thermal analysis techniques. By analyzing data obtained by thermal analysis techniques, TAK is able to provide kinetic parameters, estimate the thermal stability and life span of materials, and the best operation conditions of polymers, quantitatively describe the reaction rate and reaction mechanisms, and provide supporting information for estimating properties of energetic materials and combustibles [2].

Interests in TAK were awakened in the early 20th century, and tremendous developments occurred during the recent decades. TAK has been developed for no less than one hundred analytical methods and applied in various fields. It is capable of quantitatively characterizing reactions and phase change processes, determining the most probable reaction mechanisms, and extracting activation energies and pre-exponential factors of solid state reactions.

### *1.2 Kinetic Triplets and Equations*

Non-isothermal, heterogeneous thermal analysis kinetics originated from the theory of isothermal and homogenous gas or liquid phase kinetics, the basis of which had been established by the end of 19th century. Its description equation is

$$\frac{dc}{dt} = k(T)f(c) \quad (1.1)$$

where  $c$  is the concentration,  $t$  is the time,  $T$  is temperature,  $k(T)$  is the rate constant that dependent on temperature, and  $f(c)$  is the reaction mechanism. In isothermal and homogenous reactions it is often represented by  $f(c) = (1 - c)^n$ .

Early solid state kinetic studies were carried out under isothermal conditions [3-5], and used the following kinetic equation

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1.2)$$



where  $\alpha$  is the extent of reaction expressed by

$$\alpha = \frac{m_0 - m}{m_0 - m_f} \quad (1.3)$$

Expression 1.3 is analogous to molar concentrations of gas reactants and/or products, of which  $m$  is the mass of the reactant, the subscripts  $0$  and  $f$  designate the initial and final states, respectively, and  $f(\alpha)$  is the reaction model related to the solid reaction mechanism. Unlike in gas, molecular motion is highly restricted in solids and reactions are dependent on local structure and activity; some of the models are derived strictly according to their mechanistic basis such as nucleation, geometrical contraction, diffusion, and reaction order [6, 7]. -Most common reaction models are listed in Table 1.1.

The temperature dependence of the rate of solid state reactions is typically parameterized through the Arrhenius equation [8]

$$k(T) = A \exp(-E / RT) \quad (1.4)$$

where  $A$  is the pre-exponential factor,  $E$  is the activation energy, and  $R$  is the universal gas constant.

The use of the Arrhenius equation to parameterize temperature dependence has generated problems of interpreting experimentally determined values of  $E$  and  $A$ , and have been criticized from a physical standpoint [9, 10]. Reference [10] has stressed that the Arrhenius equation is only meaningfully applicable to reactions that take place under homogeneous conditions. However, as pointed out in Ref. [11], thermal decomposition has been demonstrated successfully [12, 13] in the framework of an activated theory from an Arrhenius-like equation for the temperature dependence of the process. Moreover, the Arrhenius equation is useful for describing  $k(T)$  of many thermally activated, heterogeneous solid state reactions such as diffusion [14], nucleation

and nuclei growth [15], presumably because the system has to overcome an energy barrier and the energy distribution along the relevant coordinate is controlled by Boltzmann statistics. In addition, Galwey and Brown [16] have demonstrated that the statistics of Fermi-Dirac and Bose-Einstein give rise to Arrhenius-like equations, even in cases where the density of available state is sparse. Therefore, Ref. [11] concluded that the use of the Arrhenius equation is justifiable in terms of a rational parameterization, and its use and physical interpretation are on a sound theoretical basis.

*Table 1.1 Expressions of functions of the most common reaction mechanisms*

Number	Model	Differential form $f(\alpha)$	Integral form $G(\alpha)$
Nucleation models			
1	Power law $P_1$	1	$\alpha$
2	Power law $P_{3/2}$	$(2/3)\alpha^{-1/2}$	$\alpha^{2/3}$
3*	Power law $P_2$	$2\alpha^{1/2}$	$\alpha^{1/2}$
4*	Power law $P_3$	$3\alpha^{2/3}$	$\alpha^{1/3}$
5*	Power law $P_4$	$4\alpha^{3/4}$	$\alpha^{1/4}$
Sigmoidal rate equations			
6	Avarami-Erofe'ev $A_{3/2}$	$(3/2)(1-\alpha)[- \ln(1-\alpha)]^{1/3}$	$[- \ln(1-\alpha)]^{2/3}$
7*	Avarami-Erofe'ev $A_2$	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$[- \ln(1-\alpha)]^{1/2}$
8*	Avarami-Erofe'ev $A_3$	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$[- \ln(1-\alpha)]^{1/3}$
9*	Avarami-Erofe'ev $A_4$	$4(1-\alpha)[- \ln(1-\alpha)]^{3/4}$	$[- \ln(1-\alpha)]^{1/4}$
10	Prout-Tomkins $A_u$	$\alpha(1-\alpha)$	$\ln \alpha/(1-\alpha) $
Geometrical contraction models			
11*	Contracting area R2	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
12*	Contracting volume R3	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
Diffusion models			
13*	1D Diffusion $D_1$	$1/2\alpha$	$\alpha^2$
14*	2D Diffusion $D_2$	$[- \ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha) + \alpha$
15*	3D Diffusion-Jander $D_3$	$(3/2)(1-\alpha)^{2/3}/[1-(1-\alpha)^{1/3}]$	$[1-(1-\alpha)^{1/3}]^2$
16*	Ginstling-Brounshtein $D_4$	$(3/2)/[(1-\alpha)^{-1/3}-1]$	$\frac{1-(2\alpha/3)}{-(1-\alpha)^{2/3}}$
17	Zhuravlev, lesokin, Tempelman $D_5$	$(3/2)(1-\alpha)^{4/3}/[(1-\alpha)^{-1/3}-1]$	$[(1-\alpha)^{-1/3}-1]^2$
18	Anti-Jander $D_6$	$(3/2)(1+\alpha)^{2/3}/[(1+\alpha)^{1/3}-1]$	$[(1+\alpha)^{1/3}-1]^2$
Reaction-order models			
19	One-third order $F_{1/3}$	$(3/2)(1-\alpha)^{1/3}$	$1-(1-\alpha)^{2/3}$
20	Three-quarters order $F_{3/4}$	$4(1-\alpha)^{4/3}$	$1-(1-\alpha)^{1/4}$
21	One and a half order $F_{3/2}$	$2(1-\alpha)^{4/2}$	$(1-\alpha)^{-1/2}-1$
22*	First-order $F_1$	$1-\alpha$	$-\ln(1-\alpha)$
23*	Second-order $F_2$	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
24*	Third-order $F_3$	$(1-\alpha)^3$	$[(1-\alpha)^{-2}-1]/2$

As pointed out in Ref. [11], Vallet studied the first kinetic evaluations of non-isothermal data that were carried out at a constant heating rate,  $\beta = dT/dt$ . To extract values of the kinetic parameters, Vallet suggested replacing the temporal differential in Eq. (1.2) by

$$dt = dT / \beta \quad (1.5)$$

Note the transformation of Eq. (1.5) implicitly contains an assumption that the change in experimental conditions from isothermal to non-isothermal does not affect reaction kinetics; this assumption may have serious implications for multi-step reaction kinetics [11].

Based on the aforementioned theories, the equation of heterogeneous solid state reaction rate under isothermal condition can be described as

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (1.6)$$

which under non-isothermal conditions with a constant heating rate leads to

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (1.7)$$

The parameters of  $E$ ,  $A$ , and  $f(\alpha)$  are often called the kinetic triplet, which are to be determined during the kinetic analyses of solid state reactions.

Currently, the core of TAK is to study the kinetics of non-isothermal solid state reactions (including physical effects). The reason for using non-isothermal conditions is because of the difficulty to attain strict isothermal conditions, especially during the initial stage of a reaction process; using isothermal conditions is also more time consuming. Moreover, theoretically, a thermal experimental curve obtained under non-isothermal conditions could carry information equivalent to that in multiple data curves obtained from isothermal conditions.

Almost all currently existing methods start from Eq. (1.6) and Eq. (1.7), but quite different results for the kinetic values are often given even by different researchers for a simple reaction. A typical example is the activation energy for dehydrating calcium oxalate monohydrate ( $C_2H_2CaO_5$ ), a representative example of a single-step reaction: literature values for activation energy range from less than 50 kJ/mol to more than 200 kJ/mol [17]. This wide variation has been shown to be influenced by experimental conditions [18]. However, none of the currently available thermal analysis techniques is capable of providing experimental data without important influences from the experimental conditions, even with strict control of the heating program, sample size, and initial mass. Especially, disparate heating programs that are required for some methods may affect solid-state kinetics by influencing physical processes of the reaction, like diffusion, adsorption, and desorption of gaseous products or reactants from the solid surface. Therefore, effects of experimental conditions, especially of the heating program, on the apparent model function should be examined extensively. Recall that current solid-state kinetic theory came from classical kinetic concepts of homogeneous reactions, and the usage and interpretation of the Arrhenius equation in solid state kinetics were supported by both empirical tests and theoretical examinations [19-21]. In homogeneous reactions, the thermodynamic meaning of activation energy is the heat absorbed in the process of transforming inactive molecules into active ones.

In addition, more than one hundred methods have been developed with a great difference in both methodology and applicability, and the accuracy and reliability of them needs to be carefully examined. More importantly, a comprehensive method needs to be developed that surmounts the influences of experimental procedures and enables simplification of them, while offering more accurate and repeatable kinetic parameters.

### *1.3 Outline of Dissertation*

This study contains six (6) chapters, the structure of which is organized as follows.

Chapter 1 introduces the study of solid state thermal analysis kinetics, the development of a general kinetic equation, and the task of thermal analysis kinetics.

Chapter 2 presents, methodically, a review of previous methods for evaluating kinetic parameters of solid state reactions, including the model fitting method, invariant kinetic parameter method, and model free methods.

Chapter 3 uses two specific examples to give a detailed analysis of previous methods, which is useful for better understanding about how previous studies compare the accuracy of model free methods, and their achievements and problems.

Chapter 4 is the main focus of this study. Firstly, it shows theoretically that the activation energy for complex reactions is both functions of reaction degree and heating programs. Model free methods that try to extract dependences of activation energy on conversion degree without considering the dependences of heating programs are problematic. Then, an analysis of the invariant kinetic parameters method is presented and discussed, and an incremental version of it is described. Based on the incremental, invariant kinetic parameters method and model free method, a comprehensive method is proposed that predicts the degree of the dependencies of activation energy on heating programs, selects reliable values of activation energy, and extracts values of the variable pre-exponential factor.

Chapter 5 gives an additional analysis of the accuracy of previous model free methods by considering the influence of the isoconversional principle.

Finally, Chapter 6 makes a conclusion of this study.

## CHAPTER 2: PREVIOUS METHODS AND COMPARISONS

In the past decades, a variety of methods have been developed for extracting single pair of or variable kinetic parameters for solid state reactions from thermal stimulated experimental data (TGA, DSC, DTA etc.) that could be unified and visualized as the conversion curves of  $\alpha$  and/or  $d\alpha/dT$  as a function of temperature or time. These methods have been categorized generally into model fitting methods and model free methods.

### 2.1 General Equation and Temperature Integral

Nearly all the thermal analysis methods start from the general differential kinetic Eqs. (1.6) and (1.7) or the integral forms of them,

$$g(\alpha) = \int_0^\alpha \frac{1}{f(\alpha)} d\alpha = A \int_0^t \exp\left(-\frac{E}{RT(t)}\right) dt \quad (2.1)$$

For a linear heating program,  $\beta = dT/dt$ , the above equation leads to

$$g(\alpha) = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT = \frac{AE}{\beta R} \int_x^\infty \frac{e^{-x}}{x^2} dx = \frac{AE}{\beta R} p(x) \quad (2.2)$$

where “ $x$ ” denotes  $E/RT$ , and  $p(x)$  is the temperature integral. Note that the derivation of the above equation involves an assumption that  $E$  must be a constant with respect to  $\alpha$ .

For a specific value  $x$ , the temperature integral,  $p(x)$ , has no analytical solution but has been approximated by hundreds of possibilities [22-27]. Doyle [22-24] suggested a linear approximation of the logarithm of  $p(x)$ ,

$$\log p(x) = -0.4567x - 2.315 \quad (2.3)$$

which is equivalent to

$$p(x) = \exp(-1.0518x - 5.330) \quad (2.4)$$

The approximation given by Coats and Redfern [25] is,

$$p(x) = \frac{\exp(-x)}{x^2} \left( 1 - \frac{2}{x} \right) \quad (2.5)$$

A more popular, fourth order approximation is given by Senum and Yang [26],

$$p(x) = \frac{\exp(-x)}{x^2} \frac{x^4 + 18x^3 + 86x^2 + 96x}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (2.6)$$

Analyses of accuracies of the approximations have been discussed [28, 29], with the conclusion that the fourth order Senum and Yang approximation is the most accurate. Other approximations result in greater errors although they may be more convenient to apply than the Senum and Yang approximation. It should be kept in mind that these analyses are based on the assumption that the value of  $x = E / RT$  is a constant.

## 2.2 Model Fitting Methods

Model-fitting methods are the major methods used during analyses of thermal analysis kinetics in which TG and DSC experimentation determine mass or heat change as a function of temperature or time. A model-fitting method is a one that fits different reaction models  $f(\alpha)$  or  $g(\alpha)$  into the general kinetic equation, Eq. (1.7) or Eq. (2.2), and values of the activation energy and pre-exponential factor are calculated by regression analyses [1]. Then, different groups of kinetic triplet values are used to fit one of the above equations, and the curves generated by the equation with the best to the actual experimental curves would be considered the proper one to be selected. For brevity, all equations in this study are derived with a linear heating rate because it is the most commonly used approach, although an arbitrary heating program can be derived by replacing  $(1/\beta)d\alpha/dT$  with  $d\alpha/dt$ . In the following, the Gorbachev [30] and Coats-Redfern methods

[25] are presented and discussed to give a better understanding of the detailed procedure associated with model-fitting methods.

From the temperature integral  $p(x)$ , one gets:

$$\begin{aligned}
p(x) &= \int_{\infty}^u \frac{e^{-x}}{x^2} dx \\
&= \frac{e^{-x}}{x^2} \Big|_{\infty}^x - \int_{\infty}^x e^{-x} dx^{-2} \\
&= \frac{e^{-x}}{x^2} - \int_{\infty}^x 2x^{-3} de^{-x} \\
&= \frac{e^{-x}}{x^2} - \frac{2}{x^3} e^{-x} + \int_{\infty}^x e^{-x} (-6)x^{-4} dx \\
&= \frac{e^{-x}}{x^2} - \frac{2}{x^3} e^{-x} + \int_{\infty}^x 6x^{-4} de^{-x} \\
&= \frac{e^{-x}}{x^2} - \frac{2}{x^3} e^{-x} + \frac{6}{x^4} e^{-x} \Big|_{\infty}^x - \int_{\infty}^x e^{-x} d \frac{6}{x^4} \\
&= \dots = \\
&= \frac{e^{-x}}{x^2} \left( 1 - \frac{2!}{x} + \frac{3!}{x^2} - \frac{4!}{x^3} + \dots \right) \tag{2.7}
\end{aligned}$$

Then Eq. (2.2) leads to

$$\int_0^T \exp\left(-\frac{E}{RT}\right) dT = \frac{E}{R} \frac{e^{-x}}{x^2} \left( 1 - \frac{2!}{x} + \frac{3!}{x^2} - \frac{4!}{x^3} + \dots \right) \tag{2.8}$$

Using the first two terms leads to the following approximation of the temperature integral



$$\int_0^T \exp\left(-\frac{E}{RT}\right) dT = \frac{ET^2}{R} \left(1 - \frac{2RT}{E}\right) \exp\left(-\frac{E}{RT}\right) \quad (2.9)$$

Equation 2.9 is the Coats-Redfern approximation.

Multiplying the term of  $(1 + 2RT / E)$  to both sides gives,

$$\int_0^T \exp\left(-\frac{E}{RT}\right) dT = \frac{\frac{ET^2}{R} \left(1 - \left(\frac{2RT}{E}\right)^2\right)}{1 + \frac{2RT}{E}} \exp\left(-\frac{E}{RT}\right) \quad (2.10)$$

In most cases  $T$  is in a moderate range and  $E$  is bigger than 60kJ/mol so that the term  $2RT / E \ll 1$  and equation 2.10 simplifies to

$$\int_0^T \exp\left(-\frac{E}{RT}\right) dT = \frac{\frac{ET^2}{R} \exp\left(-\frac{E}{RT}\right)}{1 + \frac{2RT}{E}} = \frac{ET^2}{E + 2RT} \exp\left(-\frac{E}{RT}\right) \quad (2.11)$$

This equation is the Gorbachev approximation.

Combining Eq. (2.2) and Eq. (2.11) leads to

$$\ln \left[ \frac{g(\alpha)}{T^2} \right] = \ln \left[ \frac{AR}{\beta(E + 2RT)} \right] - \frac{E}{RT} \quad (2.12)$$

If we approximate the first term on the right hand side as a constant, for a proper  $g(\alpha)$  a plot of  $\ln \left[ g(\alpha) / T^2 \right]$  and  $1/T$  will be a straight line or linear function from which can be obtained the values of  $E$  and  $A$  from the slope and (0,0) intersect, respectively. If the first term cannot be approximated as a constant, Eq. (2.12) can be transformed to

$$\ln \left[ \frac{g(\alpha)(E + 2RT)}{T^2} \right] = \ln \left( \frac{AR}{\beta} \right) - \frac{E}{RT} \quad (2.13)$$

Then use of iteration and the least square method enables the calculation of  $E$ ,  $A$  and a logically reasonable  $g(\alpha)$ . This approach is called the Gorbachev method [30].

If Eq. (2.2) and Eq. (2.9) are combined, and set  $f(\alpha) = (1 - \alpha)^n$  while using a first order approximation of  $P(x)$ , the following equation is obtained

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \frac{RT^2}{E} \left( 1 - \frac{2RT}{E} \right) \exp \left( -\frac{E}{RT} \right) \quad (2.14)$$

Taking the logarithm of both sides (if  $n \neq 1$ ) gives,

$$\ln \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right] = \ln \left[ \frac{AR}{\beta E} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (2.15)$$

If  $n = 1$ , then

$$\ln \left[ \frac{-\ln(1-\alpha)}{T^2} \right] = \ln \left[ \frac{AR}{\beta E} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (2.16)$$

The above two equations are the Coats-Redfern method. Since in most cases  $E/RT \gg 1$ ,  $(1 - 2RT/E) \approx 1$  and the first term on the right hand side of the above two equations is approximately a constant. Plotting  $\ln \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right]$  with respect to  $1/T$  when  $n \neq 1$  or plotting  $\ln \left[ \frac{-\ln(1-\alpha)}{T^2} \right]$  with respect to  $1/T$  when  $n = 1$ , a straight line is obtained if the value of  $n$  is chosen properly and the value of the activation energy is obtained

from the slope. In cases where the above two equation fails to satisfy  $(1 - 2RT / E) \approx 1$ , the following evaluation functions may be applied:

$$\Omega = \sum_{i=1}^L [LHS \text{ term of Eq.3.15} - RHS \text{ terms of Eq.3.15}]^2$$

$$\Omega = \sum_{i=1}^L [LHS \text{ term of Eq.3.16} - RHS \text{ terms of Eq.3.16}]^2$$

where *LHS* and *RHS* designate left hand side and right hand side, respectively.

The use of the above two evaluation functions to calculate a minimum value then gives the values of  $E$ ,  $A$  and  $n$ . If  $n \neq 1$ , another procedure is to transform Eq. (2.11) and Eq. (2.12) to,

$$\ln \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2 (1-n) \left(1 - \frac{2RT}{E}\right)} \right] = \ln \left( \frac{AR}{\beta E} \right) - \frac{E}{RT} \quad (2.17)$$

If  $n = 1$ , the following equation is obtained,

$$\ln \left[ \frac{\ln(1 - \alpha)}{T^2 \left(1 - \frac{2RT}{E}\right)} \right] = \ln \left( \frac{AR}{\beta E} \right) - \frac{E}{RT} \quad (2.18)$$

The values of  $E$ ,  $A$  and  $n$  can be obtained by applying an iteration or least squares method, the approach of which is called the Coats-Redfern method [25, 31]. If the value of  $n$  is close to 0, Eq. (2.18) leads to

$$\ln \left( \frac{\alpha}{T^2} \right) = \ln \left[ \frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right) \right] - \frac{E}{RT} \quad (2.19)$$

Then, a plot of  $\ln(\alpha / T^2)$  against  $1/T$  gives the value of  $E$  from the slope and the value of  $A$  from the (0, 0) intercept.

Combining Eq. (2.2) and the first order approximation of the temperature integral,  $p(x) = e^{-x} / x^2$ , and doing some transformations give another form of Coats-Redfern integral,

$$\ln \left[ \frac{g(\alpha)}{T^2} \right] = \ln \left( \frac{AR}{\beta E} \right) - \frac{E}{RT} \quad (2.20)$$

A plot of  $\ln(g(\alpha)/T^2)$  as a function of  $1/T$  gives the values of  $E$  and  $A$  from the slope and intercept, respectively. [2]

Though a great number of model fitting methods have been developed by researchers, the principle of these methods is the same as in the discussion heretofore: fit different reaction models into the kinetic equation and calculate the activation energy and pre-exponential factor, and then select the model which gives the best fit. All of these model fitting methods give a single pair of values for the activation energy and pre-exponential factor. In general, model-fitting methods have been strongly criticized [2, 32-38] because almost any  $f(\alpha)$  can be used to fit the experimental data satisfactorily even though drastic variations in the kinetic parameters occur; no good criterion exists to distinguish which result best reflects or describes actual physiochemical processes occurring during the reactions..

### *2.3 Invariant Kinetic Parameters Method*

Model-fitting methods involve the use of different reaction models to fit one single conversion curve or multiple curves, and then attempt to determine the kinetic parameters  $E$  and  $A$  by regression analyses. When a model-fitting method is applied to a single-heating rate test, widely varying values of the activation parameters are obtained when using different model functions

that can be correlated to the so-called “compensation effect” relation [39-45]:

$$\ln A = a + bE \quad (2.21)$$

where  $a$  and  $b$  are constants. It has been theoretically and experimentally postulated that  $b = 1/RT_{max}$  and in some literature,  $a = \beta E / RT_{max}^2$ , where the index  $max$  means the maximum reaction rate [45-50].

The invariant kinetic parameter (IKP) method, suggested by Lesnikovich and Levchik [40, 46, 51], employs the compensation effect. Since the linear regression lines, represented by Eq. (2.21), for several sets of different heating rates,  $\beta_j$ , tend to intersect at a point or a narrow common area, the kinetic parameters,  $\ln A_{inv}, E_{inv}$ , can be obtained by,

$$\ln A_{inv} = a_j + b_j E_{inv} \quad (2.22)$$

where the subscript  $j$  refers to the parameters of Eq. (2.21) obtained at different heating rates  $\beta_j$ .

## 2.4 Model Free Method

Methodically, model free methods can be classified into three categories: differential isoconversional, integral isoconversional and modulated thermogravimetry methods [52].

### 2.4.1 Isoconversional Principle

All isoconversional methods originate from the so called “isoconversional principle” that assumes reaction rates at a given conversion degree are only a function of temperature [53]; this principle forms the cornerstone of isoconversional analyses [1, 54, 55]. Taking the logarithmic derivative of the reaction rate of the general kinetic equation, Eq. (1.7), at a given  $\alpha$ , one gets

$$\left[ \frac{\partial \ln(d\alpha / dt)}{\partial T^{-1}} \right]_{\alpha} = \left[ \frac{\partial \ln k(T)}{\partial T^{-1}} \right]_{\alpha} + \left[ \frac{\partial \ln f(\alpha)}{\partial T^{-1}} \right]_{\alpha} \quad (2.23)$$

Note that at a given  $\alpha$ ,  $f(\alpha)$  remains constant and the second term on the right hand side of the above equation is zero. Thus,

$$\left[ \frac{\partial \ln(d\alpha / dt)}{\partial T^{-1}} \right]_{\alpha} = -\frac{E_{\alpha}}{R} \quad (2.24)$$

In order to obtain the activation energy,  $E_{\alpha}$ , three-to-five experimental tests at different heating protocols, such as at different heating rates, have to be performed. Of particular importance is that the procedure for extracting activation energy values does not require any assumption about or determination of the reaction model. For this reason, isoconversional methods are often called model-free methods. However, it has to keep in mind that although they do not require the reaction model to be identified, they do assume that the conversion dependence of the rate follow the same reaction model of  $\alpha = const$ .

A large number of isoconversional methods have been developed. In general, the methodology of model free methods can be classified into three categories: differential isoconversional [56-58], integral isoconversional and modulated thermogravimetry methods [52]; integral isoconversional methods include regular integral methods [59-66] and advanced (or “incremental” in some studies) integral methods [67-71].

#### 2.4.2 Differential Isoconversional Methods

The differential isoconversional methods start directly from Eq. (1.7). A classic differential isoconversional method is the Friedman (FR) method [56], which is derived by taking logarithms of both sides of the general kinetic equation under different heating protocols,  $\beta_i$ ,

$$\ln\left(\beta_i \frac{d\alpha}{dT}\right) = -\frac{E}{RT_i} + \ln A + \ln f(\alpha) \quad (2.25)$$

The index  $i$  is used to denote various temperature programs and  $T_i$  is the temperature at which the given conversion degree,  $\alpha$ , is reached under the corresponding heating program. Using the isoconversional principle, the term  $\ln A + \ln f(\alpha)$  in Eq. (2.25) remains unchanged for a given  $\alpha$ ; then, a plot of  $\ln[\beta_i(d\alpha/dT)]$  against  $1/RT_i$  determines the value of  $E_\alpha$ . However, the FR method and other differential isoconversional methods are very sensitive to experimental noise, resulting in large deviations of  $E_\alpha$ , which limits their application in assessing solid state reactions [54].

### 2.4.3 Regular Integral Methods

Regular integral methods start from the integral form of the general kinetic equation, Eq. (2.2). In past decades, a variety of regular integral methods have been developed. This section presents in detail the methodology of some of the most popular methods.

#### 2.4.3.1 Ozawa-Flynn-Wall Method

The Ozawa-Flynn-Wall (OFW) method [72, 73] starts from Eq. (2.2) and employs the Doyle approximation [22-24] of  $p(x)$  to yield,

$$\ln \beta_i = -1.052 \frac{E}{RT_i} + \ln \frac{AE}{Rg(\alpha)} - 5.331 \quad (2.26)$$

The value of  $E_\alpha$  is then evaluated from the slope of the linear plot of  $\ln \beta_i$  against  $1/RT_i$ .

Note that the OFW method involves two systematic errors sources. First, it starts from Eq. (2.2), which involves the assumption that  $E$  must remain constant with respect to  $\alpha$ , while for complex

reactions  $E$  varies with  $\alpha$ . Second, even if  $E$  is a constant, the OFW method still contains the error sources associated with the Doyle approximation [74] of  $p(x)$ .

#### 2.4.3.2 Vyazovkin Method

The method [67] proposed by Vyazovkin also starts from the integral form of the general kinetic equation,

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A_\alpha}{\beta_i} \int_0^{T_\alpha} \exp\left(\frac{-E_\alpha}{RT_i}\right) dt = \frac{A_\alpha}{\beta_i} A_\alpha J[E_\alpha, T_i] \quad (2.27)$$

It employs a given conversion and a set of experiments performed under  $n$  arbitrary heating programs:

$$\frac{A_\alpha}{\beta_1} J[E_\alpha, T_1] = \frac{A_\alpha}{\beta_2} J[E_\alpha, T_2] = \dots = \frac{A_\alpha}{\beta_n} J[E_\alpha, T_n] \quad (2.28)$$

Numerically, after canceling  $A_\alpha$  the value of  $E_\alpha$  can be determined by minimizing the following function:

$$\sum_{i=1}^n \sum_{j \neq i}^n \frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \quad (2.29)$$

Both the model fitting method and IKP method, as well as some other methods such as the Kissinger method [61], provide only a single pair of  $E$  and  $A$  while the value of  $E$  obtained by an isoconversional method varies with the progress of conversion degree,  $\alpha$ . Vyazovkin recommended the concept of “variable activation energy” in a review article [75] entitled ‘kinetic concepts of thermally stimulated reactions in solids: a view from a historical perspective’ but it has aroused strong controversies [76-78]. For example, Galwey [78] gave critical scrutiny of the consequences of using the concept to the theory of the subject. It stated that in some systems the



initial solid state reactant would have melted before the reaction of interest or the kinetic behavior pattern would have been adequately explained by contributions from complex or secondary controls. Therefore, it argued that the supporting information provided in the article [75] was insufficient, unsatisfactory and unnecessary for introducing the concept of variable activation energy. It also claimed that, although considerable theoretical problems exist in current understanding of reactions proceeding in solid phases, the long term development of the subject is best approached by individually identifying and quantitatively determining the contributing factors controlling or influencing the rate of any reaction of interest. It concluded that the introduction of variable activation energy was a retrograde step, unlikely to progress science through the development of theory, and does not recommend to use. In a short article [79], Vyazovkin replied [80] that for the condensed phase the free energy of activation did not have to be the free energy or enthalpy of activation but, rather, a function of temperature dependent properties of the reaction medium; hence, it claimed that the term of variable activation energy, which is often called ‘actual, effective, empirical and not merely theoretical’, was a reasonable compromise between the complexity of solid reactions and oversimplified methods used to describe their kinetics. Vyazovkin expressed the viewpoint that, by accepting variable activation energy as a practical compromise, people would forego the methods producing single values of the activation energy and begin using multiple run methods (such as isoconversional methods) that allow for detecting reaction complexity [81]. And in recent years, the terms ‘variable activation energy’ and ‘model free methods’ have become popular and widely used.

#### 2.4.3.3 Li-Tang Method

Li and Tang [64-66] proposed an isoconversional method for the analysis of thermoanalytical data. It firstly transforms the general equation into the following equation,

$$\int_0^\alpha \left( \ln \frac{d\alpha}{dt} \right) d\alpha = \int_0^\alpha \left( \ln \beta \frac{d\alpha}{dT} \right) d\alpha = - \int_0^\alpha \frac{E}{TR} d\alpha = - \frac{E}{R} \int_0^\alpha \frac{d\alpha}{T} + G(\alpha) \quad (2.30)$$

where  $G(\alpha) = \alpha \ln A + \int_0^\alpha [\ln f(\alpha) d\alpha]$ . Because of the isoconversional principle applied in model free methods,  $G(\alpha)$  would be a constant for several different heating programs for a given  $\alpha$ ; a plot of  $\int_0^\alpha \ln(d\alpha/dt) d\alpha$  against  $\int_0^\alpha (1/T) d\alpha$  would determine the values of activation energy from the slope of the linear plot. Like the FR method, the Li-Tang (LT) method removes systematic errors associated with approximating the exponential integral. However, the derivation of Eq. (2.26) also involves the assumption that  $E$  must be a constant with a change in  $\alpha$ . Note that this method is more tolerant of noise than the FR method because the FR method uses the differential data within plots of  $\ln[\beta_i(d\alpha/dT)]$  versus  $1/RT_i$ ; in the LT method, the logarithms followed by the integration decreases the influence of noise.

Budruga et al. [82] pointed out that it is difficult to determine initiation temperatures of a reaction when using the LT method and recommended a similar equation with a non-zero lower limit of  $\alpha$  for integration,

$$\int_{\alpha_1}^\alpha \left( \ln \beta \frac{d\alpha}{dT} \right) d\alpha = -\frac{E}{R} \int_{\alpha_1}^\alpha \frac{d\alpha}{T} + G(\alpha) \quad (2.31)$$

where the lower limit of integral could be  $\alpha_1 > 0$ , and  $G(\alpha) = (\alpha - \alpha_1) \ln A + \int_{\alpha_1}^\alpha [\ln f(\alpha) d\alpha]$ .

However, it has been shown that the activation energy obtained by this method depends on the lower limit of integration,  $\alpha_1$ , and the activation energy is missed when  $\alpha < \alpha_1$  [82]. Thus, Budruga et al. considered the LT method unsuitable for determining the dependence of  $E$  as a function of conversion degree [82].

#### 2.4.3.4 Kissinger-Akahira-Sunose Method

The Kissinger-Akahira-Sunose (KAS) method [61, 83] employs the Coats-Redfern [25]

approximations of  $p(x)$  to yield,

$$\ln \frac{\beta}{T_i^2} = \ln \frac{AR}{Eg(\alpha)} - \frac{E}{RT_i} \quad (2.32)$$

The value of  $E_\alpha$  can be evaluated by plotting the left side of the equation versus  $1/RT_i$ .

#### 2.4.4 Advanced Integral Methods

In the derivation of Eq. (2.2) for regular methods, it is assumed that  $E$  must be a constant; this assumption is especially problematic if multiple reaction and/or complex reaction mechanisms are involved. To avoid this disadvantage, advanced integral methods have been developed that start from a modified version of the integral form of the general kinetic equation,

$$g(\alpha - \Delta\alpha, \alpha) = \int_{\alpha - \Delta\alpha}^{\alpha} \frac{1}{f(\alpha)} d\alpha = \frac{A}{\beta} \int_{T_{\alpha - \Delta\alpha}}^{T_\alpha} \exp\left(-\frac{E}{RT}\right) dT \quad (2.33)$$

where  $\Delta\alpha$  is a small reaction segment. Since the integration is applied to a small segment of conversion degree, it is reasonable to take  $E$  as a constant.

##### 2.4.4.1 Advanced Vyazovkin Method

The modified Vyazovkin method [67] assumes  $E$  to be constant only for a small segment  $\Delta\alpha$  and uses integration over small time segments for Eq. (2.27),

$$\int_{\alpha - \Delta\alpha}^{\alpha} \frac{d\alpha}{f(\alpha)} = A_\alpha \int_{t_{\alpha - \Delta\alpha}}^{t_\alpha} \exp\left(\frac{-E_\alpha}{RT_i(t)}\right) dt = A_\alpha J[E_\alpha, T_1(t_\alpha)] \quad (2.34)$$

The procedure utilizes a given conversion and a set of experiments performed under  $n$  arbitrary heating programs:

$$A_\alpha J[E_\alpha, T_1(t_\alpha)] = A_\alpha J[E_\alpha, T_2(t_\alpha)] = \dots = A_\alpha J[E_\alpha, T_n(t_\alpha)] \quad (2.35)$$

Numerically, after canceling  $A_\alpha$ , the value of  $E_\alpha$  can be determined by minimizing the following function:

$$\sum_{i=1}^n \sum_{j \neq i}^n \frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \quad (3.36)$$

#### 2.4.4.2 Advanced Li-Tang Method

During the deviation of the LT method or the procedure improved by Budrugaac [82],  $E$  and  $A$  should be independent of the conversion degree. Otherwise the integration from 0 or  $\alpha_1$  to the current  $\alpha$  will lead to systematic errors. However, systematic errors can be minimized if the equation is integrated over a very small interval of conversion degree,  $\Delta\alpha$ , since the activation energy can be regarded as constant within this very small segment. Thus, Eq. (2.30) can be converted into,

$$\int_{\alpha-\Delta\alpha}^{\alpha} \left( \ln \frac{d\alpha}{dt} \right) d\alpha = -\frac{E}{R} \int_{\alpha-\Delta\alpha}^{\alpha} \frac{d\alpha}{T} + G(\alpha) \quad (2.37)$$

where:

$$G(\alpha) = \Delta\alpha \ln A + \int_{\alpha-\Delta\alpha}^{\alpha} [\ln f(\alpha)] d\alpha \quad (2.38)$$

in which,  $\alpha$  varies from  $3\Delta\alpha/2$  to  $1-\Delta\alpha/2$  with a step  $\Delta\alpha = 1/(m+1)$ , and where  $m$  is the number of the equidistant values of  $\alpha$ . Plotting the left side of Eq. (2.38) versus the integration of the reciprocal of the temperature should give a linear plot with  $E_\alpha$  obtained from the slope of the regression line.

#### 2.4.5 *Modulated Thermogravimetry Methods*

Modulated thermogravimetry methods [84-91] use nonlinear heating rate programs during thermal analyses. Since they are rarely used, this section presents only a brief discussion about their methodology. For example, the temperature-jump method [91] modulates the temperature by making it quickly increase from one value to another at a certain moment in time; during this 'jump' transition it is assumed that the extent of conversion remains unchanged. The value of  $E_{\alpha}$  at the given conversion degree is then obtained from a single heating program rather than multiple ones. In fact, the modulated thermogravimetry method indeed uses the isoconversional principle, and the test results can be taken as experimental realization of the principle [1]. Other modulated programs [92, 93] may employ other temperature modulation forms such as  $T = T_0 + \beta t + L \sin(2\pi\omega t)$ , where  $\omega$  and  $L$  are the frequency and amplitude of the modulation. However, all of them cannot avoid depending upon the isoconversional principle.

### **CHAPTER 3: MODIFICATION OF REGULAR LI-TANG METHOD AND ORTEGA METHOD**

Differential methods have been considered to be potentially more accurate than integral methods (like the OFW method) because differential methods do not employ any approximations [2]. However, the practical use of differential methods unavoidably involves some inaccuracy: first, if differential methods are applied to assess differential data from DSC or DTA significant inaccuracy may be introduced because of the difficulty to accurately determine the data baseline. Second, experimental noise could lead to significant errors to applying the differential methods like FR and may also introduce inaccuracies when the raw data are smoothed. A major advantage of the integral methods is that they avoid these limitations due to the usage of integral data. It should also be noted that, in the derivation of regular integral methods,  $E$  must be independent of  $\alpha$  or otherwise the integration from 0 to  $\alpha$  in Eq. (2.2) would result in serious systematic errors [29, 94]. All regular integration methods [61, 64-66, 72, 73, 95-97] are prone to the same problems, some of which are also influenced by the temperature integral approximation. Fortunately, this kind of limitation can be overcome by using the advanced Vyazovkin (AIC) method [67]. Other recently developed methods [58, 68, 70, 98-100] have made minor modifications to the AIC method to decrease computational efforts. Overall, the key idea behind these incremental methods is to calculate  $E_\alpha$  within a small segment.

This chapter discusses two examples to make a clear understanding of the above general comments on model free methods. In the first example, a simple and precise incremental isoconversional integral method based on Li-Tang (LT) method is proposed for kinetic analysis of solid thermal decomposition in order to evaluate the activation energy as a function of conversion degree. This new approach overcomes the limitation of the LT method and eliminates the problem of the calculated activation energy being influenced by the lower limit of integration. Shown is the dependence of activation energy on conversion degree evaluated by this new method that is

consistent with results obtained by the Friedman (FR) method and the modified Vyazovkin method for the kinetic analysis of both simulated nonisothermal data and experimental data from the decomposition of strontium carbonate. Because the new method is free from approximating the temperature integral and not sensitive to kinetic data noise, it is believed to be more convenient for assessing nonisothermal kinetic data acquired during solid decomposition.

The second example examines the average linear integral isoconversional method developed by Ortega and its improvement. Because evaluations of the activation energies of solid state reactions may be hindered by experimental noise and the uncertainties associated with selecting appropriate reaction segments, this research suggested a procedure, called the modified Ortega method, which can avoid or minimize these hindrances. A more consistent dependence of the activation energy on the extent of reaction conversion was found when using this modified Ortega method to assess both simulated and experimental data and these results were more in-line with those calculated using the modified Vyazovkin method and the Friedman method.

### 3.1 Advanced Li-Tang Method

#### 3.1.1 Methodology of Advanced Li-Tang Method

The integral form of the general kinetic equation is,

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT = \frac{AE}{\beta R} p(x) \quad (3.1)$$

where  $p(x)$  is the temperature integral, which has no analytical solution. In the classic integral isoconversional methods, such as the Ozawa-Flynn-Wall method (OFW) [72, 73], the approximations of  $p(x)$  [23, 25, 26] should be adopted, the result of which is the introduction of systematic errors in calculating the activation energy [101].

To avoid the usage of the temperature integral approximation, Li and Tang [64, 66, 97] proposed an isoconversional method for analyzing thermal analytical data. Their method takes the logarithm and integrates both sides of Eq. (3.1),

$$\int_0^\alpha \left( \ln \frac{d\alpha}{dt} \right) d\alpha = \int_0^\alpha \left( \ln \beta \frac{d\alpha}{dT} \right) d\alpha = -\frac{E}{R} \int_0^\alpha \frac{d\alpha}{T} + G(\alpha) \quad (3.2)$$

where

$$G(\alpha) = \alpha \ln A + \int_0^\alpha [\ln f(\alpha)] d\alpha \quad (3.3)$$

Because  $G(\alpha)$  is constant for a given  $\alpha$  for different heating programs, a plot of  $\int_0^\alpha \ln(d\alpha/dt) d\alpha$  against  $\int_0^\alpha (1/T) d\alpha$  will be a straight line and the value of the activation energy  $E_\alpha$  can be obtained from the slope of the line.

In agreement with the Friedman (FR) method [56], the Li-Tang method (LT) avoids systematic errors introduced by the temperature integral approximations during the calculation of activation energy. Moreover, this method is more tolerant of data noise in calculating activation energy than the Friedman method because the data sets of  $\int_0^\alpha \ln(d\alpha/dt) d\alpha \sim \int_0^\alpha (1/T) d\alpha$  of the LT method are less sensitive to raw data noise than those of  $\ln(d\alpha/dt) \sim 1/T$  of the Friedman method.

Budrugaec et al [82] pointed out that it is difficult to determine the initiation point of a solid reaction when using the LT method, and thus recommended an improved version of Eq. (3.2) with a non-zero lower limit of  $\alpha$  for integration,

$$\int_{\alpha_1}^\alpha \left( \ln \frac{d\alpha}{dt} \right) d\alpha = -\frac{E}{R} \int_{\alpha_1}^\alpha \frac{d\alpha}{T} + G(\alpha) \quad (3.4)$$



where the lower limit of the integral is  $\alpha_1 > 0$ , and

$$G(\alpha) = (\alpha - \alpha_1) \ln A + \int_{\alpha_1}^{\alpha} [\ln f(\alpha)] d\alpha \quad (3.5)$$

However, it has been shown that the activation energy obtained by this improved method depends on the lower limit of integration,  $\alpha_1$ , and the activation energy with  $\alpha < \alpha_1$  is missed [82]. Thus, Budrugaec et al. considered that the LT method was not suitable to find the dependence of  $E = E(\alpha)$  [82].

In this dissertation, an incremental version of the LT method, which is independent of the lower limit of integration, is proposed and verified by numerical and experimental examples. The values of activation energy calculated by this new method are compared with those obtained by other isoconversional methods, such as the LT method and its improved version by Budrugaec et al., the OFW method, the FR method and the modified Vyazovkin method (AIC) [67]).

In the deviation of the LT method or the procedure improved by Budrugaec et al.,  $E$  and  $A$  should be independent of the conversion degree. Otherwise, the integration from 0 or  $\alpha_1$  to a current  $\alpha$  value will lead to systematic errors. However, the systematic error can be minimized if Eq. (1) is integrated over a very small interval of conversion degree,  $\Delta\alpha$ , since the activation energy can be regarded as constant within a very small segment. Thus Eq. (3.2) can be changed to

$$\int_{\alpha-\Delta\alpha}^{\alpha} \left( \ln \frac{d\alpha}{dt} \right) d\alpha = -\frac{E}{R} \int_{\alpha-\Delta\alpha}^{\alpha} \frac{d\alpha}{T} + G(\alpha) \quad (3.6)$$

where

$$G(\alpha) = \Delta\alpha \ln A + \int_{\alpha-\Delta\alpha}^{\alpha} [\ln f(\alpha)] d\alpha \quad (3.7)$$

in which  $\alpha$  varies from  $3\Delta\alpha/2$  to  $1-\Delta\alpha/2$  with a step  $\Delta\alpha = 1/(m+1)$ , where  $m$  is the number of the equidistant values of  $\alpha$ . The plot of the left side of Eq. (3.7) versus the integration of the reciprocal of temperature should be a linear and  $E_\alpha$  can be obtained from the slope of the regression line.

Obviously, the above incremental isoconversional method avoids the problem of the LT method having its calculated activation energy dependent on the lower limit of integration. Hence, this new method is expected to give more consistent results with those from Friedman method (for noise-free data) or the modified Vyazovkin method.

### 3.1.2 Numerical Applications

This section will verify the advantage of the new incremental isoconversional method by numerical examples. Unlike experimental data on solid state reactions, the simulated data are not affected by noise and therefore are most suitable to test the newly proposed method. To evaluate the performance of the new method, the FR and AIC methods are also used to analyze the simulated data and the results are compared. The FR method is chosen because it is directly based on the general kinetic equation, and thus gives reliable activation energy values for the simulated data which are not encumbered by noise. Similarly, the AIC method is chosen because it is believed to be an accurate integral isoconversional method although it is complex to perform [67]. It is noted that this approach to test the quality of an isoconversional method appears in many published manuscripts [58, 67, 68, 96, 98, 102].

In this dissertation, a process that involves two parallel reactions and a variation in the effective activation energy is simulated. The overall kinetic equation of this process is described as:

$$\frac{d\alpha}{dT} = \frac{A_1}{\beta} \exp\left(-\frac{E_1}{RT}\right)(1-\alpha)^2 + \frac{A_2}{\beta} \exp\left(-\frac{E_2}{RT}\right)(1-\alpha) \quad (3.8)$$

where  $E_1 = 80 \text{ kJ/mol}$ ,  $A_1 = 10^8 \text{ min}^{-1}$ ,  $E_2 = 160 \text{ kJ/mol}$ ,  $A_2 = 10^{16} \text{ min}^{-1}$ ; four linear heating rates,  $\beta_{1-4} = 1, 2, 4, 8 \text{ K/min}$ , are used. Note that equations similar to Eq. (3.8) are used in the aforementioned papers [58, 67, 68, 96, 98, 102] but with different Arrhenius parameters or model functions.

The dependence of the apparent activation energy as a function of the conversion degree obtained by aforementioned isoconversional methods is displayed in Fig. 3.1. It indicates that:

-The  $E_\alpha$  dependence calculated by the new method is practically identical to that estimated by FR method and AIC method, i.e.  $E_{new} \approx E_{AIC} \approx E_{FR}$ ;

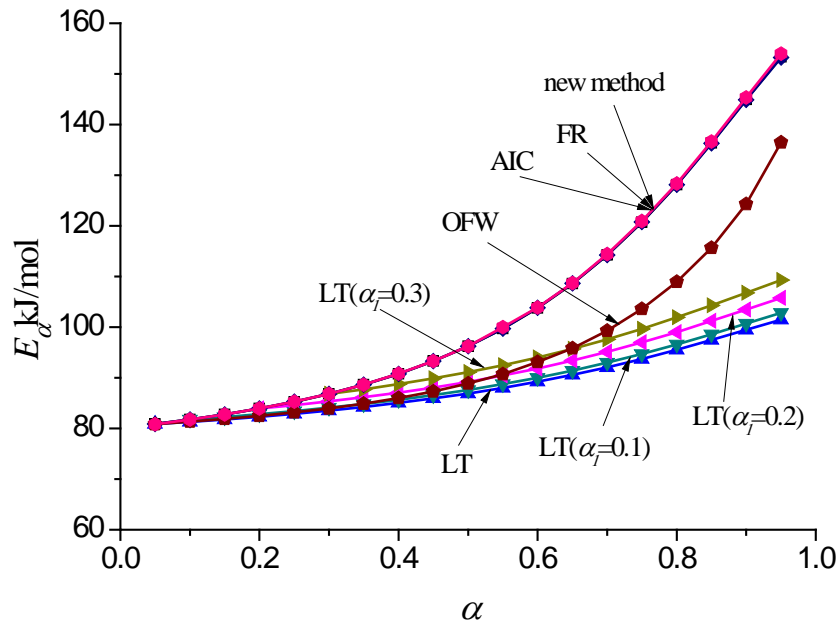


Figure 3.1  $E_\alpha$  dependencies evaluated for the simulated process by Li-Tang method with different lower limit of the integral,  $\alpha_l$ , as well as by OFW, AIC, FR and the new method

-The  $E_\alpha$  dependence estimated by the LT method (Eq. (3.2)) and the version improved by Budrugaec et al. (Eq. (3.4)) deviates noticeably from the dependence estimated by the FR method;

-As noted by Budrugaec et al.[82] , the activation energy values obtained by LT method depend on the lower limit of the integral  $\alpha_1$ . With the increases of the lower limit of  $\alpha_1$  , the information of  $E_\alpha$  for  $\alpha < \alpha_1$  will be lost.

These simulated data suggest that the new method gives reliable activation energy when  $E$  varies with the degree of conversion. It can be concluded that the new method is much better than the regular LT method and the method improved by Budrugaec.

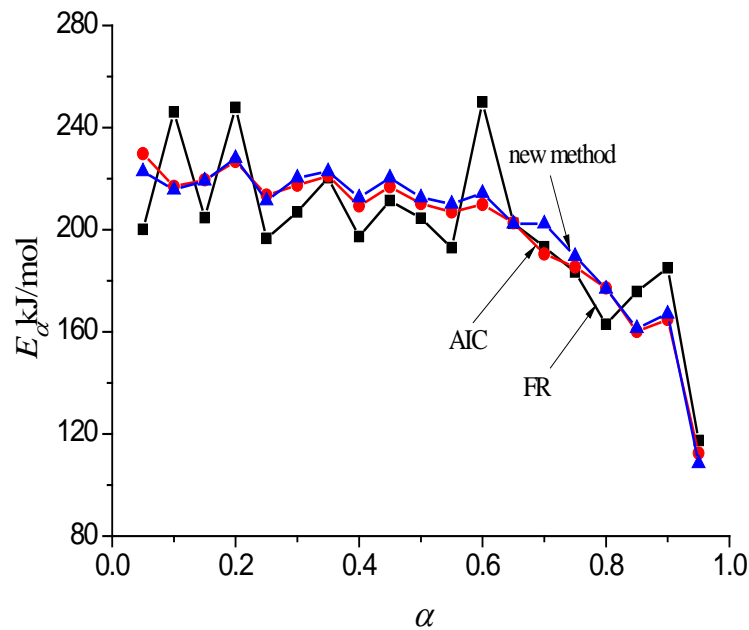


Figure 3.2  $E_\alpha$  dependencies evaluated for the  $SrCO_3$  decomposition by the new method, FR method and AIC method

### 3.1.3 Experimental Example

The thermal decomposition of strontium carbonate ( $SrCO_3$ ), which is used as the experimental example in this dissertation, was carried out in a 50 ml/min flow of  $N_2$  with heating rates of 0.5, 5, 7.5 K/min from room temperature (300K) to 1000K on a Shimadzu DTG-60H TGA/DTA Analyzer. The  $SrCO_3$  sample (purity of >99.99%) was supplied by Tianjin Guangfu at the Fine Chemical Research Institute. The sample was dried for two hours at 450°C and then between 23.8-24.3 mg was loaded into the TGA/DTA sample holder. Although heating rates of 0.5, 5, 7.5 K/min were to be used during the testing, actual heating rate values were calculated from the recorded sample temperature against time.

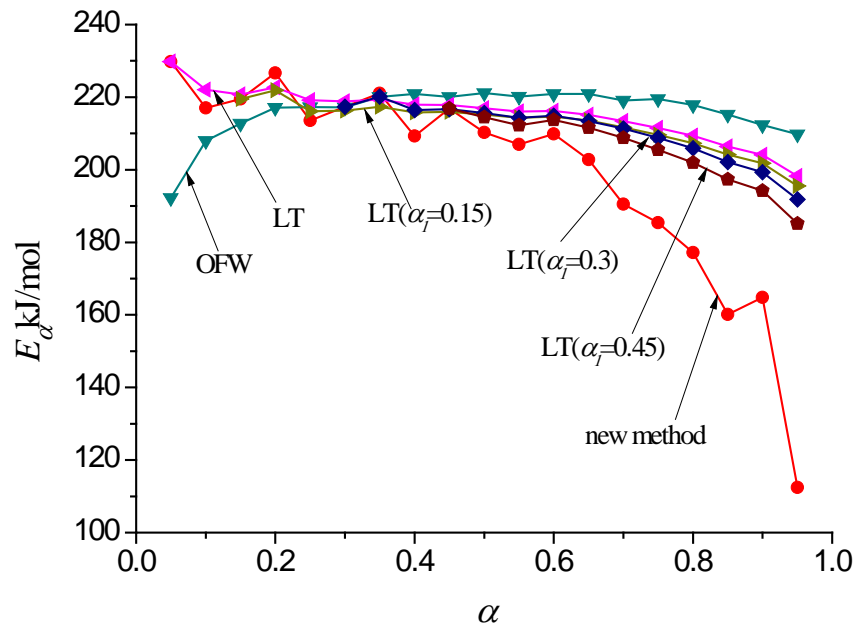


Figure 3.3  $E_\alpha$  dependencies obtained for the  $SrCO_3$  decomposition by the new method and Li-Tang method with different lower integral limit,  $\alpha_1$ , and by OFW method

The dependence of activation energy on the conversion degree obtained by aforementioned isoconversional methods is shown in Fig. 3.2 and Fig. 3.3. From Fig. 3.2, it can be seen that the activation energy decreases with the increasing conversion degrees. The results obtained by the

new method and AIC method are consistent, while those obtained using the FR method seem less consistent, perhaps because of effects of experimental noise. Taking the values calculated by the Modified Vyazovkin method as a reference, the overall standard deviation of the E values determined by new method was 4.14 while the overall standard deviation of the values calculated by FR method was 17.79. Moreover, from Fig. 3.3 it can be seen that:

-the OFW method gave much lower values near the onset ( $\alpha < 0.15$ ) of the reaction, and then rather stable values for  $\alpha > 0.15$ .

-the LT method gave consistent values in the beginning of the process but also led to rather stable values for  $\alpha > 0.15$ . As expected, the dependence of  $E_\alpha$  values obtained by the Budrugaec et al. method depended on the lower limit  $\alpha_1$  in Eq. (3.4).

-The values of the activation energy obtained by the OFW method, LT method, and the method improved by Budrugaec et al. differed considerably from the results obtained by AIC (Fig. 3.2).

From Figs. 3.2 and 3.3 it can be shown that the proposed new approach has distinct advantages over some integral isoconversional methods (OFW, LT *etc.*). It can be concluded that the new approach is capable of providing consistent values of activation energy obtained by AIC even if E varies strongly with the conversion degree.

### 3.2 Modified Ortega Method

#### 3.2.1 Methodology of Modified Ortega Method

Recently, Ortega developed a simple average integral isoconversional method [98] (the original Ortega method) for the most frequently used linear heating program,  $\beta = dT(t)/dt$ , of nonisothermal experiments, which is based on the integral form of the general kinetic equation,

$$g(\alpha) = \int_0^\alpha \frac{1}{f(\alpha)} d\alpha = A \int_0^t \exp\left(-\frac{E}{RT}\right) dt \quad (3.9)$$

It leads to

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T \exp\left(\frac{-E}{RT}\right) dT \quad (3.10)$$

For a small segment  $\Delta\alpha$ , Eq. (3.10) can be approximated by

$$g(\alpha - \Delta\alpha, \alpha) = \frac{A}{\beta} \int_{T_{\alpha-\Delta\alpha}}^{T_\alpha} \exp\left(\frac{-E_\alpha}{RT}\right) dT \approx \frac{A\Delta T}{\beta} \exp\left(-\frac{E_\alpha}{RT_\alpha}\right) \quad (3.11)$$

where  $\Delta T = T_\alpha - T_{\alpha-\Delta\alpha}$ .

Taking the log of Eq. (3.11) yields

$$\ln g(\alpha - \Delta\alpha, \alpha) \approx \ln\left(\frac{\Delta T}{\beta}\right) + \ln A - \frac{E_\alpha}{RT_\alpha} \quad (3.12)$$

For a given conversion and set of  $n$  experiments carried out at different linear heating programs

$\beta_i$  ( $i=1, \dots, n$ ), Eq. (3.12) leads to

$$\ln\left(\frac{\beta_i}{\Delta T_{\alpha,i}}\right) = \text{cons.} - \frac{E_\alpha}{RT_{\alpha,i}} \quad (3.13)$$

Then a plot of  $\ln(\beta_i / \Delta T_{\alpha,i})$  versus  $1 / RT_{\alpha,i}$  will be a straight line and the value of  $E_\alpha$  can be determined from the slope of the line.

Using a traditional integral isoconversional method, such as the Ozawa-Flynn-Wall (OFW) method [72, 73], creates system errors when the value of  $E$  varies with the conversion degree  $\alpha$ .

To avoid these errors, the Ortega method and some other newly developed methods [67, 68, 70] also use small integral segments,  $\Delta\alpha$ . However, when  $\Delta\alpha$  is small, the use of a single temperature  $T_\alpha$  prevents accurate characterization of the reaction segment and creates a source of systematic error. Hence, the Ortega method requires accurate values of  $T_{\alpha-\Delta\alpha}$  and  $T_\alpha$ , and potentially large  $\Delta\alpha$ , to minimize the influence of temperature measurement noise; errors in the temperature interval  $\Delta T$  compromise the accuracy of  $E_\alpha$  values. The accuracy of the improved

version of the Ortega method is examined using both numerical and experimental examples, and some recommendations for using this method are discussed in the following.

The derivation of Eq. (3.11) imposes the integration range from  $\alpha - \Delta\alpha$  to  $\alpha$ . Because of the importance of selecting an appropriate temperature to characterize the temperature segment when using the modified Ortega method, the integration of Eq. (3.11) with respect to  $\alpha$  is changed between  $\alpha - \Delta\alpha / 2$  and  $\alpha + \Delta\alpha / 2$ , which yields

$$g(\alpha - \Delta\alpha / 2, \alpha + \Delta\alpha / 2) = \frac{A}{\beta} \int_{T_{\alpha - \Delta\alpha/2}}^{T_{\alpha + \Delta\alpha/2}} \exp\left(\frac{-E_\alpha}{RT}\right) dT = \frac{A}{\beta} \exp\left(-\frac{E_\alpha}{RT_\varepsilon}\right) \Delta T \quad (3.14)$$

where  $\Delta T = T_{\alpha + \Delta\alpha/2} - T_{\alpha - \Delta\alpha/2}$ ,  $T_{\alpha - \Delta\alpha/2} \leq T_{\varepsilon n} \leq T_{\alpha + \Delta\alpha/2}$ .

As the second step, a number,  $n$ , of temperatures,  $T_{\varepsilon n}$ , are selected to characterize the temperature for different reaction segments; hence,  $T_{\varepsilon n}$  varies from  $T_{\alpha - \Delta\alpha/2}$  to  $T_{\alpha + \Delta\alpha/2}$  with the step  $h = \Delta\alpha / (n - 1)$  and  $n$  an odd number, as shown below:

if  $n = 1$ ,  $T_{\varepsilon 1} = T_\alpha$

if  $n = 3$ ,  $T_{\varepsilon 1} = T_{\alpha - \Delta/2}$ ,  $T_{\varepsilon 2} = T_\alpha$ ,  $T_{\varepsilon 3} = T_{\alpha + \Delta/2}$

if  $n = 5$ ,  $T_{\varepsilon 1} = T_{\alpha - \Delta/2}$ ,  $T_{\varepsilon 2} = T_{\alpha - \Delta/4}$ ,  $T_{\varepsilon 3} = T_\alpha$ ,  $T_{\varepsilon 4} = T_{\alpha + \Delta/4}$ ,  $T_{\varepsilon 5} = T_{\alpha + \Delta/2}$

...

Finally, the characteristic temperature of the aforementioned  $n$  temperatures is defined as

$$T_\varepsilon = \frac{1}{n} \sum_{i=1}^n T_{\varepsilon i} \quad (3.15)$$



Thereby, noise created by temperature measurements when using small  $\Delta\alpha$  can be minimized because a relatively large reaction segment  $\Delta\alpha$  is used for a large number  $n$  temperatures. For a set of experiments carried out at different heating rates, Eq. (3.13) can be modified to

$$\ln\left(\frac{\beta_i}{\Delta T_{\alpha,i}}\right) = \text{cons.} - \frac{E_\alpha}{RT_\varepsilon} \quad (3.16)$$

The activation energy,  $E_\alpha$ , is obtained from a plot of  $\ln(\beta_i / \Delta T_{\alpha,i})$  against  $1/RT_\varepsilon$ .

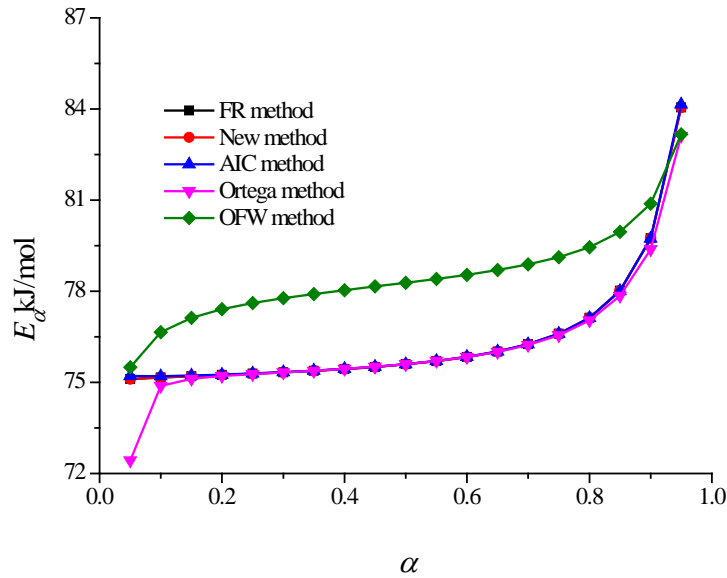


Figure 3.4 Dependence of  $E_\alpha$  on the value  $\alpha$  evaluated by FR, AIC, OFW, the original Ortega method, and the modified Ortega method with  $\Delta\alpha=0.04$

It is proposed that this modified Ortega method can minimize the systematic error caused by large  $\Delta\alpha$  segments and increase tolerance to experimental noise as  $n$  is increased. In the following section, the modified Ortega method [71] is assessed for the case of  $n = 5$ .

### 3.2.2 Results and Discussion

Both simulated and experimental data were assessed to validate the modified Ortega method. The first simulation procedure described below used two parallel reactions without noise: one was a first order reaction and the other a second order reaction. In the second simulation discussed below, a single step reaction with noise was assessed to explore effects of noise on the calculated  $E_\alpha$  values. As for applicability of the modified Ortega method to experimental data, data during the decomposition of strontium carbonate ( $SrCO_3$ ) were analyzed using the modified Ortega and other methods.

#### 3.2.2.1 Simulation without Noise

The modified Ortega method was compared to the original Ortega method, and the Friedman (FR) and modified Vyazovkin (AIC) methods, when using simulated data. The FR method is known to be very sensitive to experimental noise that can lead to serious deviations, but without noise it can give reliable activation energies. Similarly, the AIC method is known to be one of the most accurate integral isoconversional methods with good tolerance of noise although it is more complex to perform. Because it was considered beneficial to compare results when using the modified Ortega method and the Ortega, FR and AIC methods with a more traditional integral method, the OFW method was also used to calculate activation energies.

For a process having two parallel reactions, the activation energy varies with  $\alpha$  and the overall kinetic equation is described as

$$\frac{d\alpha}{dT} = \frac{A_1}{\beta} \exp\left(-\frac{E_1}{RT}\right)(1-\alpha) + \frac{A_2}{\beta} \exp\left(-\frac{E_2}{RT}\right)(1-\alpha)^2 \quad (3.17)$$

where  $E_1=100$  kJ/mol,  $A_1=10^9$  min<sup>-1</sup>,  $E_2=75$  kJ/mol,  $A_2=10^8$  min<sup>-1</sup>; four linear heating rates of  $\beta_{1-4}=2, 4, 6, 8$  K/min were studied.

Figure 4.4 compares the dependence of calculated  $E_\alpha$  values as a function of  $\alpha$  for the five different isoconversional methods when an integral segment  $\Delta\alpha = 0.04$ . The following summarizes the findings:

- The  $E_\alpha$  dependence determined by the modified Ortega method leads to practically the same result estimated by FR and AIC methods;
- The  $E_\alpha$  dependence calculated by the original Ortega method had larger systematic errors as compared to its dependence calculated by the FR method; and
- The  $E_\alpha$  dependence obtained by OFW method differed noticeably from the results calculated by other methods, because traditional isoconversional methods that assume  $E$  is independent of  $\alpha$  lead to a large systematic error when  $E$  varies with  $\alpha$  [16, 17].

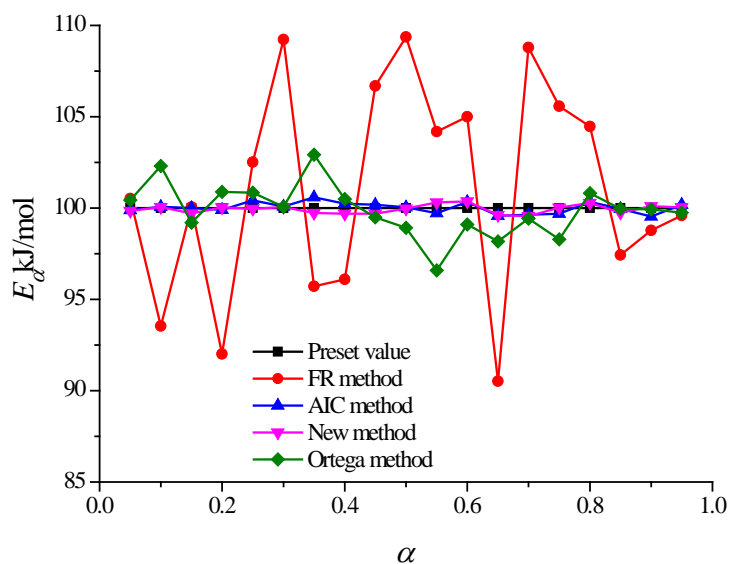


Figure 3.5 Dependence of  $E_\alpha$  on the value  $\alpha$  for the simulated single step reaction FR, AIC, and the original Ortega method with  $\Delta\alpha = 0.01$ , and the modified Ortega method with  $\Delta\alpha = 0.04$

### 3.2.2.2 Simulation with Noise

To evaluate the effect of noise on the value of  $E_\alpha$ , a small-order, random temperature noise ( $-0.01$  to  $0.01$  K) was introduced into the simulated data when using a single step reaction:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right)(1-\alpha) \quad (3.18)$$

where  $E=100$  kJ/mol (a setting value),  $A = 10^9$  and  $\beta_{1-4} = 2, 4, 6, 8$  K/min.

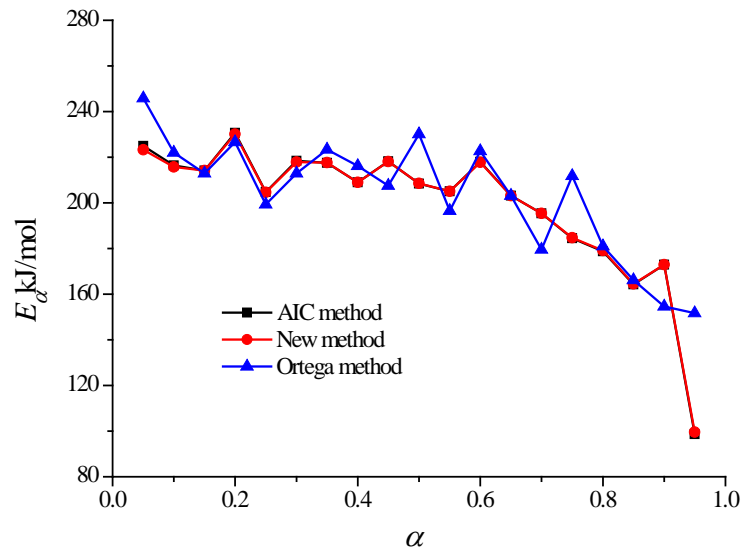


Figure 3.6 Dependence of  $E_\alpha$  on the value  $\alpha$  obtained for the experiments of  $\text{SrCO}_3$  decomposition by AIC, the modified Ortega method, and the original Ortega method, all with  $\Delta\alpha = 0.04$

Figure 3.5 compares the results, and the following summarizes them:

-The  $E_\alpha$  dependence estimated by the modified Ortega method ( $\Delta\alpha = 0.04$  in this simulation) gave results consistent with the AIC method if relatively large segments  $\Delta\alpha$  were used;

-The  $E_\alpha$  dependence calculated by both the original Ortega method ( $\Delta\alpha = 0.01$ ) and FR method led to noticeable deviations;

-Also, the original Ortega method led to larger deviations as smaller  $\Delta\alpha$  segments were used.

### 3.2.2.3 Experimental Application

The thermal decomposition of  $SrCO_3$  [70] was examined again, using a  $N_2$  flow rate of 50 ml/min and three different heating rates: 2.379, 4,734, and 7.007  $K\text{min}^{-1}$ ; the data were acquired using a Shimadzu DTG-60H simultaneous TGA/DTA analyzer. The results from analyzing the data using the five different methods were then assessed to check on the accuracy of the dependence of  $E_\alpha$  on the value of  $\alpha$ .

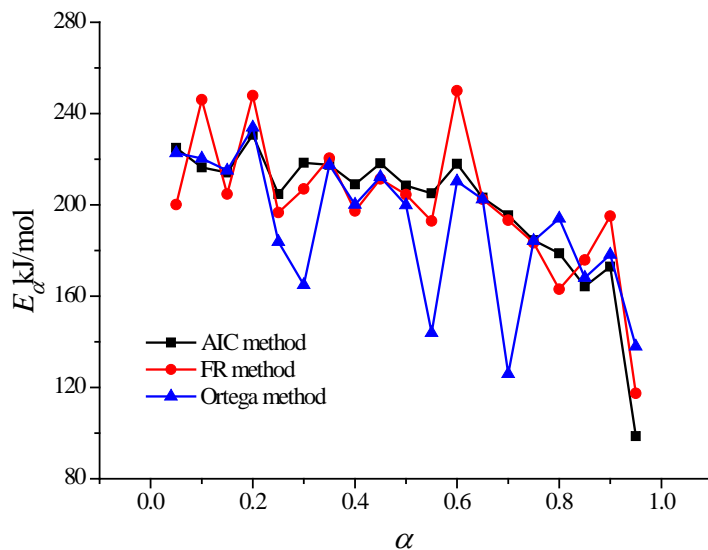


Figure 3.7 Dependence of  $E_\alpha$  on the value  $\alpha$  obtained for the experiments of  $SrCO_3$  decomposition by AIC, FR and Ortega method all with  $\Delta\alpha=0.04$

For  $\Delta\alpha = 0.04$ , Fig. 3.6 shows that the  $E_\alpha$  dependence calculated by the modified Ortega method and AIC methods agreed very well, while the original Ortega method data deviated from the modified Ortega method and AIC data due to the expected influence of systematic error and experimental noise. Taking the values obtained by the AIC method as the reference benchmark, the standard deviation (SD) of  $E_\alpha$  calculated by the modified Ortega method was  $SD = 0.53$ ; in contrast, the original Ortega method resulted in  $SD = 17.14$ , more than 30 times larger. Figure 3.7 shows that both FR and OFW methods largely disagreed with the benchmark AIC method.

### 3.3 Conclusions

The original Ortega's average integral isoconversional method only uses the upper temperature limit to characterize selected reaction segments to evaluate the activation energy for solid state reactions. In this study, a modified procedure based on the original method was developed without any additional assumptions. The modified method chose larger reaction segments and several temperature values rather than a single temperature to characterize the integral segment. Using the modified Ortega method not only eliminated systematic errors but also effectively reduced the influence of experimental noise. The validity of the modified Ortega method was shown by both simulated and experimental data.

During the development of the modified Ortega method, it was found that certain specifications for the analyses were important in providing the best results, and did not impart unwanted errors or misrepresentations of the actual data. These specifications included: (1) The segment of temperature to characterize temperature corresponding to  $\alpha$  should not be too small, i.e.  $\Delta\alpha \geq 0.04$ , and (2) the number of characteristic temperatures used should be  $n \geq 5$ .

An incremental isoconversional method has been developed based on Li-Tang method without any additional assumptions. The incremental version not only avoided the integration of the rate equation and lowered the effects of noise which are encountered in Friedman method, but also

eradicating the limitation of Li-Tang method that the activation energy would depend on lower limit of the integration. Moreover, the procedure was very simple and gave consistent activation energy values with those obtained by Friedman and the modified Vyazovkin methods.

However, it should be kept in mind that original LT, Ortega methods, the modified version of them, and all other isoconversional methods, are based on the isoconversional principle, the influences of which are not taken into consideration in the analyses of this chapter. Therefore, in next chapter, additional examinations of the conclusions in this chapter are given and a comprehensive method is proposed which is able to take advantage and avoid the limitations of these methods.

## CHAPTER 4: COMPREHENSIVE METHOD BASED ON MODEL-FREE AND IKP METHODS TO EVALUATE KINETIC PARAMETERS

Evaluating  $E_\alpha$  without any previous knowledge of  $f(\alpha)$  is considered a substantial advantage of using model free methods. Moreover, having an variable activation energy,  $E_\alpha$ , that varies as a function of conversion degree,  $\alpha$ , is believed beneficial for revealing the complexities inherent to solid-state kinetics [35, 36]. However, the phenomenon of  $E$  varying with  $\alpha$  and the inconsistencies in results obtained during various studies [17] have caused debate and controversy [103, 104]. Explanations of these inconsistencies have often focused on the complexities associated with solid state experiments [105-107] and the introduction of systematic errors associated with computational methods, one of which is the approximation made during integration, as shown in Eq. (2.2) [108]. To perform model free analysis accurately, great care should be taken to ensure that each experiment is performed at the same conditions with constant mass and size of samples, and constant gas purge rate, etc. Variations in experimental conditions can be minimized and systematic errors associated with computational methods can be eliminated by using incremental approaches such as the AIC and the MLT methods. However, although some studies [11] showed that the results obtained by isoconversional methods depend on the heating rate, few in-depth assessments of the validity of the isoconversional principle have been published even though it is the foundation of model free methods - as embodied by Eq. (2.24). To begin such an assessment, this study used a linear heating program to provide critical information for assessing the isoconversional principle. More importantly, a comprehensive method is proposed that extracts more meaningful and reliable kinetic parameters of solid state reactions.

The structure of this chapter is set as follows. In Section 4.1, a theoretical approach is suggested that is used to assess whether the “isoconversional principle” of Eq. (2.24) is valid for single step and complex reactions. In Section 4.2, the traditional IKP method is modified to simultaneously determine variable activation energies and pre-exponential factors for complex reactions. In



Section 4.3 a comprehensive method is proposed that is based on both isoconversional and IKP methods.

#### 4.1 Critical Analysis of Model Free Methods

The overall kinetic equations of parallel independent reactions are given as,

$$\frac{d\alpha}{dT} = c \frac{d\alpha_1}{dT} + (1-c) \frac{d\alpha_2}{dT} = c \frac{A_1}{\beta} \exp\left(-\frac{E_1}{RT}\right) f_1(\alpha_1) + (1-c) \exp\left(-\frac{E_2}{RT}\right) f_2(\alpha_2) \quad (4.1)$$

where  $c \in (0,1)$  is the contribution percentage of the first reaction to the change in the overall reaction,  $\alpha = c\alpha_1 + (1-c)\alpha_2$ . Then, the ‘‘apparent’’, ‘‘overall’’, ‘‘empirical’’ or ‘‘global’’ [54] activation energy for expressing the activation energy at a given  $\alpha$  is,

$$E_\alpha = \frac{c \frac{d\alpha_1}{dT} E_1 + (1-c) \frac{d\alpha_2}{dT} E_2}{c \frac{d\alpha_1}{dT} + (1-c) \frac{d\alpha_2}{dT}} = \frac{c \frac{d\alpha_1}{dT} E_1 + (1-c) \frac{d\alpha_2}{dT} E_2}{\frac{d\alpha}{dT}} = f_1 E_1 + f_2 E_2 \quad (4.2)$$

where  $f_1$  and  $f_2$  are contribution percent of the overall reaction rate  $d\alpha / dT$ , and  $f_1 + f_2 = 1$ .

It is expected that, for a given conversion degree, the value of  $f_1$  and  $f_2$  will vary with heating rate; consequently,  $E$  is not only a function of  $\alpha$  but also a function of  $\beta$ , as is shown explicitly in the following simulations.

Consider a simple case in which the values of  $Af(\alpha)$  for two reactions are the same, i.e.,

$$\frac{d\alpha}{dT} = \frac{1}{\beta} \left( c \exp\left(-\frac{E_1}{RT}\right) + (1-c) \exp\left(-\frac{E_2}{RT}\right) \right) Af(\alpha) \quad (4.3)$$

Because temperatures vary with  $\beta$  for a given  $\alpha$ , the ratio of  $c \exp(-E_1 / RT)$  -to-  $(1-c) \exp(-E_2 / RT)$  of Eq. (4.3) will vary and then the ratio of  $f_1$  -to-  $f_2$  will also change with  $\beta$ . Therefore,  $E_\alpha$  is expected to also vary with  $\beta$ , that is

$$E_{app} = E(\alpha, \beta) \quad (4.4)$$

where  $E_{app}$  is defined as the overall or apparent energy for the complex reaction at given  $\alpha$  and  $\beta$ . Similarly, it is reasonable to express the pre-exponential factor as

$$A_{app} = A(\alpha, \beta) \quad (4.5)$$

Therefore, the starting point of model free methods in which  $E_{app} = E(\alpha)$  is problematic, which implies the isoconversional principle embodied by Eq. (2.24) cannot be used without taking into considerations the heating programs.

Similar analyses are possible for other types of complex reactions, such as parallel competitive reactions:

$$\frac{d\alpha}{dT} = \frac{A_1}{\beta} \exp\left(-\frac{E_1}{RT}\right) f_1(\alpha) + \frac{A_2}{\beta} \exp\left(-\frac{E_2}{RT}\right) f_2(\alpha) \quad (4.6)$$

and reversible reactions [109],  $M \leftrightarrow N$  :

$$\frac{d\alpha_M}{dT} = -\frac{d\alpha_N}{dT} = \frac{A_M}{\beta} \exp\left(-\frac{E_M}{RT}\right) f_1(\alpha_M) - \frac{A_N}{\beta} \exp\left(-\frac{E_N}{RT}\right) f_2(\alpha_N) \quad (4.7)$$

where  $\alpha_M$  and  $\alpha_N$  are the corresponding conversion degrees of substance  $M$  and  $N$ . In other words, for complex reactions the dependence of  $E_\alpha$  on  $\beta$  has to be tested if the method that gives activation energies as a function of conversion degree.

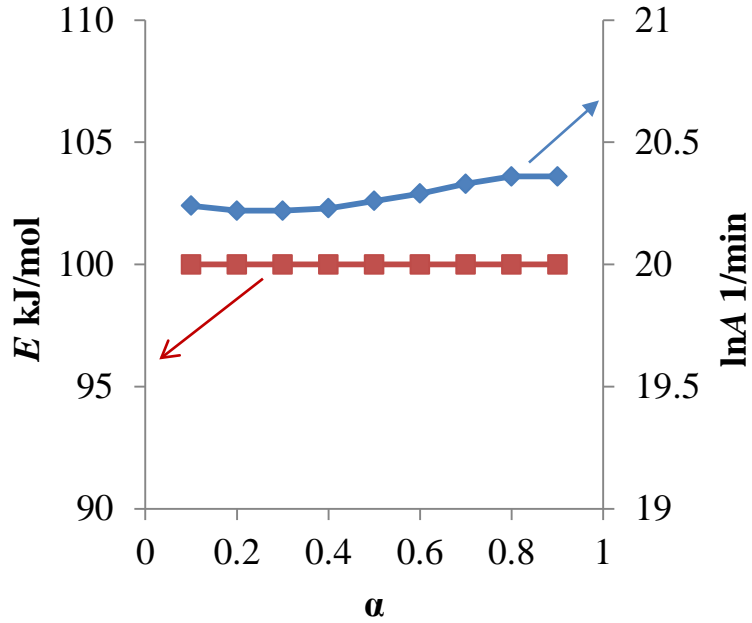


Figure 4.1 The dependences of  $E$  and  $\ln A$  on  $\alpha$  of a single step reaction determined by IIKP method

#### 4.2 Analysis of IKP Method

Eqs. (2.21) and (2.22) lead to,

$$\ln A_{inv} = \frac{\beta E_{inv}}{RT_{max}^2} + \frac{1}{RT_{max}} E_{inv} \quad (4.8)$$

where the subscript “*max*” means the maximum reaction rate, and “*inv*” refers to invariant parameters, which historically have been calculated by applying a model-fitting method to a full reaction range, that is,  $\alpha \in (0,1)$ , in a single experimental run. The compensation relations still hold if a model-fitting method is applied to a small reaction segment  $\Delta\alpha$ , i.e., from  $\alpha - \Delta\alpha$  to  $\alpha$ : the characteristic temperature can be approximated as the mean temperature of the selected computation segment. Therefore, the incremental IKP (IIKP) method has a wider applicability

than the IKP method, the possibility of which is seen by considering a simple first order reaction described by:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right)(1-\alpha) \quad (4.9)$$

where  $E = 100$  kJ/mol,  $\ln A = 20.7$  and  $\beta_{1-4} = 5, 10, 15, 20$  K/min. The values obtained by using the IIKP method are shown in Fig. 4.1 for an increment of 0.1 and computation range  $\Delta\alpha = 0.05$  for each point. It can be seen that the values of  $E$  and  $\ln A$  are quite reliable at all points. Applications of the IIKP method to complex reactions will be discussed in the following section.

#### 4.3 Proposition of a Comprehensive Method

A schematic for applying the IIKP principle to complex reactions at three different heating rates is shown in Fig. 4.2. Considering the parallel independent reactions represented by Eq. (4.1), for a given heating program,  $\beta$ , the temperature of the two reactions is the same at any overall conversion degree,  $\alpha = c\alpha_1 + (1-c)\alpha_2$ . If the two reactions are assumed to be decoupled, then each reaction would have individual invariant points,  $(\ln A_1, E_1)$  and  $(\ln A_2, E_2)$ , as is shown in Fig. 4.2. For a given  $\beta_i$ , the slopes of the compensation lines for two reactions would be identical, i.e.,

$$b_{i1} = b_{i2} = b_i = \frac{1}{RT_\alpha}, \quad i = 1, 2, 3 \quad (4.10)$$

Therefore, the equations for two reactions can be described as:

for reaction 1-

$$\begin{aligned}
 \ln A_1 &= b_1 E_1 + a_{11}, & \text{for } \beta_1 \\
 \ln A_1 &= b_2 E_1 + a_{21}, & \text{for } \beta_2 \\
 \ln A_1 &= b_3 E_1 + a_{31}, & \text{for } \beta_3
 \end{aligned}
 \tag{4.11}$$

for reaction 2-

$$\begin{aligned}
 \ln A_2 &= b_1 E_2 + a_{12}, & \text{for } \beta_1 \\
 \ln A_2 &= b_2 E_2 + a_{22}, & \text{for } \beta_2 \\
 \ln A_2 &= b_3 E_2 + a_{32}, & \text{for } \beta_3
 \end{aligned}
 \tag{4.12}$$

where  $b_1, b_2, b_3, a_{11}, a_{21} \dots$  are constants.

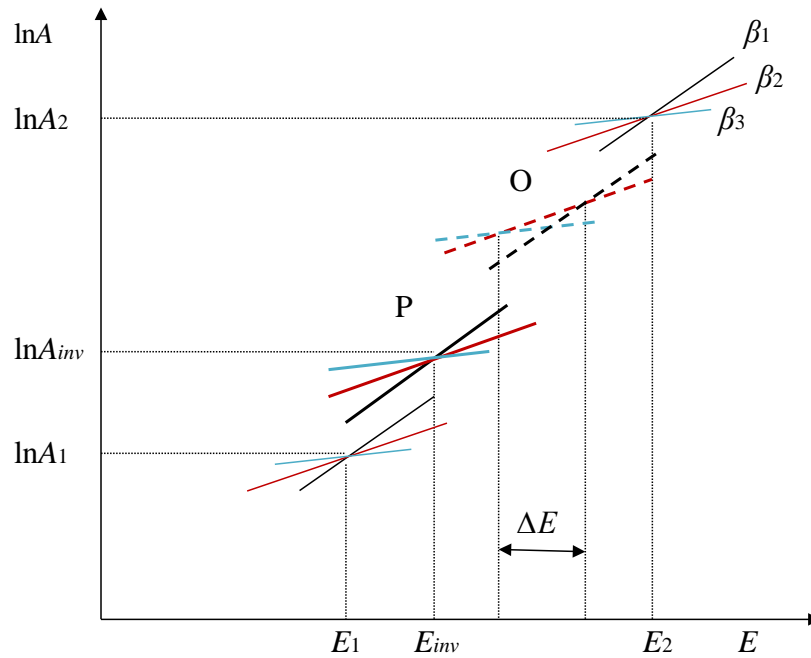


Figure 4.2 Schematic of IIKP principle for complex reactions

Note the coefficients of  $E$  for a specific  $\beta$  in Eqs. (4.11) and (4.12) are the same. Taking  $\beta_1$  as an example, the two lines from Eqs. (4.11) and (4.12) are parallel; the combination line is determined by the contribution ratio,  $f_{11} : f_{12}$ , of their intercept values, which leads to a combination of  $f_{11}a_{11} + f_{12}a_{12}$ . The overall Eq. (4.1) for a given  $\beta_i$  produces the following:

$$\begin{aligned}
\ln A &= b_1 E + f_{11} a_{11} + f_{12} a_{12}, & \text{for } \beta_1 \\
\ln A &= b_2 E + f_{21} a_{21} + f_{22} a_{22}, & \text{for } \beta_2 \\
\ln A &= b_3 E + f_{31} a_{31} + f_{32} a_{32}, & \text{for } \beta_3
\end{aligned} \tag{4.13}$$

From Eq. (4.2), if the contribution percentage remains unchanged,  $f_{i1} : f_{i2} = m$ , for different  $\beta_i$ , or if the contribution percentage changes within a narrow range the three lines determined by Eq. (4.13) intersect at a common point P  $((mE_1 + E_2)/(1+m), (m \ln A_1 + \ln A_2)/(1+m))$  (see Fig. 4.2) or within a narrow range (Case 1). Otherwise, the three lines intersect in a wider range,  $\Delta E$ , or have no obvious common intersection (Case 2). Note that the ‘‘apparent’’ or ‘‘overall’’ activation energy  $E_{app}$  is determined by the contributions percentage of two individual reactions, and the activation energy at given  $\alpha$  for the Case 1 is independent or weakly dependent on  $\beta$  whereas for Case 2 it is strongly depend on  $\beta$ .

Taking the log of the general kinetic equation, Eq. (1.7), and differentiating over  $1/T$ , and then rearranging it yields,

$$\frac{\partial \ln \left( \beta \frac{d\alpha}{dT} \right)}{\partial T^{-1}} = -\frac{E_\alpha}{R} + \frac{\partial \ln A}{\partial T^{-1}} + \frac{\partial \ln f(\alpha)}{\partial T^{-1}} \tag{4.14}$$

If a common point  $P$  or narrow range of it exists, then  $\ln A$  has no or only a weak dependence on  $T$ , in which case the term  $\partial \ln A / \partial T^{-1} = 0$ . Moreover, considering the assumption of isoconversional methods that the reaction model remains unchanged for different heating rates, the last term in Eq. (4.14),  $\partial \ln f(\alpha) / \partial T^{-1}$ , can also be zero. Because the compensation equation, Eq. (2.21), does not contain  $f(\alpha)$ , the phenomenon of the compensation effect would determine that the reaction models would have no, or weak, dependence on heating rate. Therefore, for Case 1, it is reasonable that the activation energy at a given  $\alpha$  has no or weak

dependence on heating rates and the isoconversional principle gives reliable  $E_\alpha$ . These conclusions suggest the IIKP principle can be used to judge the reliability of the values.

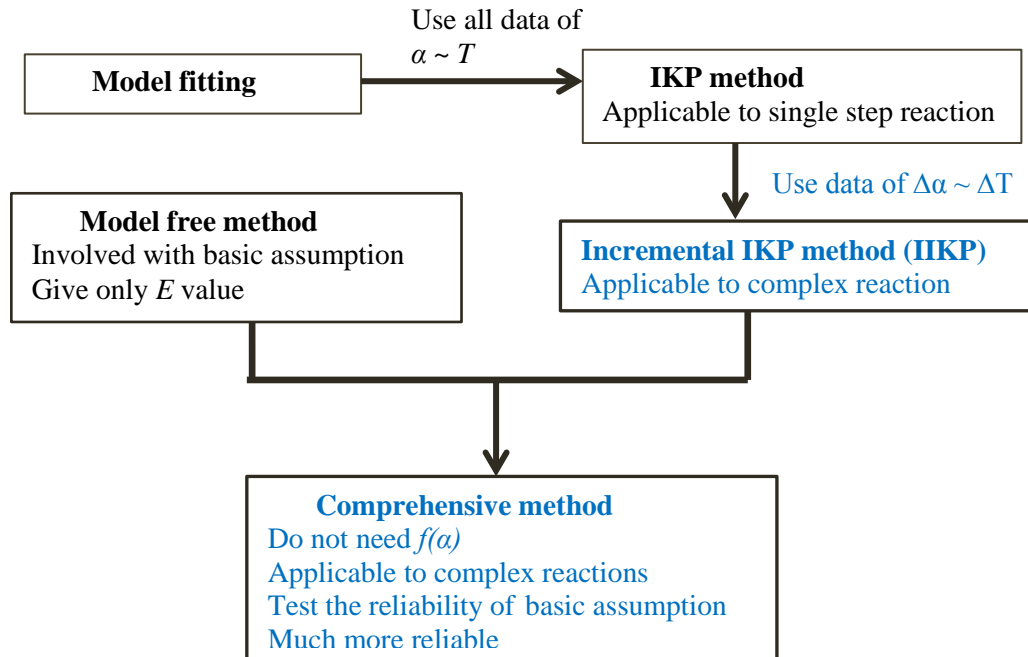


Figure 4.3 Flow chart of comprehensive method

Thereby, it is clear that the new comprehensive method based on model free and IIKP methods can be proposed, the relationship of which with previous methods are shown in the flow chart above, in which the blue texts indicates the contributions by the author. The chart shows that the combination of model free method and IIKP method generates a comprehensive method [110], which has obvious advantages over previous methods. The steps of the comprehensive method are described below:

1. Use an incremental model free method to determine values of  $E_\alpha$  as a function of  $\alpha$  ;
2. Use the IIKP method to calculate both  $E_\alpha$  and  $A_\alpha$  and check whether the compensation lines at different heating rates intersect at a common point or within a narrow range. If so, the

corresponding value calculated in step 1 is reliable and can be selected, otherwise the value will be discarded according to IIKP principle;

3. Use the compensation effect as evidenced by the values determined in step 2 to predict the values of  $A_\alpha$  for the selected values of  $E_\alpha$  (this step is discussed more in the simulation section).

It is suggested that the comprehensive method can be applied successfully to other types of complex reactions, such as parallel dependent reactions. Moreover, it is worth mentioning that the IIKP principle can be used for arbitrary heating program experiments by replacing  $\beta d\alpha / dT$  with  $d\alpha / dt$  in the related equations.

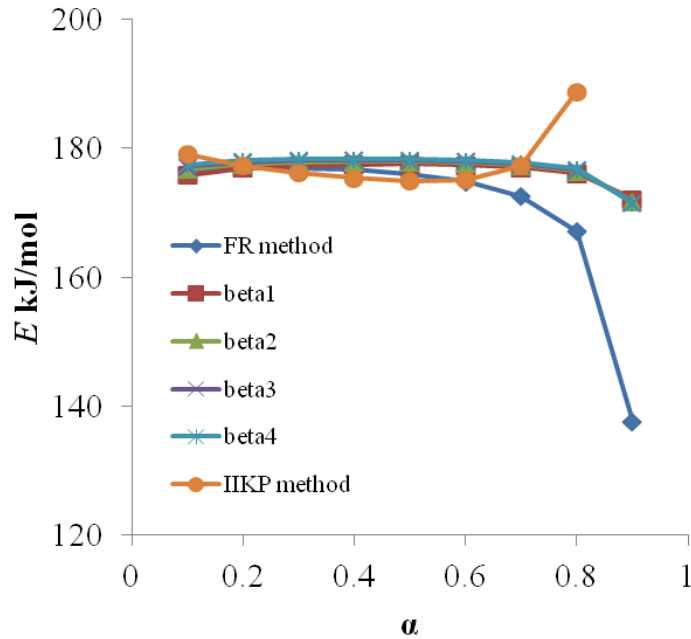


Figure 4.4 Values of activation energy determined by FR and IIKP methods for simulation test S1(The meaning of beta1-4 is the true values calculated by Eq. (4.2) for  $\beta_{1-4}$ ; it applies to Figs. 4.4-4.9)



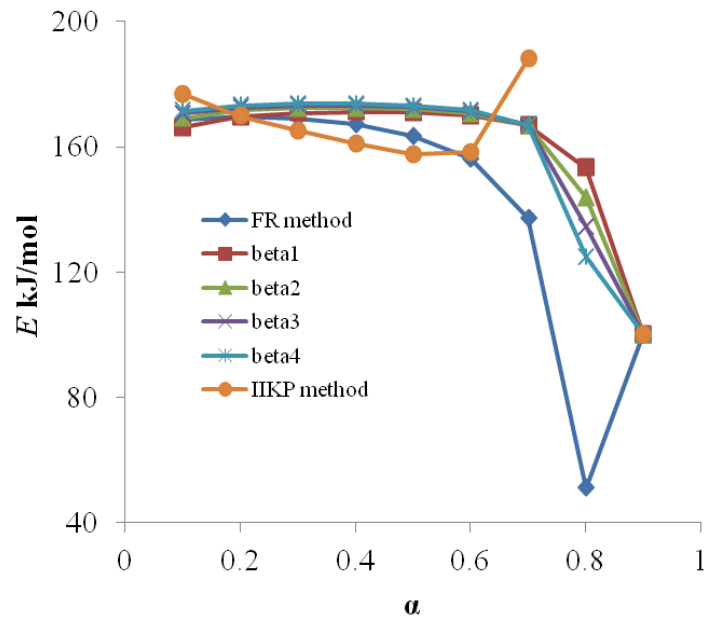


Figure 4.5 Values of activation energy determined by FR and IIKP methods for simulation test S2

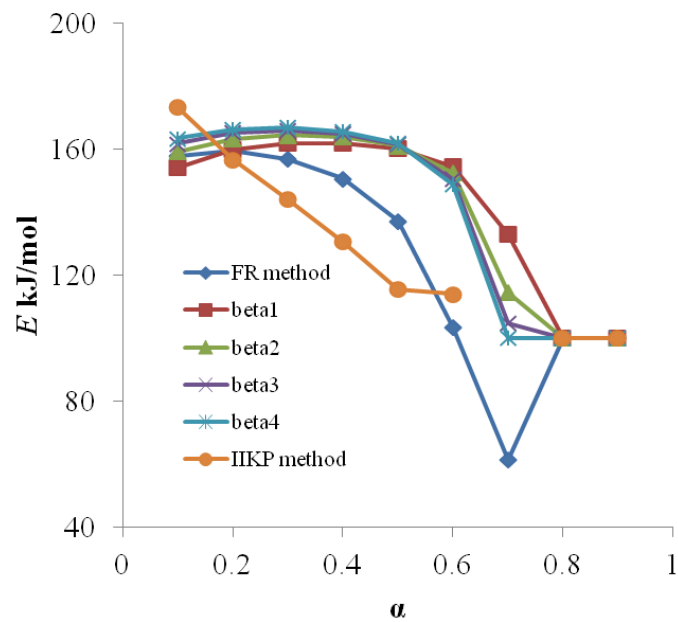


Figure 4.6 Values of activation energy determined by FR and IIKP methods for simulation test S3

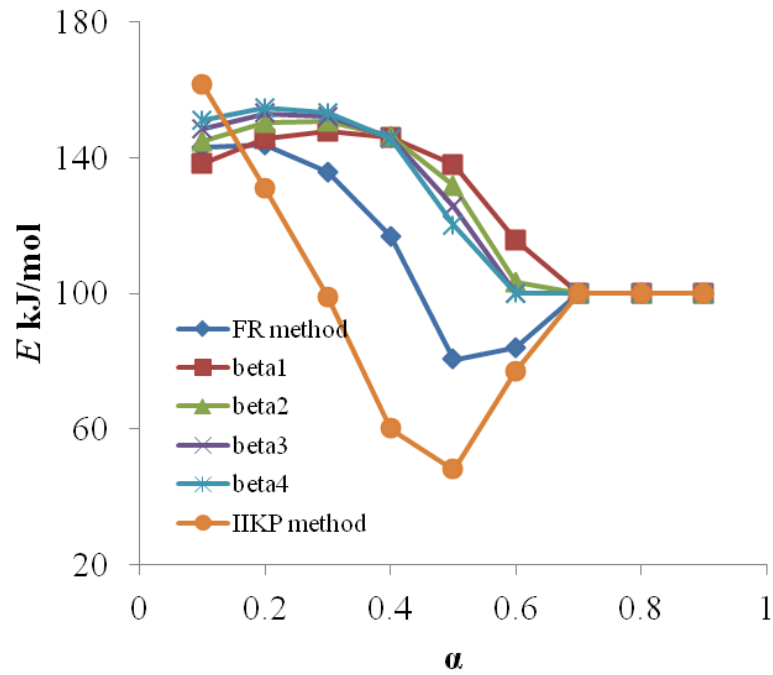


Figure 4.7 Values of activation energy determined by FR and IIKP methods for simulation test S4

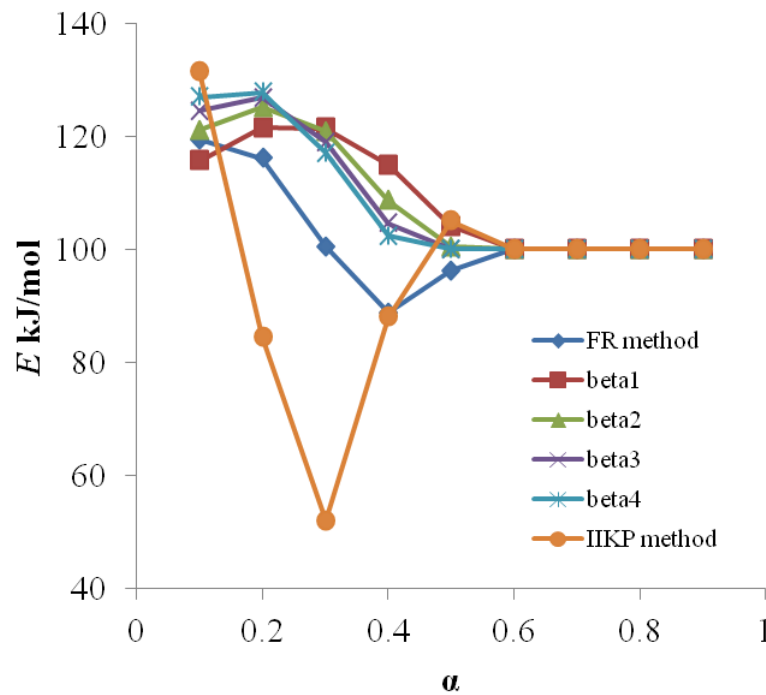


Figure 4.8 Values of activation energy determined by FR and IIKP methods for simulation test S5

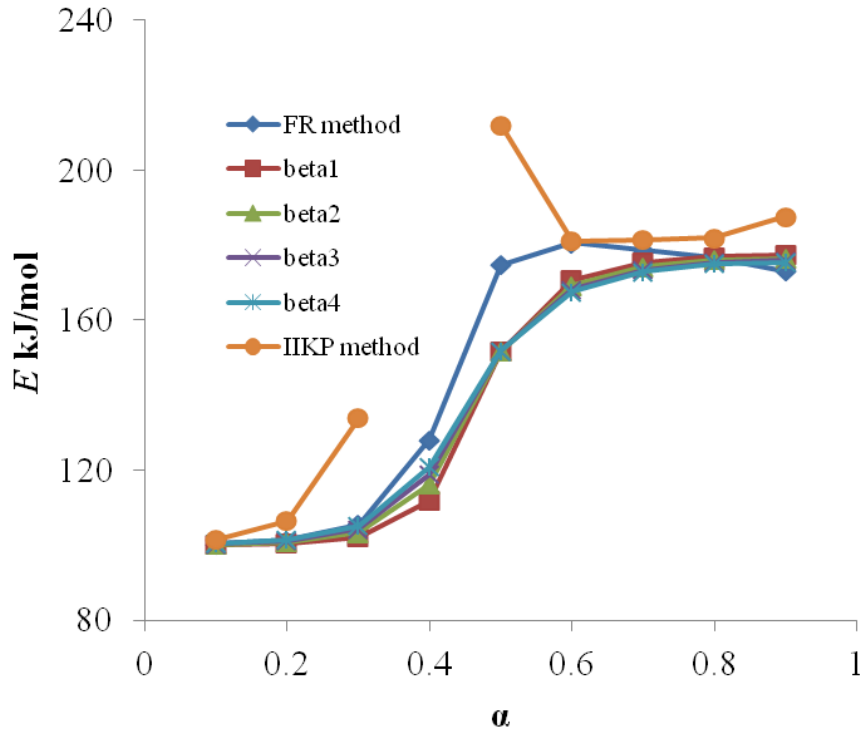


Figure 4.9 Values of activation energy determined by FR and IIKP methods for simulation test S6

#### 4.4 Simulation Validations

A parallel independent reaction was simulated that involved two different reactions, as given by the following:

$$\frac{d\alpha}{dT} = c \frac{A_1}{\beta} \exp\left(-\frac{E_1}{RT}\right) (1-\alpha_1)^2 + (1-c) \frac{A_2}{\beta} \exp\left(-\frac{E_2}{RT}\right) (1-\alpha_2) \quad (4.15)$$

where  $\beta_{1-4} = 5, 10, 15, 20$  K/min,  $\ln A_1 = 18.42 \text{ min}^{-1}$ ,  $E_1 = 100$  kJ/mol,  $\ln A_2 = 36.84 \text{ min}^{-1}$ ,  $E_2 = 180$  kJ/mol, and the contributions  $c = 0.1, 0.3, 0.5, 0.7, 0.9$  for tests S1-S5 respectively. The reactions involving S1-S5 may be heavily or totally overlapped. A test S6 with no heavily overlapped reaction was designed with  $\ln A_2 = 28.78$ .

The test S7 simulated a competitive parallel reaction:

$$\frac{d\alpha}{dT} = \frac{A_1}{\beta} \exp\left(-\frac{E_1}{RT}\right)(1-\alpha)^2 + \frac{A_2}{\beta} \exp\left(-\frac{E_2}{RT}\right)(1-\alpha) \quad (4.16)$$

where the values of the parameters were identical to those for S1-S5 except  $\ln A_2 = 35.69$ .

The invariant values of  $E$  and  $\ln A$  determined by the IIKP method are shown in Table 2.

To enable reliable comparisons, the isoconversional method used for calculation was the FR method. Among the isoconversional methods, it is directly derived from the kinetic equation of Eq. (1.7) [52], and can give the most reliable values of  $E_\alpha$  when  $E_\alpha$  is not dependent on  $\beta$ .

The values of  $E_\alpha$  shown in Figs. 4.4-4.10 were calculated using Eq. (4.2) for every heating rate along with the values of  $E_\alpha$  calculated by the FR method and IIKP method (only the most frequently used models were applied, noted as ‘\*’ in Table 4.1). The major results from the S1-S7 tests are presented below:

1. The apparent activation energy values were dependent on the heating rates. If a dominant reaction existed - for example for S1 where  $c = 0.1$  or S5 where  $c = 0.9$ , the dependence of  $E_\alpha$  on  $\beta$  was weak; if no dominant reaction existed, this dependence was strong.
2. The use of an isoconversional method cannot recognize dependencies of  $E_\alpha$  on  $\beta$ , and it can lead to serious errors even when a dominant reaction exists.
3. The values determined by the IIKP method and the isoconversional method were directly correlated, and accordingly to the relation of the compensation lines, three cases are presented below:

Case 1: A common intersection point (P in Fig. 4.2) or a narrow intersection domain was found for which  $\Delta E < 5\text{kJ}$  (empirically). The values of  $E_\alpha$  did not depend or weakly depended on  $\beta$ ; hence,  $E_\alpha$  values calculated by the isoconversional method were reliable;

Case 2: A relatively large range (noted as ‘\*’ in Table 4.1) in the intersection domain was found. The values of  $E_\alpha$  may have a dependency on  $\beta$ ; the values obtained by the isoconversional method may be acceptable;

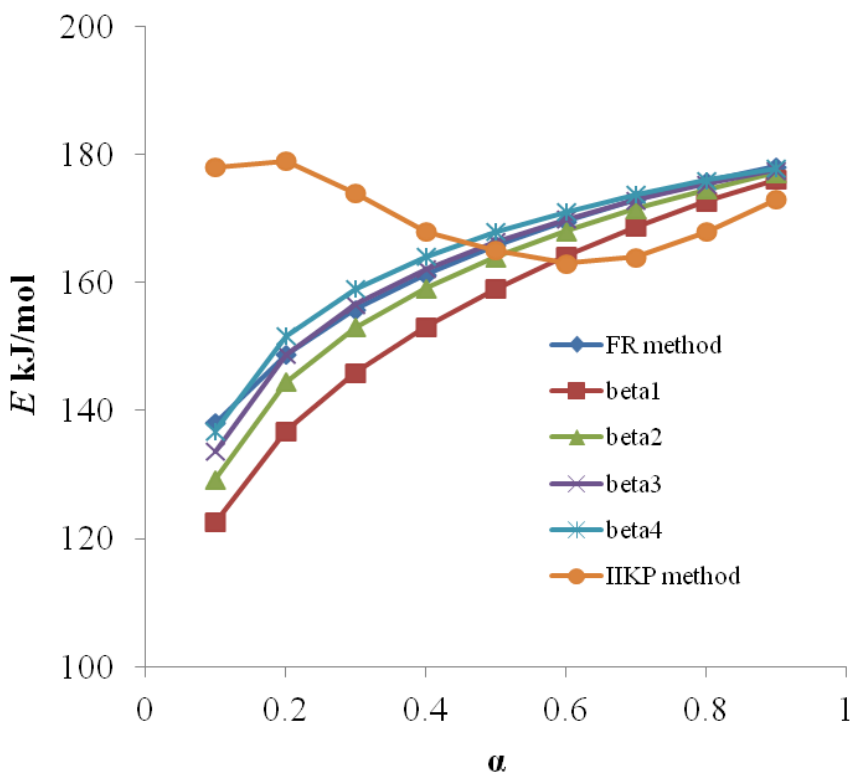


Figure 4.10 Values of activation energy determined by FR and IIKP methods for simulation test S7

Case 3: The compensation lines were widely separated or were randomly intersected over a wide range,  $\Delta E \geq 20\text{kJ}$  for example. Hence,  $E_\alpha$  was strongly dependent on  $\beta$ ; hence, the values obtained were not reliable – and are not presented herein.

4. From the previous discussion, it can be recognized that when results are obtained that reflect the Case 3 situation, and in many cases the Case 2 situation, the starting point of estimating activation energy on the given conversion degree is problematic for any model free method, independent of whether linear heating rates or nonlinear heating programs were implemented.

*Table 4.1 The values of  $E_{inv}$  and  $A_{inv}$  obtained by IIKP method*

	$\alpha$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
S1	$E$	179.1	177.3	176.2	175.4	174.9	175.1	177.3	188.8*	—
	$\ln A$	36.05	35.65	35.4	35.22	35.13	35.21	35.77	38.42	—
S2	$E$	176.8	169.8	165.2	160.9	157.5	158.2*	188.0*	—	100.0
	$\ln A$	35.27	33.78	32.76	31.81	31.07	31.26	37.85	—	19.03
S3	$E$	173.2	156.7	144.2	130.5*	115.6*	114.0*	—	100.0	100.0
	$\ln A$	34.14	30.68	27.97	25	21.75	21.5	—	18.31	18.58
S4	$E$	161.5	131.0	99.0*	60.0*	48.0*	77.0*	100.0	100.0	100.0
	$\ln A$	31.20	24.88	18.12	9.85	7.08	13.02	17.68	17.94	18.18
S5	$E$	131.4	84.5*	52.0*	88.0*	105.0	100.0	100.0	100.0	100.0
	$\ln A$	24.35	14.75	7.95	14.64	18.05	17.23	17.43	17.69	17.93
S6	$E$	101.5	106.5	134	—	212*	181*	181.5	181.9	187.6
	$\ln A$	16.31	16.02	19.42	—	33.35	28.06	28.7	28.78	29.8
S7	$E$	178.0*	179.0	174.0	168.0	165.0	163.0	164.0	168.0	173.0
	$\ln A$	34.53	34.98	34.14	32.99	32.38	31.93	32.05	33.77	33.67

5. When the reactions were partially separated, such as for S1 and S5, or when the reactions were insignificantly overlapped, such as for S6, the  $E$  and  $A$  values are considered reliable at the beginning and/or ending points for both methods. Also, it can be expected that the IIKP method can be used to extract representative single pairs of  $E$  and  $A$  for similarly well-separated reactions. For S7, the trends for the competitive reactions were the same as for S1-S5.

6. The  $E_{\alpha}$  values as determined by the IIKP method deviated from true values to a much greater degree than by the model free method when a dependence of  $E_{\alpha}$  on  $\beta$  existed. This situation occurred because the slopes of the compensation lines (the coefficients  $b$  in Eqs. (2.21), (2.22) and (4.8)) were very close. When the heating rate increased from 5 K/min to 40 K/min (most experimental range), the temperature gap,  $\Delta T_m$ , generated for a given  $\alpha$  was generally about 40K, while the characteristic temperature  $T_m$  tended to be more than 600K. In this situation, the

order of the change of coefficient  $b$  was much smaller than that of  $a$ . For example, in the simulated data of Eq. (4.9) when the heating rate increased from 5 K/min to 20 K/min the temperature at  $\alpha = 0.5$  increased about 30 K (533 to 565 K). These variation ranges can be estimated from:

$$b = \frac{1}{RT} \in (2.257 \times 10^{-4}, 2.129 \times 10^{-4})$$

$$a = \ln \frac{E}{RT^2} \in (-3.162, -3.279)$$

It is to be realized that even a small change in the relative contribution percentage,  $f_{i1} : f_{i2}$  in Eqs. (4.11) and (4.12), significantly influenced  $f_{i1}a_{i1} + f_{i2}a_{i2}$  in Eq. (4.13) as compared to the much smaller differences of the slopes,  $b_i$ ; the result of this influence was that the calculated  $E_{inv}$  and  $\ln A_{inv}$  values were noticeably deviated from true values. In general, calculations using isoconversional methods are based on regression analysis such as least square approaches, and the results are less influenced by changes in  $f_{i1} : f_{i2}$  than is the IIKP method. For this reason, the IIKP principle was used to judge the reliability of values obtained by the model free method rather than directly selecting the values extracted by the IIKP method.

Moreover, it was found that the values of  $\ln A_{inv}$  and  $E_{inv}$  obtained by using the IIKP method at different conversion rates were linearly correlated. It is probable this linear relation explains the existence of single pair values of  $(\ln A_{inv}, E_{inv})$  that can be determined by using the IKP method. Because of linearity, it is possible to predict values of  $\ln A_{\alpha}$  for the selected  $E_{\alpha}$  values. As an example, if the S3 test was selected for determining  $\ln A_{\alpha}$ , the conversion degrees selected would be  $\alpha = 0.1, 0.2, 0.3, 0.8, 0.9$ , and the corresponding  $E_{\alpha} = 157.89, 159.54, 156.98, 99.99, 100.01$  kJ/mol. By using the linear relation and interpolation analysis, the values of pre-exponential

factor are then:  $\ln A_\alpha = 30.94, 31.29, 30.74, 18.31, 18.31 \text{ min}^{-1}$ . Similar calculations could be accomplished for the other tests.

#### 4.5 Experimental Validation

The thermal decomposition of high purity (> 99%) calcium carbonate ( $\text{CaCO}_3$ ) was carried out in a 40 ml/min flow of  $\text{N}_2$  using 4.97, 9.92, 14.85, 19.83 K/min linear heating program from room temperature to 1150K on a NETZSCH STA 409C Analyzer. To minimize variability between the experiments, the sample was carefully weighted to be between 7.750-to-7.890 mg before decomposition testing at the different heating rates.

To apply the comprehensive method, two incremental isoconversional methods (AIC, MLT) and the FR method were applied to analyze the experimental data. Considering that the selection and use of a reaction model can influence the accuracy of the IKA method, all the reaction models listed in Table 1.1 were applied to the experimental data. Data from models having poor fitting (coefficient < 0.97) were discarded, and the remaining data were selected for determining  $E$  values and then  $A$  values with the IKA method. It can be seen in Fig. 4.11 that:

1. The AIC and MLT methods produced identical  $E_\alpha$  dependencies so their curves were merged in the figure, while the FR method resulted in certain deviations from the AIC and MLT methods because the FR method is more sensitive to experimental noise;
2. As expected, the  $E_\alpha$  dependencies calculated using the IKA method deviated more seriously than the AIC and MLT methods. According to the intersection area of the four regression lines obtained at a given conversion degree, the values determined by the IKA method were divided into three levels. The first level was four compensation lines for a given point that intersected over a narrow range (< 10 kJ/mol) for which the  $E_\alpha$  values calculated by the isoconversional methods were reliable; the second level was four lines that intersected over a range of 10 to 20



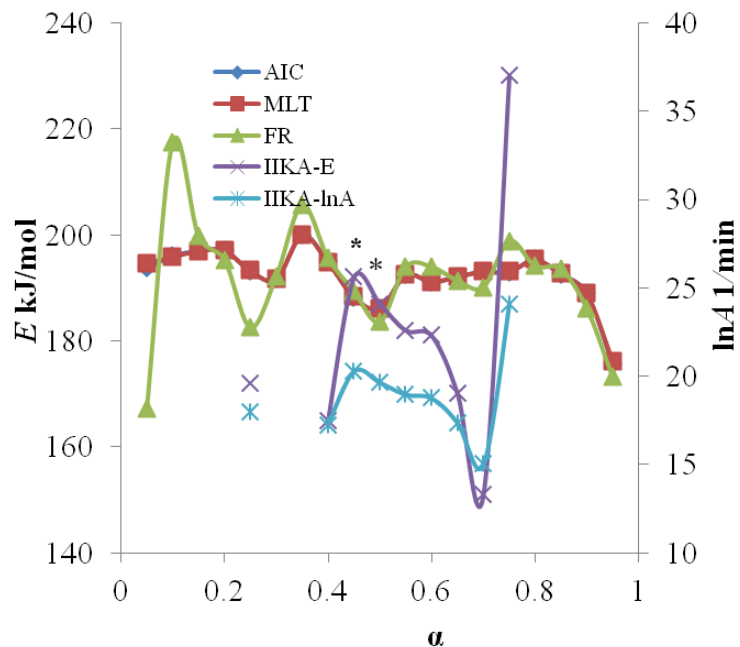


Figure 4.11 Values of activation energy obtained by different methods for experiment data

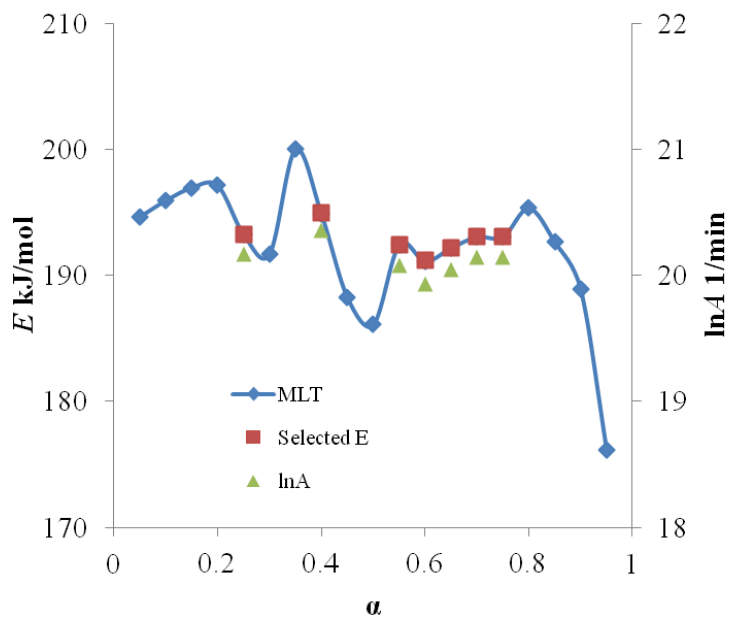


Figure 4.12 Values of selected activation energy determined by comprehensive method

kJ/mol (noted with ‘\*’), for which the  $E_\alpha$  values calculated by isoconversional methods may not be reliable; and, the third level was four lines that intersected over a range greater than 20kJ or did not have a common area, the results were not reliable (not displayed).

3. The  $\ln A_\alpha$  values calculated by the IKA method varied with  $\alpha$  and provided a reasonable compensation relation with  $E_\alpha$  that gave  $\ln A_\alpha = 0.1126E_\alpha - 1.5944$ .

In this study, the range of  $E_\alpha$  values as determined by the AIC and MLT methods was  $175 \leq E_\alpha \leq 200$  kJ/mol; these values are in agreement with previous studies [111, 112] of the decomposition of  $CaCO_3$  in which the range was  $170 \leq E_\alpha \leq 210$  kJ/mol. However, as discussed herein, these values are considered problematic because they include unreliable values. Only by applying the comprehensive method proposed in this study is it possible to obtain the reliable  $E_\alpha$  values displayed in Fig. 4.12 with a range of  $191.15 \leq E_\alpha \leq 194.91$  kJ/mol. Using the relation determined for  $\ln A_\alpha$ ,  $\ln A_\alpha = 0.1126E_\alpha - 1.5944$ , that was calculated by the IKA method and for which  $E_\alpha$  varied with  $\alpha$  with a reasonable compensation relation, the values of  $\ln A_\alpha$  for the selected  $E_\alpha$  at corresponding reaction degrees were  $19.93 \leq \ln A \leq 20.36 \text{ min}^{-1}$ . These reliable  $E_\alpha$  and  $\ln A_\alpha$  values encompass a very narrow range and can be reasonably approximated as constants with  $E = 192.5$  kJ/mol and  $\ln A = 20.15 \text{ min}^{-1}$ .

#### 4.6 Conclusion

Many methods that have been developed to obtain activation energies of solid-state reactions consider  $E$  to be a function only of  $\alpha$ . However, after a theoretical study along with examples presented herein, it is proposed that for complex reactions the values of  $E$  is not only a function of  $\alpha$  but also a function of the heating programs. This dependency needs to be considered when methods are used to obtain  $E_\alpha$  dependencies.

It is generally believed that the IKA method requires more computation than other methods and yet provides only single pair of  $E$  and  $A$ ; as a consequence, the IKA method is rarely used in kinetic studies. However, it has been determined that the potential applications and benefits of this method are underestimated. This research has shown the development and use of the IKA method that is based on the original IKA method and gives variable  $E_\alpha$  and  $A_\alpha$  values for solid state reactions. It can provide reliable values of  $E_\alpha$  and  $A_\alpha$  at any given reaction degree for single-step reactions for simulation data. For experimental data that can be complex reactions and have a variety of influencing factors such as experimental noise, sample weight and sample size IKA can be used to successfully determine the reliability of values obtained by model free methods, after which a comprehensive method based on IKP and method free methods is proposed.

This comprehensive method was tested on both simulation and experimental data of the decomposition of  $CaCO_3$  and provided results showing noticeable advantages over other methods. It can: evaluate the reliability of the results calculated by model free methods; determine the dependence of  $E$  on the heating programs used; select reliable  $E$  and provide variable  $A$  values for complex reactions; and to a certain degree, help to judge the quality of the experimental data.

## CHAPTER 5: ACCURACY OF ISOCONVERSIONAL METHODS WITH A CONSIDERATION OF BASIC ASSUMPTION

The comprehensive method proposed in Chapter 4 has many advantages over other existing methods including isoconversional methods. However, it takes time for people to accept a newly developed method especially when the current isoconversional methods are widely applied in almost every field that thermal kinetic analysis is used. In this chapter results are given to compare the accuracy of existing isoconversional methods by considering the influence of the isoconversional principle, which is often called the basic assumption. This discussion is helpful for researchers to select a better isoconversional method that matches with the incremental invariant kinetic parameters method for different types of complex reactions.

### *5.1 Previous Comments about Isoconversional Methods*

A conclusion of the ICTAC Kinetic Project [32] was that the kinetic analysis of heterogeneous reactions should use an isoconversional method because it is able to evaluate the activation energy without any prior knowledge of reaction model. For complex reactions  $E$  varies with  $\alpha$ . Studies [29, 94, 113, 114] examining the accuracy of the different types of isoconversional methods conclude that:

1. the differential methods [56, 58] are very sensitive to experimental noise, resulting in large deviations of activation energy [54]; for simulation data that do not contain experimental noise, these methods allow the evaluation of the exact value of activation energy;
2. the regular integral methods [61, 64, 72, 73, 83, 95-97] have good tolerance of noise but, compared to the “exact” values obtained by the differential methods, they lead to significant systematic errors because they involve the use of approximations of the temperature integral and assume  $E$  is a constant in the integration of the Eq. (3.2) [94];

3. the advanced integral methods [67, 68, 70, 98, 99, 115] that use small integration ranges of the variables not only have good tolerance of experimental noise but also produce values in agreement with those obtained by the use of differential methods.

The advanced integral methods are highly recommended and have become popular. For example, leading up to Jan. 2014, the most popular advanced integral method (AIC) [67] was that proposed by Vyazovkin in 2001; it was cited more than 400 times on Google Scholar. Most of these citations relate to obtaining activation energies of various solid reactions, while some use it along with the Friedman differential (FR) method [56] as a standard to analyze the reliability of other methods, especially newly developed ones [52, 68, 70, 98, 116, 117]. To the authors' knowledge of the literature review, all publications have agreed that the advanced integral methods (including the differential methods if data do not contain noise) are more accurate than other isoconversional methods.

The conclusions concerning the accuracy of isoconversional methods correlate directly to the basic assumption; they may be not reliable if this assumption is problematic. By theoretical and simulation analyses, this study provides critical information concerning the generally accepted conclusions about these models and provides some recommendations about using isoconversional methods to evaluate the activation energies of parallel independent reactions and competitive reactions.

For brevity, this study focuses on the Friedman (FR) [56], Ozawa-Flynn-Wall (OFW) [72, 73] and Kissinger-Akahira-Sunose (KAS) [61, 83], and AIC methods because they are representative and the most popularly-used differential, regular integral, and advanced integral isoconversional methods, respectively.

### *5.2 Error Sources of Isoconversional Methods*

The overall kinetic equation of a competitive reaction is given as,

$$\frac{d\alpha}{dT} = \frac{d\alpha_1}{dT} + \frac{d\alpha_2}{dT} = \frac{A_1}{\beta} \exp\left(-\frac{E_1}{RT}\right) f_1(\alpha) + \frac{A_2}{\beta} \exp\left(-\frac{E_2}{RT}\right) f_2(\alpha) \quad (5.1)$$

Then

$$E_\alpha = \frac{d\alpha_1/dT}{d\alpha/dT} E_1 + \frac{d\alpha_2/dT}{d\alpha/dT} E_2 = f_1 E_1 + f_2 E_2 \quad (5.2)$$

where the contribution percent  $f_1 + f_2 = 1$ .

Some authors [117] suggest the contribution ratio  $f_1 : f_2$  should be dependent on the heating rate, in which case  $E$  is not only a function of  $\alpha$  but also of  $\beta$ , i.e.,

$$E_{app} = E(\alpha, \beta) \quad (5.3)$$

where  $E_{app}$  is defined as the overall or apparent energy for a complex reaction at given  $\alpha$  and  $\beta$ .

The same dependence is obtained for other types of complex reactions like parallel independent reactions. However, the starting point inherent to isoconversional methods is to obtain  $E$  as a function only of  $\alpha$ . This is a problematic assumption that would introduce error into any of the isoconversional methods, and is labeled as “error source 1” (ES1) in the following discussion.

The reason that the AIC and FR methods are considered to provide “exact” values is that they may use small ranges of  $\Delta\alpha$  or  $\Delta\alpha$  close to zero, and so they only suffer from ES1. Comparatively, the OFW and KAS methods have two additional error sources (ES2 and ES3, as discussed in the following):

ES2: employing the temperature integral approximation leads to inaccurate values of  $E$ ; many analyses [29, 108] have been carried out on this topic. It was concluded that the KAS method offers significant improvements in accuracy of  $E$  values relative to the OFW method because it uses a more accurate approximation[54];

ES3: the integration from 0 to  $\alpha$  in Eq. (2.2) assumes  $E$  is a constant; otherwise it would introduce significant systematic errors.

Therefore, the following equation can represent the essence of the differences in error for the AIC and FR methods relative to the OFW and KAS methods:

$$|ES1| < |ES1 + ES2 + ES3| \quad (5.4)$$

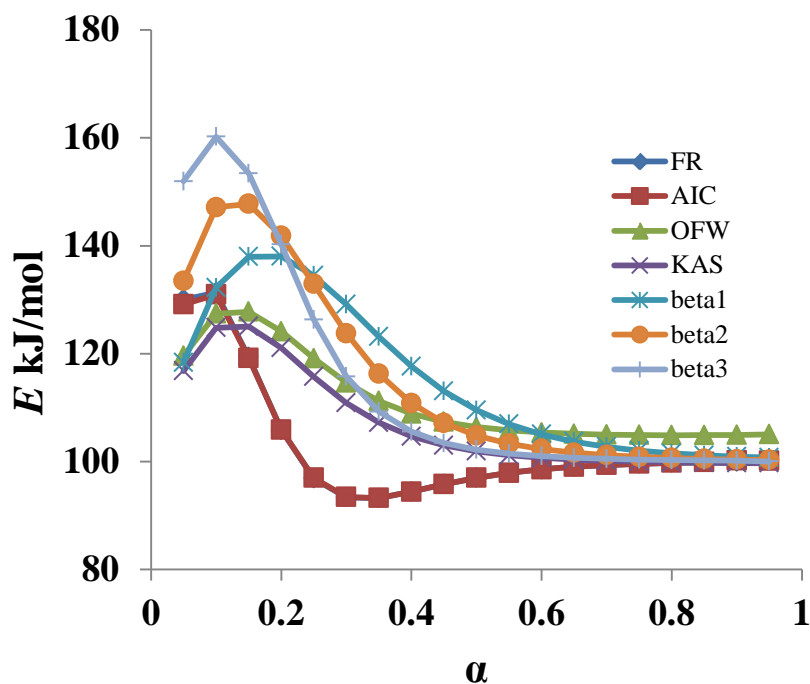


Figure 5.1 Simulation results obtained from test T1, (beta1-3 are true values for different  $\beta_i$ ; it also applies all Figures)

However, the term  $ES2 + ES3$  does not have to increase, a priori, the overall value of  $|ES1 + ES2 + ES3|$ . Actually, in some cases, the source of error for the AIC and FR methods may be singular and lead to more serious errors than for the OFW and KAS methods.

In general, the isoconversional methods try to obtain a one dimensional parameter  $E_\alpha$ , usually labeled as the “apparent”, “overall”, “empirical” or “global” activation energy, to characterize a

two dimensional parameter  $E(\alpha, \beta)$ . It is proposed that no isoconversional method can provide “exact”  $E_\alpha$  values; instead, the accuracy of an isoconversional method should be judged by its overall performance when testing one kind of reaction as compared to the overall performance of other isoconversional methods on the same reaction.

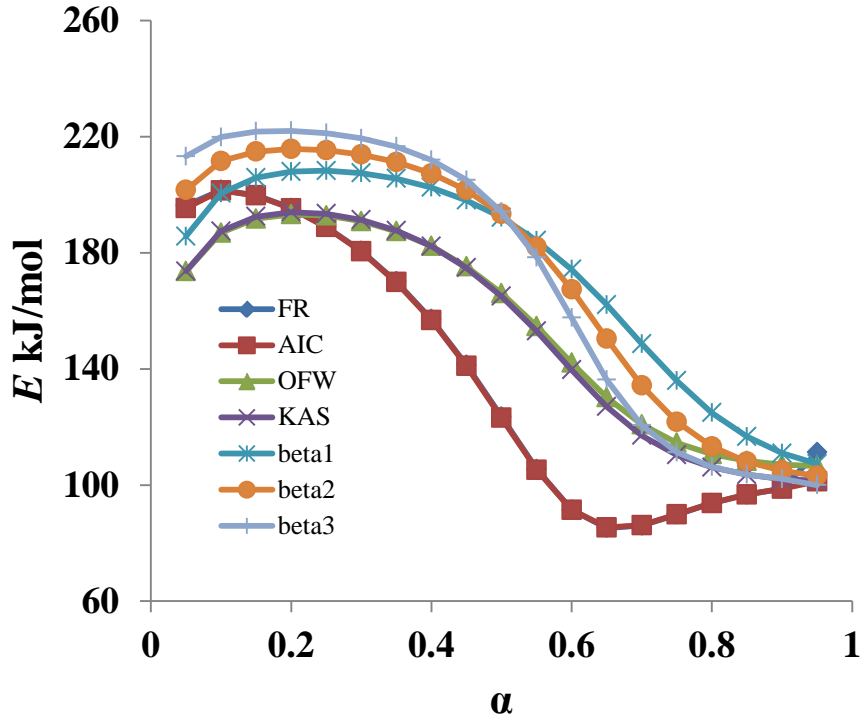


Figure 5.2 Simulation results obtained from test T2

### 5.3 Simulations and Analysis

#### 5.3.1 Parallel Independent Reaction

A parallel independent reaction is simulated that has two different reactions, as given below:

$$\frac{d\alpha}{dT} = c \frac{A_1}{\beta} \exp\left(-\frac{E_1}{RT}\right) (1-\alpha_1)^2 + (1-c) \frac{A_2}{\beta} \exp\left(-\frac{E_2}{RT}\right) (1-\alpha_2) \quad (5.5)$$



where  $\beta_{1-3} = 5, 10, 20$  K/min,  $A_1 = 10^{20.5} \text{ min}^{-1}$ ,  $E_1 = 240$  kJ/mol,  $A_2 = 10^8 \text{ min}^{-1}$ ,  $E_2 = 100$  kJ/mol, and  $c = 0.1, 0.5, 0.9$ , for tests T1-T3 respectively. For test T4,  $c = 0.5$ , and the value of  $A_1$  is  $10^{19.5}$ . The reactions T1-T3 involve different contributions and are totally or heavily overlapped. Two tests with partly overlapped reactions are labeled as T5 and T6, for which  $c = 0.5$ , and the value of  $A_1$  is  $10^{18.5}$  and  $10^{23} \text{ min}^{-1}$ , respectively.

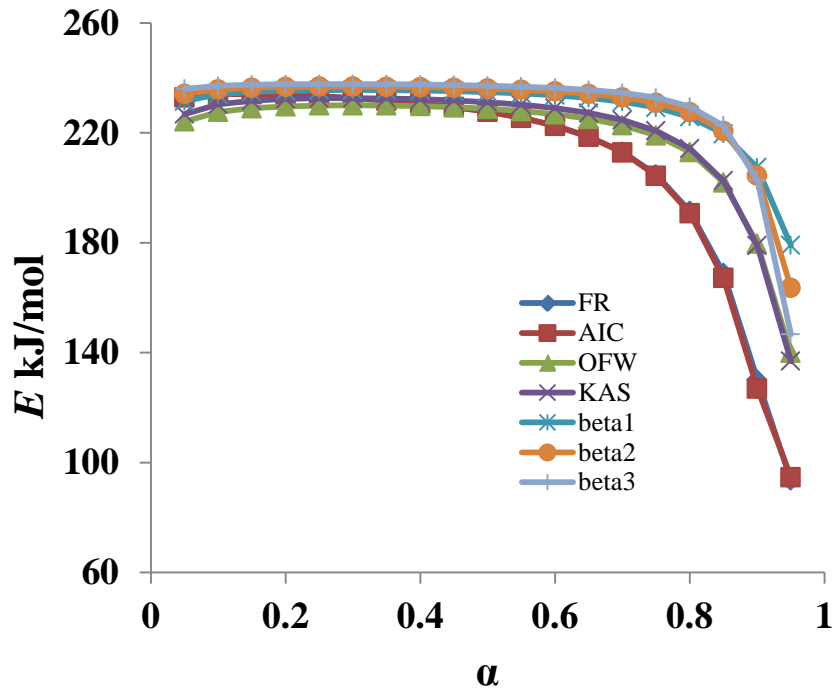


Figure 5.3 Simulation results obtained from test T3

The true values of  $E_\alpha$  for different  $\beta_i$  that are calculated using Eq. (5.2) and the values determined by various methods are shown in Figs. 5.1-5.6. The major results from the T1-T6 tests are presented below:

1. The apparent activation energies have strong dependency on the heating rates. If no dominant reaction exists - for example, for T2 where  $c = 0.5$ , the average differences between 5 K/min and 20 K/min heating rates,

calculated by  $\overline{\Delta E} = \frac{1}{19} \sum_{i=1}^{19} |E_{\beta_{3,i}} - E_{\beta_{1,i}}|$ , was 14.74 while the maximum

difference attained was 28.09 kJ/mol. If a dominant reaction existed, the dependence was relatively weak; for example, for T1 where  $c = 0.1$ , the average difference was 8.62 kJ/mol.

2. The use of the FR and AIC methods led to almost the same dependencies of  $E_\alpha$  on  $\alpha$ , as indicated in the figure by their lines having been merged; the use of the OFW and KAS methods led to same trends of  $E_\alpha$  variation with  $\alpha$  and was not able to detect if advantages existed for using the KAS method relative to the OFW method; the accuracy of the temperature integral is trivial and does not require attention as compared to the errors introduced by the basic assumption of the isoconversional methods;

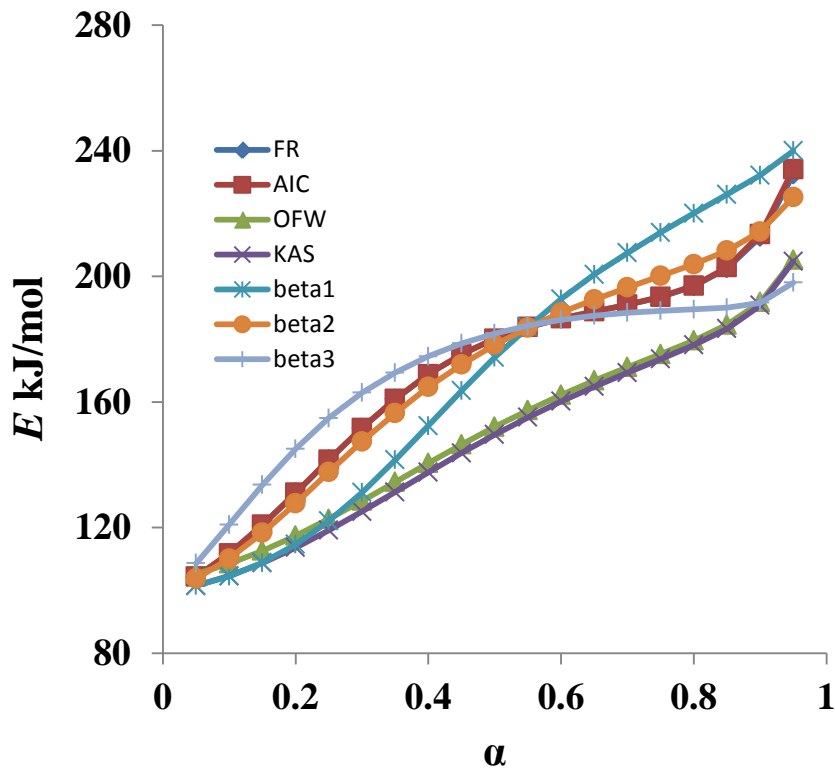


Figure 5.4 Simulation results obtained from test T4

3. In all tests except for T4, the behaviors of the OFW and KAS results were better than of the FR and AIC results in evaluating the dependencies of  $E_\alpha$  on  $\alpha$  for parallel independent reactions. Specifically, if the reactions were partly overlapped, the use of the OFW and KAS methods was

better than the use of the FR and AIC methods. If the reactions were totally or heavily overlapped, the dependences of  $E_\alpha$  on  $\alpha$  obtained by the FR and AIC methods may seriously deviate from the true values, as is observed in Figs. 5.1-5.3 where dependences obtained by the FR and AIC methods were far from any of the three true  $E_\alpha$  lines; in contrast the dependencies obtained by OFW and KAS methods did not have suffer from this inaccuracy. For T4, the behavior of the FR and AIC results was a little better than of the OFW and KAS methods, but they also captured true overall trends of the dependencies of  $E_\alpha$  on  $\alpha$ .

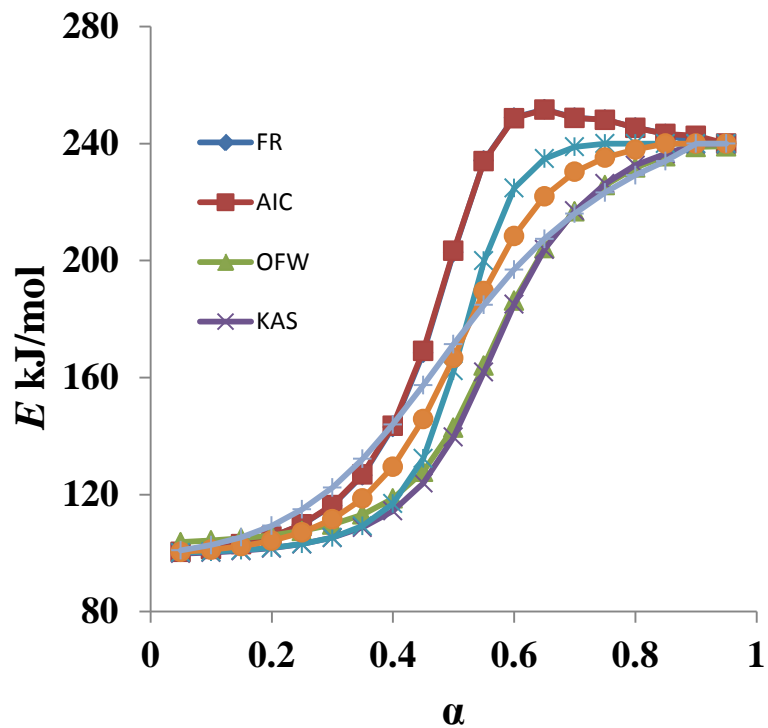


Figure 5.5 Simulation results obtained from test T5

4. The use of the FR and AIC methods led to false values that were smaller or bigger than both  $E_1$  and  $E_2$ , and even more questionable values were found in simulations using other parameters

(these are not shown for brevity). In contrast, the use of the OFW and KAS methods never suffered from these significant problems.

5. When the reactions were partially separated- as for T5 and T6- the  $E_\alpha$  values were considered reliable at the beginning and/or ending points for all methods; when the contribution of one of the reactions was dominant- as for T1 and T3 – the  $E_\alpha$  values for the dominating reaction could be obtained by all the methods.

Hence, in summary, the OFW and KAS methods gave better results than the values obtained by the FR and AIC methods; Eq. (6.4) was not suitable for use with parallel independent reactions; and, the introduction of ES2 and ES3 for the OFW and KAS methods a flattened or “averaged” influence decrease the error caused by ES1.

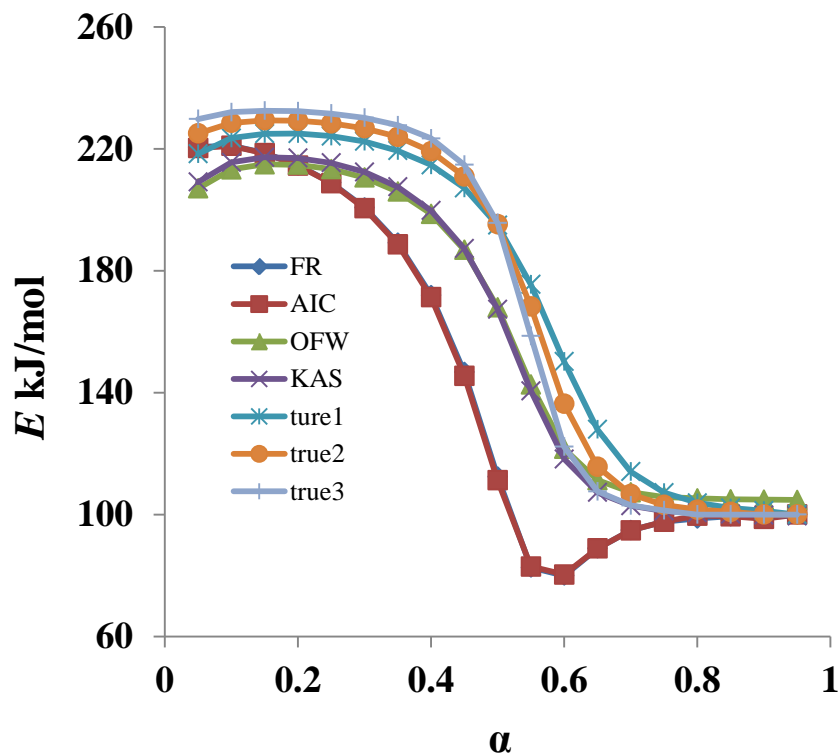


Figure 5.6 Simulation results obtained from test T6

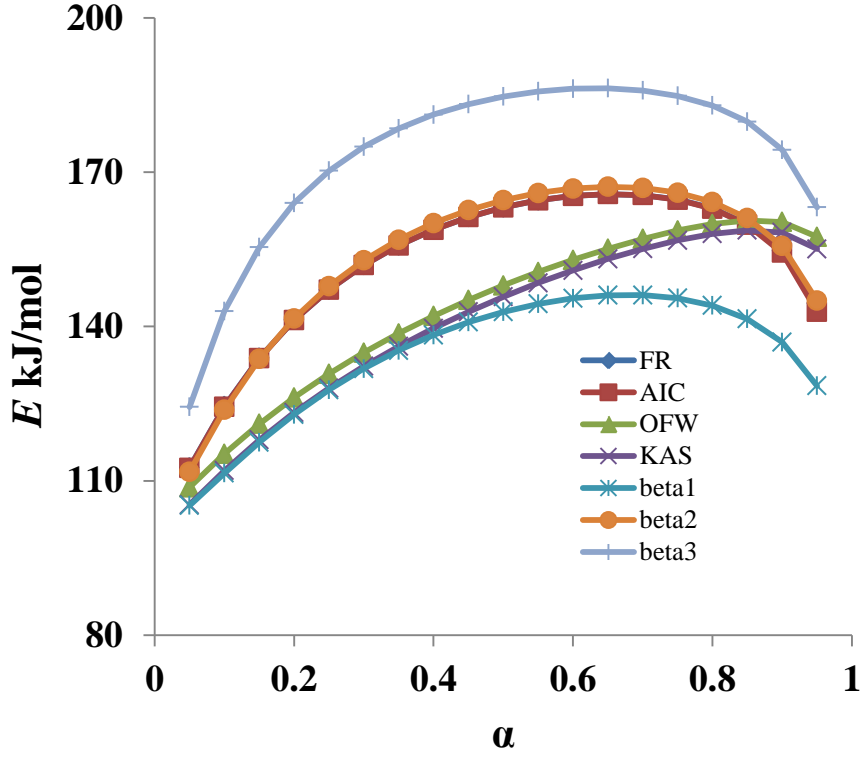


Figure 5.7 Simulation results obtained from test T7

### 5.3.2 Parallel Competitive Reaction

A parallel competitive reaction is simulated that has two different reactions, as given by:

$$\frac{d\alpha}{dT} = \left(\frac{d\alpha}{dT}\right)_1 + \left(\frac{d\alpha}{dT}\right)_2 = \frac{A_1}{\beta} \exp\left(-\frac{E_1}{RT}\right)(1-\alpha_1)^2 + \frac{A_2}{\beta} \exp\left(-\frac{E_2}{RT}\right)(1-\alpha_2) \quad (5.6)$$

where  $\beta_{1-3} = 5, 10, 20 \text{ K/min}$ ,  $A_1 = 10^{20.5} \text{ min}^{-1}$ ,  $E_1 = 240 \text{ kJ/mol}$ ,  $A_2 = 10^8 \text{ min}^{-1}$  and  $E_2 = 100 \text{ kJ/mol}$ . The two reactions in this Test (T7) were equally weighted, which means that in the overall reaction  $(d\alpha/dT)_1 \sim (d\alpha/dT)_2$  and no dominating reaction existed. Another two tests were conducted where one dominating reaction existed (T8) that had  $A_1 = 10^{19.5} \text{ min}^{-1}$ ; using this  $A_1$  value led to  $(d\alpha/dT)_1 \ll (d\alpha/dT)_2$ , i.e. the reaction was dominated by reaction 2. The

other test with a dominating reaction (T9) had  $A_1 = 10^{22} \text{ min}^{-1}$ ; using this  $A_1$  value led to  $(d\alpha/dT)_1 \gg (d\alpha/dT)_2$ , i.e. the reaction was dominated by reaction 1.

1. The values of  $E_\alpha$  had strong dependencies on the heating rates independent of whether a dominating reaction existed or not: the average  $E_\alpha$  differences when using 5 K/min, 10 K/min and 20 K/min for T7-T9 were 30.70, 13.09, and 17.10 kJ/mol, respectively, and the maximum differences were 34.46, 18.14, 32.13 kJ/mol at  $\alpha = 0.35, 0.70, 0.05$ , respectively;

The true values of  $E_\alpha$  and the values obtained by various methods are shown in Figs. 5.7-5.9. A discussion of the results from the T7-T9 tests is presented below.

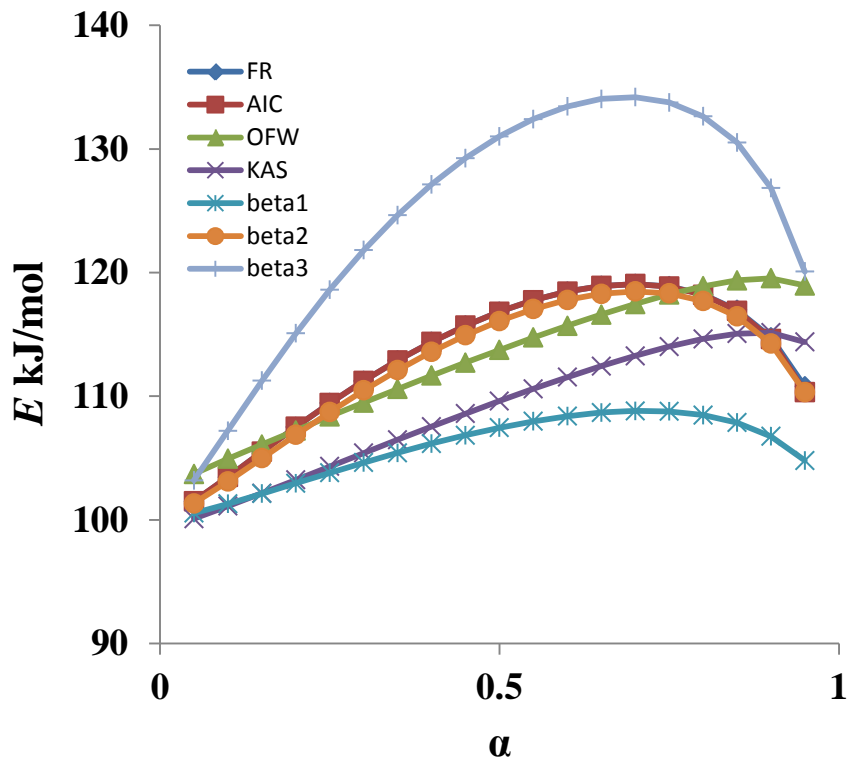


Figure 5.8 Simulation results obtained from test T8

2. The behaviors of the FR and AIC results for evaluating the dependencies of  $E_\alpha$  on  $\alpha$  for parallel competitive reactions were better than of the OFW and KAS results. The use of the FR

and AIC methods also led to the same dependencies of  $E_\alpha$  on  $\alpha$ . Comparatively, the use of the OFW and KAS methods also captured the overall trend of the dependencies but caused over smoothing of the true values.

In these tests, the dependency of  $E_\alpha$  on  $\alpha$  obtained by the FR and AIC methods were almost identical to the dependency on true values of  $\beta_2$ . It is worth noting, however, that this observation does not mean to imply that the same trends could be expected for cases that use different values and model functions. However, the dependence of  $E_\alpha$  on  $\alpha$  for competitive reactions obtained by the FR and AIC methods tended to be better than that obtained by the OFW and KAS methods; this observation then suggests Eq. (6.4) holds for competitive reactions.

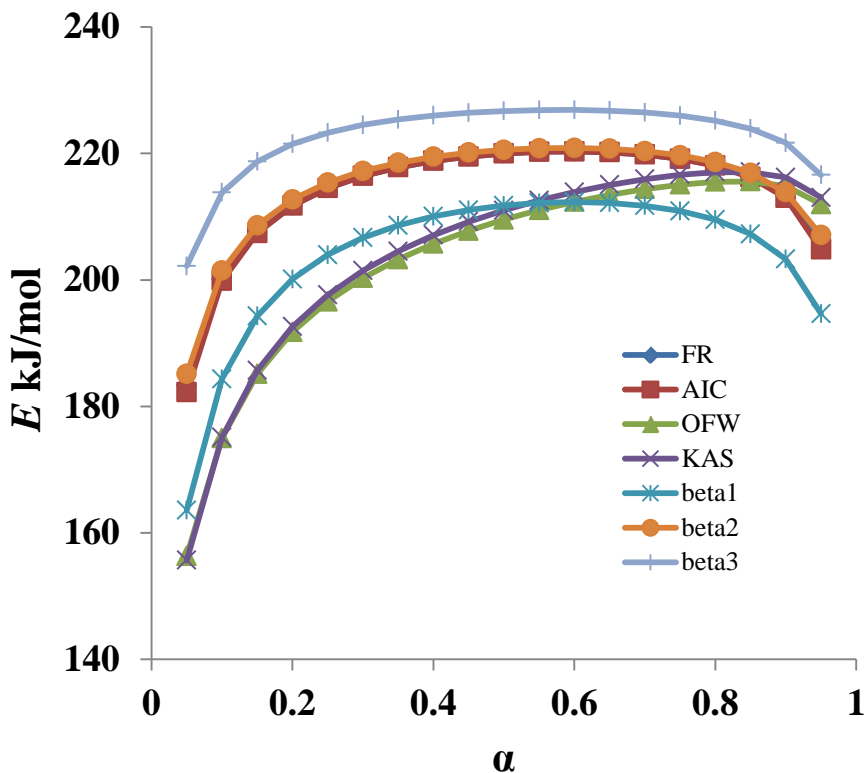


Figure 5.9 Simulation results obtained from test T9

Galway [118] collected 404 sets of  $E$  and  $A$  values from a wide range of solid state reactions for which the range of pre-frequency factors and activation energies for a majority of the reactions were within  $60 \leq E \leq 300$  kJ/mol and  $10^6 \leq A \leq 10^{19}$  min<sup>-1</sup>, respectively. During this study, many simulation tests using various combinations of  $\beta_i$  and  $f(\alpha)$ , and of  $E$  and  $A$ , were performed besides those values that were discussed in the previous sections. The overriding result of these simulations was that the behaviors discussed for reactions T1-T9 also held for these other simulations. Therefore, it is reasonable to conclude that the results of T1-T9 have common and important significance.

#### *5.4 Conclusion*

Studies of the accuracy of using isoconversional methods to evaluate the activation energy from non-isothermal solid state reaction data have concluded that the advanced integral isoconversional methods (and the differential ones if no noise involved) are more accurate than the regular integral ones. This research suggests this conclusion is problematic; the use of regular isoconversional methods involve a temperature integral approximation and the assumption that  $E$  is constant over the integration from 0 to  $\alpha$ , but has failed to consider the influence of the basic assumption on isoconversional methods.

This study showed that there are three kinds of error sources involved in various isoconversional methods: the basic assumption (ES1); the temperature integral approximation (ES2); and the assumption that  $E$  is constant over the integration from 0 to  $\alpha$  (ES3). The differential methods, such as the FR method, and the advanced integral ones, such as the AIC method, suffer from source ES1; the regular integral methods such as the OFW and KAS methods suffer from all three (ES1, ES2 and ES3). However, this study for the first time gave critical insight into information about the generally accepted idea that advanced integral isoconversional methods (and



differential ones if the data do not contain noise) are more accurate than the regular integral isoconversional methods.

Simulations have been carried out for parallel independent reactions and competitive reactions. The results of these simulations were: the idea that the FR and AIC methods would give exact values of  $E_\alpha$  was not correct; for parallel independent reactions the use of the OFW and KAS methods was better than the use of FR and AIC methods; for competitive reactions, the use of the FR and AIC methods was better than the use of the OFW and KAS methods; the error introduced by the source of temperature integral approximation was much less important than the other two sources and can be neglected for complex reactions.

Therefore, if one wants to apply an isoconversional method, the following recommendations are made. Additional studies testing the accuracy of the isoconversional methods or the reliability of newly developed methods should use the true values of the heating programs rather than the values determined by the advanced integral methods or the differential ones. Studies should also give more attention to the basic assumption inherent to the isoconversional methods and the assumption that  $E$  is a constant over the integration range from 0 to  $\alpha$  rather than the simplified the temperature integral. Finally, the use of the AIC and FR methods should yield to the use of regular integral methods such as the OFW and KAS methods for parallel independent reactions.

Based on theoretical and simulation analyses, it is proposed that the use of advanced methods is better than regular ones for competitive reactions, but for parallel independent reactions this research shows for the first time that the use of regular integral methods is better than the use of the advanced integral ones.

## CHAPTER 6: CONCLUSION

This study talked in detail of model-fitting, model free and invariant kinetic parameters methods that have been developed, and proposed a comprehensive method based on previous methods for obtaining kinetic parameters for solid state reactions. The conclusions are as follows:

Firstly, this study examined the advantages and disadvantages of previously existing methods. Model-fitting methods are easy to apply and are able to obtain single pair values for the activation energy and pre-exponential factor. However, model-fitting methods are highly unreliable because they require an existing knowledge of reaction mechanism, which is difficult to tell in most situations. Model free methods originated from the isoconversional principle, which is often called the basic assumption. This assumption provides model free methods - the freedom to avoid the usage of pre-knowledge of reaction mechanism. Additionally, model free methods are able to provide variable values of activation energy as a function of reaction degree. Previous studies comparing the reliability of those methods have not paid attention to the influence of the basic assumption on model free methods, and therefore, earlier conclusions are problematic. The invariant kinetic parameters method is also able to provide more reliable single pair values of activation energy and pre-exponential factor than model-fitting methods, but it is not applicable for complex reactions where the kinetic parameters such as activation energy vary with reaction degree and heating programs.

Secondly, this study has determined that the benefits of the invariant kinetic parameters method are underestimated and an incremental version of the method has been developed. This incremental method is able to provide values for both the activation energy and pre-exponential factor for complex reactions. Although those values often deviates heavily from true values, this study showed that the incremental invariant kinetic parameters method can be used to successfully determine the reliability of values obtained by model free methods.

Thirdly, based on model free methods and the invariant kinetic parameters method, this study proposed a comprehensive method. This method was tested on both simulation and experimental data of the decomposition of calcium carbonate and provided results showing noticeable advantages over other methods. The comprehensive method can evaluate the reliability of the results calculated by model free methods, determine the dependence of activation energy on the heating programs used, select reliable activation energy and provide variable pre-exponential

factor values for complex reactions, and to a certain degree, help to judge the quality of the experimental data.

In addition, this work compares the accuracy of existing model free methods by considering the influence of the basic assumption. This discussion is helpful for researchers to select a better isoconversional method that matches with the incremental invariant kinetic parameters method for different types of complex reactions.

## REFERENCES

1. Vyazovkin, S. and C.A. Wight, *Kinetics in solids*. Annual Review of Physical Chemistry, 1997. 48: p. 125-149.
2. Vyazovkin, S., *Thermal analysis*. Analytical Chemistry, 2006. 78(12): p. 3875-3886.
3. Lewis, G., *Zersetzung von Silberoxyd durch Autokatalyse*. Z physik Chemie, 1905. 52: p. 310-26.
4. Macdonald, J.Y. and C.N. Hinshelwood, *CCCLXXX.—The formation and growth of silver nuclei in the decomposition of silver oxalate*. Journal of the Chemical Society, Transactions, 1925. 127: p. 2764-2771.
5. Centnerszwer, M. and B. Bruzs, *The Thermal Decomposition of Silver Carbonate*. The Journal of Physical Chemistry, 1925. 29(6): p. 733-737.
6. Khawam, A. and D.R. Flanagan, *Basics and applications of solid-state kinetics: A pharmaceutical perspective*. Journal of Pharmaceutical Sciences, 2006. 95(3): p. 472-498.
7. Khawam, A. and D.R. Flanagan, *Solid-state kinetic models: Basics and mathematical fundamentals*. Journal of Physical Chemistry B, 2006. 110(35): p. 17315-17328.
8. Arrhenius, S., *On the reaction velocity of the inversion of cane sugar by acids*. Zeitschrift für physikalische Chemie, 1889. 4: p. 226.
9. Garn, P.D. and S. Hulber, *Kinetic investigations by techniques of thermal analysis*. 1972.
10. Garn, P.D., *Kinetics of thermal decomposition of the solid state: II. Delimiting the homogeneous-reaction model*. Thermochemica Acta, 1990. 160(2): p. 135-145.
11. Vyazovkin, S. and C.A. Wight, *Isothermal and non-isothermal kinetics of thermally stimulated reactions of solids*. International Reviews in Physical Chemistry, 1998. 17(3): p. 407-433.

12. Shannon, R.D., *Activated complex theory applied to the thermal decomposition of solids*. Transactions of the Faraday Society, 1964. 60: p. 1902-1913.
13. Cordes, H.F., *Preexponential factors for solid-state thermal decomposition*. The Journal of Physical Chemistry, 1968. 72(6): p. 2185-2189.
14. AD Le Claire, *Treatise on solid state chemistry* NB Hannay (Plenum, New York), 1975. 4: p. 1.
15. Raghavan, V. and M. Cohen, *Treatise on Solid State Chemistry*. Changes of state, 1975. 5: p. 96.
16. Galwey, A.K. and M.E. Brown, *A theoretical justification for the application of the Arrhenius equation to kinetics of solid state reactions (mainly ionic crystals)*. Proceedings of the Royal Society of London. Series A: Mathematical and Physical Sciences, 1995. 450(1940): p. 501-512.
17. Vlaev, L., et al., *A comparative study of non-isothermal kinetics of decomposition of calcium oxalate monohydrate*. Journal of Analytical and applied Pyrolysis, 2008. 81(2): p. 253-262.
18. Galwey, A.K., *What is meant by the term 'variable activation energy' when applied in the kinetic analyses of solid state decompositions (crystolysis reactions)?* Thermochemica acta, 2003. 397(1): p. 249-268.
19. AD, L.C., *In Treatise of Solid State Chemistry*. ed. BN Hanney, 4:1. New York: Plenum, 1975.
20. Raghavan V and Cohen M, *In Treatise of Solid State Chemistry*. ed. BN Hanney, 5:67. New York: Plenum, 1975.
21. Andrew K. Galwey and M.E. Brown, *A Theoretical Justification for the Application of the Arrhenius Equation to Kinetics of Solid State Reactions (Mainly Ionic Crystals)* Proc. R.Soc. London Ser. A 450, 1995: p. 501-512

22. Doyle, C., *Kinetic analysis of thermogravimetric data*. Journal of applied polymer science, 1961. 5(15): p. 285-292.
23. Doyle, C.D., *Estimating isothermal life from thermogravimetric data*. Journal of Applied Polymer Science, 1962. 6(24): p. 639-642.
24. Doyle, C.D., *Series approximations to the equation of thermogravimetric data*. 1965.
25. Coats, A.W. and J.P. Redfern, *Kinetic Parameters from Thermogravimetric Data*. Nature, 1964. 201(4914): p. 68-69.
26. Senum, G.I. and R.T. Yang, *Rational approximations of the integral of the Arrhenius function*. Journal of Thermal Analysis and Calorimetry, 1977. 11(3): p. 445-447.
27. Chen, H. and N. Liu, *New approximate formula for the generalized temperature integral*. AIChE Journal, 2009. 55(7): p. 1766-1770.
28. Flynn, J.H., *The temperature integral: its use and abuse*. Thermochemica Acta, 1997. 300(1): p. 83-92.
29. Starink, M.J., *The determination of activation energy from linear heating rate experiments: a comparison of the accuracy of isoconversion methods*. Thermochemica Acta, 2003. 404(1-2): p. 163-176.
30. Gorbachev, V.M., *Mathematical analysis of thermokinetic curves*. Journal of Thermal Analysis and Calorimetry, 1975. 8( 1).
31. A. W. Coats, J.P.R., *Kinetic parameters from thermogravimetric data. II*. Journal of Polymer Science Part B: Polymer Letters, 1965. 3(11): p. 917-920.
32. Brown, M.E., et al., *Computational aspects of kinetic analysis: Part A: The ICTAC kinetics project-data, methods and results*. Thermochemica Acta, 2000. 355(1-2): p. 125-143.
33. Roduit, B., *Computational aspects of kinetic analysis. Part E: The ICTAC Kinetics Project - numerical techniques and kinetics of solid state processes*. Thermochemica Acta, 2000. 355(1-2): p. 171-180.

34. Vyazovkin, S., *Computational aspects of kinetic analysis. Part C. The ICTAC Kinetics Project - the light at the end of the tunnel?* *Thermochimica Acta*, 2000. 355(1-2): p. 155-163.
35. Khawam, A. and D.R. Flanagan, *Role of isoconversional methods in varying activation energies of solid-state kinetics - II. Nonisothermal kinetic studies.* *Thermochimica Acta*, 2005. 436(1-2): p. 101-112.
36. Khawam, A. and D.R. Flanagan, *Role of isoconversional methods in varying activation energies of solid-state kinetics - I. isothermal kinetic studies.* *Thermochimica Acta*, 2005. 429(1): p. 93-102.
37. Burnham, A.K., *Computational aspects of kinetic analysis. Part D: The ICTAC kinetics project - multi-thermal-history model-fitting methods and their relation to isoconversional methods.* *Thermochimica Acta*, 2000. 355(1-2): p. 165-170.
38. Maciejewski, M., *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.* *Thermochimica Acta*, 2000. 355(1-2): p. 145-154.
39. Koga, N. and H. Tanaka, *A kinetic compensation effect established for the thermal decomposition of a solid.* *Journal of thermal analysis*, 1991. 37(2): p. 347-363.
40. Lesnikovich, A. and S. Levchik, *Isoparametric kinetic relations for chemical transformations in condensed substances (analytical survey). I.* *Journal of Thermal Analysis and Calorimetry*, 1985. 30(1): p. 237-262.
41. Galwey, A.K. and M. Mortimer, *Compensation effects and compensation defects in kinetic and mechanistic interpretations of heterogeneous chemical reactions.* *International journal of chemical kinetics*, 2006. 38(7): p. 464-473.
42. Marcilla, A., et al., *New approach to elucidate compensation effect between kinetic parameters in thermogravimetric data.* *Industrial & engineering chemistry research*, 2007. 46(13): p. 4382-4389.

43. Koga, N., *A review of the mutual dependence of Arrhenius parameters evaluated by the thermoanalytical study of solid-state reactions: the kinetic compensation effect.* Thermochimica acta, 1994. 244: p. 1-20.
44. Koga, N., *A Review of the Mutual Dependence of Arrhenius Parameters Evaluated by the Thermoanalytical Study of Solid-State Reactions - the Kinetic Compensation Effect.* Thermochimica Acta, 1994. 244: p. 1-20.
45. Koga, N. and H. Tanaka, *A kinetic compensation effect established for the thermal decomposition of a solid.* Journal of Thermal Analysis and Calorimetry, 1991. 37(2): p. 347-363.
46. Lesnikovich, A.I. and S.V. Levchik, *Isoparametric kinetic relations for chemical transformations in condensed substances (Analytical survey). II. Reactions involving the participation of solid substances.* Journal of Thermal Analysis and Calorimetry, 1985. 30(3): p. 677-702.
47. Garn, P., *The kinetic compensation effect.* Journal of Thermal Analysis and Calorimetry, 1976. 10(1): p. 99-102.
48. Nikolaev, A.V., V.A. Logvinenko, and V.M. Gorbachev, *Special features of the compensation effect in non-isothermal kinetics of solid-phase reactions.* Journal of Thermal Analysis and Calorimetry, 1974. 6(4): p. 473-477.
49. Mianowski, A. and T. Radko, *Evaluation of the solutions of a standard kinetic equation for non-isothermal conditions.* Thermochimica Acta, 1992. 204(2): p. 281-293.
50. Budrugaec, P., *The Kissinger law and the IKP method for evaluating the non-isothermal kinetic parameters.* Journal of Thermal Analysis and Calorimetry, 2007. 89(1): p. 143-151.
51. Lesnikovich, A.I. and S.V. Levchik, *A method of finding invariant values of kinetic parameters.* Journal of Thermal Analysis and Calorimetry, 1983. 27(1): p. 89-93.



52. Mamleev, V., et al., *Three model-free methods for calculation of activation energy in TG*. Journal of Thermal Analysis and Calorimetry, 2004. 78(3): p. 1009-1027.
53. Vyazovkin, S., et al., *ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data*. Thermochimica acta, 2011. 520(1): p. 1-19.
54. Vyazovkin, S.ergey, A.K. Burnham, J.M. Criado, L.A. Pérez-Maqueda, C. Popescu, N. Sbirrazzuoli, *ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data*. Thermochimica Acta, 2011. 520: p. 1-19.
55. Vyazovkin, S., *Model-free kinetics - Staying free of multiplying entities without necessity*. Journal of Thermal Analysis and Calorimetry, 2006. 83(1): p. 45-51.
56. Friedman, H., *Kinetics of thermal degradation of char-forming pastics from thermogravimetry-application to a phenolic resin*. J Polym Sci Part C: Polym Lett 6:. 1964: p. 183-195.
57. Friedman, H.L. *Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic*. in *Journal of polymer science part C: polymer symposia*. 1964. Wiley Online Library.
58. Budrugaec, P., *Differential non-linear isoconversional procedure for evaluating the activation energy of non-isothermal reactions*. Journal of Thermal Analysis and Calorimetry, 2002. 68(1): p. 131-139.
59. Ozawa, T., *Kinetics in differential thermal analysis*. Bull Chem Soc Jpn, 1965. 38: p. 1881-1886.
60. Flynn, J.H. and L.A. Wall, *A quick, direct method for the determination of activation energy from thermogravimetric data*. Journal of Polymer Science Part B: Polymer Letters, 1966. 4(5): p. 323-328.
61. Kissinger, H.E., *Reaction Kinetics in Differential Thermal Analysis*. Analytical Chemistry, 1957. 29(11): p. 1702-1706.
62. Akahira, T. and T. Sunose, *Res. Report Chiba Inst. Technol. Sci. Technol*, 1971. 16: p. 22.

63. Vyazovkin, S., *Evaluation of activation energy of thermally stimulated solid-state reactions under arbitrary variation of temperature*. Journal of computational chemistry, 1997. 18(3): p. 393-402.
64. Li, C.-R. and T.B. Tang, *A new method for analysing non-isothermal thermoanalytical data from solid-state reactions*. Thermochemica Acta, 1999. 325(1): p. 43-46.
65. Li, C.-R. and T.B. Tang, *Isoconversion method for kinetic analysis of solid-state reactions from dynamic thermoanalytical data*. Journal of materials science, 1999. 34(14): p. 3467-3470.
66. Li, C.-R. and T.B. Tang, *Dynamic thermal analysis of solid-state reactions*. Journal of Thermal Analysis and Calorimetry, 1997. 49(3): p. 1243-1248.
67. Vyazovkin, S., *Modification of the integral isoconversional method to account for variation in the activation energy*. Journal of Computational Chemistry, 2001. 22(2): p. 178-183.
68. Tang, W., and C. Donghua, *An integral method to determine variation in activation energy with extent of conversion*. Thermochemica acta, 2005. 433(1): p. 72-76.
69. Ortega, A., *A simple and precise linear integral method for isoconversional data*. Thermochemica Acta, 2008. 474(1): p. 81-86.
70. Han, Y., H. Chen, and N. Liu, *New incremental isoconversional method for kinetic analysis of solid thermal decomposition*. Journal of thermal analysis and calorimetry, 2011. 104(2): p. 679-683.
71. Han, Y., T. Li, and K. Saito, *A modified Ortega method to evaluate the activation energies of solid state reactions*. Journal of Thermal Analysis and Calorimetry, 2013: p. 1-5.
72. Ozawa, T., *A New Method of Analyzing Thermogravimetric Data*. Bulletin of the Chemical Society of Japan, 1965. 38(11): p. 1881-1886.

73. Flynn, J.H. and L.A. Wall, *A quick, direct method for the determination of activation energy from thermogravimetric data*. Journal of Polymer Science Part B: Polymer Letters, 1966. 4( 5): p. 323-328.
74. Doyle, C., *Estimating isothermal life from thermogravimetric data*. Journal of applied polymer science, 1962. 6(24): p. 639-642.
75. Vyazovkin, S., *Kinetic concepts of thermally stimulated reactions in solids: a view from a historical perspective*. International Reviews in Physical Chemistry, 2000. 19(1): p. 45-60.
76. Galwey, A.K. and M.E. Brown, *Solid-state decompositions - Stagnation or progress?* Journal of Thermal Analysis and Calorimetry, 2000. 60(3): p. 863-877.
77. Sewry, J.D. and M.E. Brown, *Model-free "kinetic analysis?"* Thermochemica Acta, 2002. 390(1-2): p. 217-225.
78. Galwey, A.K., *What is meant by the term 'variable activation energy' when applied in the kinetic analyses of solid state decompositions (crystolysis reactions)?* Thermochemica Acta, 2003. 397(1-2): p. 249-268.
79. Vyazovkin, S., *Reply to "What is meant by the term 'variable activation energy' when applied in the kinetics analyses of solid state decompositions (crystolysis reactions)?"*. Thermochemica Acta, 2003. 397(1): p. 269-271.
80. Marcus, R., *Chemical and electrochemical electron-transfer theory*. Annual Review of Physical Chemistry, 1964. 15(1): p. 155-196.
81. Maciejewski, M., *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*. Thermochemica Acta, 2000. 355(1): p. 145-154.
82. Budrugaec, P. and E. Segal, *On the Li and Tang's isoconversional method for kinetic analysis of solid-state reactions from thermoanalytical data*. Journal of Materials Science, 2001. 36(11): p. 2707-2710.

83. Sunose, A.T., T. Res Report Chiba Inst Technol (Sci Technol.), 1971. 16: p. 22.
84. Blaine, R., *A faster approach to obtaining kinetic parameters*. American Laboratory, , 1998. Jan. 21.
85. Blaine, R. and B. Hahn, *Obtaining Kinetic Parameters by Modulated Thermogravimetry*. Journal of Thermal Analysis and Calorimetry, 1998. 54(2): p. 695-704.
86. Mamleev, V. and S. Bourbigot, *Calculation of activation energies using the sinusoidally modulated temperature*. Journal of Thermal Analysis and Calorimetry, 2002. 70(2): p. 565-579.
87. Takeo, O., *Kinetic analysis by repeated temperature scanning. Part 1. Theory and methods*. Thermochemica Acta, 2000. 356(1-2): p. 173-180.
88. Blaine, R. and S. Marcus, *Derivation of Temperature-Modulated DSC Thermal Conductivity Equations*. Journal of Thermal Analysis and Calorimetry, 1998. 54(2): p. 467-476.
89. B, R., *Prediction of the progress of solid-state reactions under different temperature modes*. Thermochemica Acta, 2002. 388(1-2): p. 377-387.
90. Ozawa, T., *Further thoughts on temperature oscillation in thermal analysis*. Journal of Thermal Analysis and Calorimetry, 2003. 73(3): p. 1013-1018.
91. Flynn, J.H., *Thermal Analysis* Academic Press, 1969. 2: p. p. 1111.
92. S. R. Sauerbrunn, B.S.C.a.M.R., Proc. 21st N. Amer. Thermal Anal. Soc. Conf. , 1992: p. p. 137.
93. Gill, P., S. Sauerbrunn, and M. Reading, *Modulated differential scanning calorimetry*. Journal of Thermal Analysis and Calorimetry, 1993. 40(3): p. 931-939.
94. Vyazovkin, S., *Two types of uncertainty in the values of activation energy*. Journal of Thermal Analysis and Calorimetry, 2001. 64(2): p. 829-835.
95. M.J, S., *A new method for the derivation of activation energies from experiments performed at constant heating rate*. Thermochemica Acta, 1996. 288(1-2): p. 97-104.

96. Vyazovkin, S., *Evaluation of activation energy of thermally stimulated solid-state reactions under arbitrary variation of temperature*. Journal of Computational Chemistry, 1997. 18(3): p. 393-402.
97. Li, C.R. and T.B. Tang, *Isoconversion method for kinetic analysis of solid-state reactions from dynamic thermoanalytical data*. Journal of Materials Science, 1999. 34(14): p. 3467-3470.
98. Ortega, A., *A simple and precise linear integral method for isoconversional data*. Thermochemica Acta, 2008. 474(1-2): p. 81-86.
99. Cai, J. and S. Chen, *A new iterative linear integral isoconversional method for the determination of the activation energy varying with the conversion degree*. Journal of Computational Chemistry, 2009. 30(13): p. 1986-1991.
100. Gao, Z., H. Wang, and M. Nakada, *Iterative method to improve calculation of the pre-exponential factor for dynamic thermogravimetric analysis measurements*. Polymer, 2006. 47(5): p. 1590-1596.
101. Chen, H.X., N. Liu, and L.F. Shu, *Error of kinetic parameters for one type of integral method for thermogravimetric measurements*. Polymer Degradation and Stability, 2005. 90(1): p. 132-135.
102. P. Budrugeac, E.S., *On the nonlinear isoconversional procedures to evaluate the activation energy of nonisothermal reactions in solids*. International Journal of Chemical Kinetics, 2004. 36( 2): p. 87-93.
103. Opfermann, J.R. and H.J. Flammersheim, *Some comments to the paper of J.D. Sewry and M.E. Brown: Model-free kinetic analysis?* Thermochemica Acta, 2003. 397(1-2): p. 1-3.
104. Galwey, A.K., *Is the science of thermal analysis kinetics based on solid foundations? A literature appraisal*. Thermochemica Acta, 2004. 413(1-2): p. 139-183.

105. Narayan, R. and M.J. Antal, *Thermal Lag, Fusion, and the Compensation Effect during Biomass Pyrolysis*. Industrial & Engineering Chemistry Research, 1996. 35(5): p. 1711-1721.
106. Grønli, M., J. Michael Jerry Antal, and G.b. Va´rhegyi, *A Round-Robin Study of Cellulose Pyrolysis Kinetics by Thermogravimetry*. Ind. Eng. Chem. Res., 1999. 38: p. 2238-2244.
107. Roura, P. and J. Farjas, *Analysis of the sensitivity and sample–furnace thermal-lag of a differential thermal analyzer*. Thermochemica Acta, 2005. 430(1-2): p. 115-122.
108. Gao, Z.M., M. Nakada, and I. Amasaki, *A consideration of errors and accuracy in the isoconversional methods*. Thermochemica Acta, 2001. 369(1-2): p. 137-142.
109. Vyazovkin, S. and W. Linert, *Kinetic analysis of reversible thermal decomposition of solids*. International Journal of Chemical Kinetics, 1995. 27(1): p. 73-84.
110. Han Y., T. Li, and K. Saito, *Comprehensive method based on model free method and IKP method for evaluating kinetic parameters of solid state reactions*. Journal of computational chemistry 2012. 33: p. 2516-2525.
111. Jansen, J. and L. Machado, *Using ordinary differential equations system to solve isoconversional problems in non-isothermal kinetic analysis*. Journal of Thermal Analysis and Calorimetry, 2007. 87(3): p. 913-918.
112. Haixiang, C., L. Naian, and Z. Weitao, *Critical study on the identification of reaction mechanism by the shape of TG/DTG curves*. Solid State Sciences, 2010. 12(4): p. 455-460.
113. Budrugaec, P., D. Homentcovschi, and E. Segal, *Critical considerations on the isoconversional methods - III. On the evaluation of the activation energy from non-isothermal data*. Journal of Thermal Analysis and Calorimetry, 2001. 66(2): p. 557-565.
114. Vyazovkin, S., *Some confusion concerning integral isoconversional methods that may result from the paper by Budrugaec and Segal Some methodological problems*

*concerning nonisothermal kinetic analysis of heterogeneous solid-gas reactions."*

International Journal of Chemical Kinetics, 2002. 34(7): p. 418-420.

115. Budrugaec, P. and E. Segal, *On the nonlinear isoconversional procedures to evaluate the activation energy of nonisothermal reactions in solids*. International Journal of Chemical Kinetics, 2004. 36(2): p. 87-93.
116. Segal, E. and P. Budrugaec, *Is there any convergence between the differential and integral procedures used in chemical kinetics, particularly in nonisothermal kinetics?* International Journal of Chemical Kinetics, 2006. 38(5): p. 339-344.
117. Criado, J., P. Sánchez-Jiménez, and L. Pérez-Maqueda, *Critical study of the isoconversional methods of kinetic analysis*. Journal of Thermal Analysis and Calorimetry, 2008. 92(1): p. 199-203.
118. Galwey, A.K., *Magnitudes of Arrhenius parameters for decomposition reactions of solids*. Thermochemica Acta, 1994. 242(0): p. 259-264.

VITA

YUNQING HAN

Previously attended University of Science and Technology of China (Hefei, China), 2008-2011.

Publications

1. Han Y., T. Li, and K. Saito, *Comprehensive method based on model free method and IKP method for evaluating kinetic parameters of solid state reactions*. Journal of computational chemistry 2012. 33: p. 2516-2525.
2. Han, Y., T. Li, and K. Saito, *A modified Ortega method to evaluate the activation energies of solid state reactions*. Journal of Thermal Analysis and Calorimetry, 2013: p. 1-5.
3. Han, Y., H. Chen, and N. Liu, *New incremental isoconversional method for kinetic analysis of solid thermal decomposition*. Journal of thermal analysis and calorimetry, 2011. 104(2): p. 679-683.