A New Adaptation of the Method of Invariant Kinetic Parameters and its Application to a Flame Retardant System

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Abstract

This thesis treats a particular flame retardant (FR) system with a new kinetic analysis method derived from the method of Invariant Kinetic Parameters (IKP). The IKP method is one of many techniques available that extract a kinetic triplet (activation energy, pre-exponential factor and function of conversion) from non-isothermal, constant heating rate thermogravimetric (TG) data. The principles and advantages of the IKP method are discussed within a broad context, as are its limitations that are shared by most other methods. Such a consolidated and critical literature review is uncommon and is designed to help the novice researcher navigate through the kinetic analysis “minefield”. Each and every step for all solid-state mechanism derivations are explained for the same purpose: To encourage the adoption of an informed and circumspect approach to often complex heterogenous kinetic analysis.

The new method improves kinetic analysis outcomes and reliability by, in part, refining the IKP. Its approach is described in such detail that the inherent complexity of this undertaking can be fully appreciated, and if possible, managed in better ways. Subroutines written in Visual Basic for Applications in Excel to realise the method are validated with synthetic data up to a complexity of two overlapped independent models. Output from the method that pertains to water evaporation and the decomposition of calcium carbonate compares favourably with expectation. Statistical analyses are integrated into the method and allow for the proper treatment of uncertainty in all applications.

Motivation for this study originated from a desire to characterise the commercial FR system, polypropylene/ tetrabromobisphenol A bis(2,3-dibromopropyl ether)/ antimony trioxide. No thorough analyses of this FR system previously existed. TG data nominally for input into the new method is correlated with differential scanning calorimetry and Fourier transform infrared spectroscopy, and the implications of these small-scale analytical techniques are illustrated with larger-scale cone calorimetry.

Benson’s Group Additivity Method applied to a characteristic exothermic weight loss during the thermal decomposition of the pure FR complements the results of the new kinetic analysis method. A proposed degradation pathway is affiliated with the nucleation and nucleus growth model of statistical significance implied as the first of three overlapped independent processes that match the pyrolysis behaviour of the FR. The synergistic effect of antimony trioxide derives from its ability to make bromine from the FR overcome the diffusive resistance of the polypropylene substrate and enter the gas phase prior to ignition. It is concluded that the FR system behaves as might have been expected from a careful interpretation of the literature.
A New Adaptation of the Method of Invariant Kinetic Parameters and its Application to a Flame Retardant System

Declaration

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission in my name for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide.

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1 Introduction

Plastic materials offer such versatile physical characteristics that they have become ubiquitous in modern society. This versatility arises primarily from the range of different chemical groups that can be substituted to the basic hydrocarbon backbone of the polymers from which plastics are derived. Generally, polymeric molecules such as these are highly flammable, which translates to dangerously high fuel loadings in living spaces. Current fire safety standards acknowledge this danger and compel the chemical (reactive) or physical (additive) incorporation of flame retardant (FR) compounds before plastic products can be distributed commercially. The goals of FRs are to improve the rate of human survival and mitigate the extent of property damage from interior fires by delaying/preventing ignition, impeding fire propagation or extinguishing combustion within plastics.

It is possible to achieve a satisfactory fire safety standard via a number of different actions. FR compounds can either interfere in the condensed (solid or melt)-phase decomposition that occurs in hot plastic or inhibit the gas-phase combustion reactions above the degrading material. Physical or chemical means can be employed in either case. It is much easier to understand and therefore design FRs to hamper the radical chemistry in the gas phase. Hence, the vast majority of FRs in use today explicitly dilute or scavenge the highly reactive hydrogen and hydroxyl radicals in this phase.

Heavily-employed brominated FR compounds, for example, have their impressive efficacy attributed to a gas-phase scavenging mechanism. Their mode of action has serious drawbacks since HBr liberated from the plastic is very acidic and can damage property that is remote from the fire affected area. Moreover, acidic smoke is a tangible hindrance to timely evacuation. Brominated FR compounds are persistent and can bioaccumulate or degrade to ultra-toxic dioxins and furans, which incites environmental and health concerns. Attention has been focussed on the particular polybrominated diphenyl ethers that have recently been banned in the European Union. The structurally different brominated FR in greatest production, tetrabromobisphenol A, and its derivatives, remain free from regulatory restrictions.

One of these derivatives, tetrabromobisphenol A bis(2,3-dibromopropyl ether) (TBBA-BDPE), finds use mixed with the synergist antimony trioxide (Sb$_2$O$_3$) as an additive FR in polypropylene. This compound is the most significant of a mere handful of brominated FRs of commercial interest that contain both aromatic and aliphatic bromine. Given that the chemical and physical mechanisms at play in the condensed phase remain poorly understood, even for the more prolific brominated FRs, an interesting
question is raised of why this mix of chemical reactivity has been deduced from the standard trial-and-error selection process. How does the presence of two distinctly different intramolecular chemical environments affect the performance of TBBA-BDPE in polypropylene? Is it merely a matter of programming the most effective release of HBr into the gas phase with Sb₂O₃, or is there something of more significance occurring in the condensed phase that has been hitherto overlooked? Some studies are suggestive of the fact that brominated FR activity has been oversimplified. Answering these questions could lead to testable predictions that may themselves suggest how to mitigate some of the negative consequences of brominated FR use.

Interactions between TBBA-BDPE, Sb₂O₃ and the polypropylene substrate in a fire scenario are naturally assumed to be complex and likely to be confounded by heat and mass transfer effects. A kinetic analysis of large-scale combustion cannot be expected to resolve fundamental kinetic triplets (activation energy, pre-exponential factor and function of conversion). For a tractable analysis, non-isothermal thermogravimetric (TG) data from suitably small samples may be input into established methods that deduce global kinetic triplets to describe the conversion to volatile products. However, the merit of such deductions is questionable; in many cases these global kinetic parameters are not fundamental and can imply an inappropriate function of conversion.

It is pertinent to ask how it is possible to judge a function of conversion as inappropriate when many of these functions have their true meanings lost in the annals of history, and moreover, are presented in their final forms in the more recent literature without any qualifications. A proper consolidation of the physical origins and salient assumptions that give rise to these indiscriminate descriptions of how conversion rate changes with conversion would be a welcome resource.

The inverse kinetic problem is inherently ambiguous largely due to the similarity of these functions of conversion, which is exacerbated in the non-isothermal case. At odds with this demand for precision, deviations between experiment and prediction are tolerated beyond what is reasonable or are sometimes not even visualised. Influential computational errors can be easily made and, furthermore, data input for analysis often consists of overlapped processes. The questions are: How is this complexity best treated? Under what circumstances can global kinetic parameters affiliated with simplified functions of conversion have meaningful relationships to TG data? Is it possible to differentiate between models that all show some degree of statistical significance? The uncertainty in the answers to these questions motivates the evaluation and refinement of current practice before attempting to infer anything from the kinetic analyses relating to this FR system.
1.1 Thesis Content

This thesis is underpinned by comprehensive literature reviews on both flame retardancy (Chapter 2) and kinetic analysis (Chapter 3). Chapter 2 begins with a broad scope that covers all the known ways in which FRs act and how their performance is tested, which then narrows to a synopsis of the specific degradation pathways of relevant compounds to finally arrive at a set of realistic expectations to validate for the FR system. Chapter 3 describes the questionable foundations of kinetic analysis and compares and contrasts the multitude of methods that are currently applied to non-isothermal TG data. Section 3.3 is linked to Appendix A2, which critically derives all the known functions of conversion that are often called upon in kinetic analysis methods.

Chapter 4 reports the makeup of the sample formulations and the experimental methodology. Chapter 5 explains in careful detail the actions taken by the new algorithm to manipulate the raw TG data into a suitable form for analysis, determine invariant kinetic parameters, refine the kinetic solutions and evaluate their correlation back to the input data. Table 5-1 illustrates the 20 solid-state mechanisms and the two variants of the random scission scheme that correspond to the derivations of Appendix A2, and lists the assumptions from those derivations. “Algorithm” and “the [kinetic analysis] method”, when not explicitly referencing previous studies, refer to the new kinetic analysis method described in Chapter 5 and/or the algorithm laid out in full in Appendix A5.

Chapter 6 assesses the performance of the method when it is required to successfully return the kinetic triplets of non-overlapped and overlapped model simulations from user inputs that are not necessarily accurate. This validation is expanded to real TG data for water evaporation and calcium carbonate decomposition.

Chapter 7 analyses the complementary experiments conducted on the elements of the FR system and selected molecular analogues of TBBA-BDPE to deduce both the role of bromine in different chemical environments and the effect of Sb2O3. This analysis is tied to the performance of the FR formulations in a fire scenario with cone calorimetry.

Chapter 8 collates the conclusions drawn from this study with respect to generic kinetic analysis and the behaviour of the FR system, and puts forward ideas for future exploration.
2 Literature Review: Flame Retardancy

The relevance of flame retardants (FRs) has increased with the growing presence of inherently flammable material in human environs. Before the proliferation of synthetic plastic products began in the 1950s (Aubert et al., 2011), fire retardancy was universally imparted to wood and textiles by applying inorganic salts (alum, gypsum, borax, etc.) to their surfaces (van Esch, 1997). Hydrophobic synthetic polymers were unable to effectively bind these unrefined inorganic salts without the assistance of suitable surfactants like fatty acids, silanes and unsaturated polymeric acids (Rothon and Hornsby, 1996, van Esch, 1997, Wilkie, 2005). Readily compatible organic FR molecules were hurriedly innovated in lieu of making the necessary refinements to these existing compounds. These new molecules commonly contained halogens or phosphate esters (Lomakin and Zaikov, 2003).

Since the 1980s, intolerable rates of death, injury and property loss have resulted in more stringent fire safety standards, and the use of FRs has increased accordingly (Bourbigot and Duquesne, 2007). At least during the middle and latter stages of the last century, the high demand for effective FRs meant that their application was not preceded by rigorous testing of environmental and health criteria. As a result, many halogenated FRs have seen extensive use followed by reactionary prohibition (e.g. polychlorinated biphenols (PCBs), tris(2,3-dibromopropyl) phosphate and polybrominated diphenyl ethers) (van Esch, 1995, Horrocks et al., 2005, DiGangi et al., 2010). Despite their flawed implementation, FRs, in conjunction with better education and safety codes for buildings, have helped to decrease the number and impact of indoor fires (Morgan and Gilman, 2012).

More demanding plastic applications, cost reduction through improved FR efficiency and concern for the environment are cited as the three drivers for the innovation of new FR formulations (Howell, 2008). Comprehensive theoretical bases for the action of effective FRs are clearly invaluable. The accusation of a to date “schematic and qualitative” (Lewin, 2005) approach to describing the more complex mechanisms by which FRs interfere with the combustion cycle, attributed to a poor understanding of high temperature reactions, is unsurprising given the applied nature of the progression in this field (Luda di Cortemiglia et al., 1986).

2.1 The Combustion Cycle

Any polymer will start to degrade endothermically with the application of sufficient heat. A thermoplastic or elastomer will soften and melt, while a thermoset will exhibit surface charring. All plastics will eventually release low molecular weight compounds into the gas phase (Tewarson, 2003).
concentration of volatile organics above the degrading polymer will increase until it is within the relevant flammability limits. Ignition will then occur provided the temperature is high enough for autoignition or an ignition source is present; this is often the very element that has supplied the external heat. Once flaming combustion is established, burning is perpetuated through a cycle of endothermic pyrolysis, exothermic oxidation and thermal feedback (Camino et al., 1991, Lyon, 2000, Morgan and Gilman, 2012). The external source of heat becomes redundant. As this generic mechanism becomes a closed loop, effective flame retardancy can be achieved by inhibiting any one of these steps, i.e. by:

- Changing the mechanism of degradation
- Shielding the polymer from heat
- Reducing the concentration/activity of combustible volatiles
- Cooling the polymer
- Delaying ignition (only relevant prior to the polymer catching fire)

2.2 Modes of Action

Flame retardants must break or significantly inhibit the combustion cycle but not degrade the physical properties of the polymer relevant to the application, nor release toxins into the environment (including smoke) nor increase costs such that the plastic is made unviable as a commercial product. The FR must be compatible with the polymer to be treated and its processing requirements (Green, 1995). A distinction is often made between the condensed and gas phases when describing FR activity. It is also common to distinguish FRs on the basis of primarily physical or chemical action or the chemical makeup of the FR compound. The most cogent way to categorise FR activity, exemplified in the monograph Environmental Health Criteria 192 (van Esch, 1997), is adopted here.

2.2.1 Physical Action

Diluent/Thermal Quencher

A FR of this type can be released into the gas phase in such a volume that the volatile organic concentration is diluted below the lean limit (van Esch, 1997, Bourbigot and Duquesne, 2007). If the plastic is subjected to heat for longer than the diluent can be evolved at a sufficient rate, then the remaining polymer will burn unimpeded (Morgan and Gilman, 2012). These “fillers”, being inorganic metallic compounds (e.g. talc and chalk (Bourbigot and Duquesne, 2007)), reduce the total fuel content of the plastic, reducing the longevity of the fire.

Fillers with a high heat capacity can also effectively sequester heat from the fire. Endothermic decomposition and the release of vapour that also possesses a high heat capacity further improve FR
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performance (Hull et al., 2011). Alumina trihydrate (ATH or aluminium hydroxide), for example, releases 34.5% of its mass as water vapour following the onset of decomposition at 230ºC. Other metal hydroxide or carbonate compounds (alum, magnesium hydroxide, hydromagnesite etc.) work according to the same principle, but have different decomposition temperatures to match with different polymer substrates (Ranken, 2009). These simplistic physical actions predictably require very high FR loadings to be effective (50 – 80%), likely affecting the desirable physical properties of the polymer, e.g. strength and flexibility (van Esch, 1997, Morgan and Gilman, 2012). Morgan and Gilman (2012) also make the point that mineral-filled polymers would be more aptly labelled “ceramic composites with polymeric binders”, considering the loading levels. However, these percentages are by weight; 60% loading of magnesium hydroxide in polypropylene is equivalent to 37% by volume (Rothon and Hornsby, 1996). Recently it has been suggested that new fibrous mineral structures, such as “whiskers” of magnesium hydroxide sulphate hydrate, have the potential to enhance the physical properties of the composites at similar loading levels (Hao et al., 2011).

Inert mineral fillers lessen the toxicity and volume of combustion gases and are environmentally benign. They also are comparatively cheap mainly because of their simplicity (Morgan and Gilman, 2012).

Protective Barrier

Exposure to heat causes certain FRs to undergo a set of temperature-programmed chemical and physical changes that lead to the formation of a protective foam layer above the condensed phase of the polymer. This barrier, which ideally has a low thermal conductivity and high thermal mass, not only shields the polymer from heat, but also impedes the migration of volatile decomposition products to the flame (Camino et al., 1991, Bourbigot and Duquesne, 2007). The natural corollary of this mechanism is that smoke production is inhibited (Ceric and Simon, 1991). This intumescent behaviour generally requires an inorganic acid source to perform the required cross-linking/esterification, a carbon-rich compound for the acid to act upon and a blowing agent to foam the char thus formed.

The system of ammonium polyphosphate and pentaerythritol is frequently exemplified; in this case, the acid source (phosphoric acid) and blowing agent (ammonia) both originate from the same component (Bourbigot and Duquesne, 2007, Morgan and Gilman, 2012). Melamine is often added to take on the role of the blowing agent source for this system (Li, B. and Xu, 2006). Oxygen-rich phosphates and phosphoric acids that migrate to the surface of the polymer further decompose to polyunsaturated chains, aromatic char and finally elemental carbon char (Lindsay et al., 2000). Loading requirements for
phosphorus-based intumescent compounds are modest compared to fillers, but are still high at 10 – 40% (Price et al., 2001).

Nanocomposites can be constructed by blending molten polymers with montmorillonite (clay) and then improving the affinity of the clay to the polymer by removing the influence of excess sodium with quaternary ammonium salts (Ranken, 2009). It is believed that the early degradation of the ammonium salts (~200ºC) triggers the migration of the subsequently hydrophilic clay to the surface where it chars and forms a barrier (Lewin, 2005). The mechanism of FR action reduces peak heat release rates by 50 – 70%, but unfortunately cannot protect the substrate from ignition adequately enough to pass a UL 94 V-0 test (Section 2.4.3) (Gann and Gilman, 2003, Bourbigot and Duquesne, 2007, Ranken, 2009). These FRs have generated much interest recently as not only do they impart flame retardancy to the polymer, they can also enhance its physical properties. Loading levels are also comparatively low (3 – 6%) and no environmental concerns have been cited (Lewin, 2005, Ranken, 2009).

Flame retardant mechanisms that result in the formation of a non-intumescent continuous solid or liquid layer also exist. Silicon-based flame retardants for polyolefins, for example, supposedly deposit silicon dioxide (sand) on the surface of the polymer (van Esch, 1997, Ranken, 2009). Furthermore, burgeoning interest in FR ionic liquids appears to have evolved from the understanding of phosphorous chemistry; triethylmethyl phosphonium dibutyl phosphate and analogous ionic liquids can be substituted for the ammonium polyphosphate in the system described previously, or be mixed with aluminium trihydrate (Xu, 2011).

### 2.2.2 Chemical Action

#### Condensed Phase

It is possible for the polymer to act as the carbon source for intumescence (Bourbigot and Duquesne, 2007, Morgan and Gilman, 2012), and in that case it is reasonable for the action to be characterised as chemical in nature. Similarly, a polymer may dehydrate or dehydrogenate under the influence of a FR compound and cyclise or cross-link (char) (Xu, 2011, Shen et al., 2012). Substitution of the polymer for the carbon source reduces the required FR loading (Zhang and Horrocks, 2003) and therefore mitigates the cost and effect on physical properties.

Degradation/molecular weight reduction of thermoplastics can be accelerated by the free radicals generated from decomposing FR compounds, causing the polymer to absorb energy through liquefaction and drip or flow away from the hot zone (Tkac and Spilda, 1981, Camino et al., 1991,
Kaspersma et al., 2002, Bourbigot and Duquesne, 2007). This mechanism is not presented as frequently as others, possibly because of its negative connotations for the structural integrity of the flame-retarded material and the fact that this mechanism also has the potential to spread the fire (Savides et al., 1979). Brominated FRs are often labelled as solely gas-phase active (Hull et al., 2011, Morgan and Gilman, 2012), even though it is easy to demonstrate that they accelerate the decomposition of the polymer (Tkac and Spilda, 1981, Kaspersma et al., 2002).

Gas Phase

Decomposition products of FRs can scavenge the very reactive volatile organic, hydroxyl and hydrogen radicals that participate in highly exothermic combustion reactions (Zhang and Horrocks, 2003), form less reactive radicals, and thereby quench the combustion process. This is a very efficient means of fire retardation and is considered the mode of action for halogenated FRs and some phosphorous-based FRs. The FRs within polymers must decompose at an appropriate moment in the combustion cycle in order to scavenge radicals to greatest effect; this point is approximately 50ºC below the polymer decomposition temperature (van Esch, 1997). In most cases, however, a programmed release of the retarding gaseous species (e.g. HBr and Br•) would be ideal in order to be consistent with the complicated decomposition within the polymer (Tkac and Spilda, 1981). Clearly this mode of action increases toxic smoke formation (Morgan and Gilman, 2012).

Antimony trioxide (Sb2O3) can be added in 2 – 10% loadings to prematurely volatilise halogens as antimony trihalide (SbX3) so that interference with the radical reactions occurs earlier in the combustion cycle (Handa et al., 1979, Savides et al., 1979, van Esch, 1997, Kaspersma et al., 2002). This tends to optimise the performance of brominated FRs and allows them to be used at loadings of less than 10% (Rychly and Rychla, 1996) rather than 10 – 20% (Zhang and Horrocks, 2003, Covaci et al., 2009). Ceric and Simon (1991) state that a mixture of 3% Sb2O3 and 6% bromine has an equivalent FR effect in polyolefins as 20% bromine.

Solid metal oxides can also disperse through the combusting gases immediately above the polymer and adsorb reactive H• and OH• radicals, but this appears to be of minor importance as Sb2O3 is not considered a FR in its own right (van Esch, 1997, Bocchini and Camino, 2010). Even so, Sb2O3 is described as a “glow inhibitor” (van Esch, 1997) and thus can be expected to delay ignition, and is also likely to stimulate char formation (Section 2.5.2).
2.3 Chemical Incorporation

Rather than physically mixing FR additives with the polymer substrate in the loading levels indicated in the previous section, the components that impart the FR effect can be bound chemically. Some polymers are inherently flame retardant due to these components already forming an integral part of the polymer, such as the charring elements in polyimides (Bourbigot and Duquesne, 2007). Halogenated polymers, such as polyvinylchloride (PVC), are also inherently flame retardant and many do not combust even in a 50% oxygen atmosphere (Tewarson, 2003).

Flame retardant compounds extraneous to the unmodified polymer that are bound chemically are called “reactives”. These compounds are generally functionalised organics, although silicon-based compounds and ionic liquids are also suitable (Bourbigot and Duquesne, 2007, Xu, 2011). Due to a much better integration level and no need to compensate for untimely FR leaching, reactive FRs are often only required in concentrations of less than 10% (Price et al., 2001, Bocchini and Camino, 2010). It has also been suggested that a FR incorporated in a reactive sense can have a different mechanism of action and degrade to different products compared to if it were merely physically mixed with the polymer (van Esch, 1995, Price et al., 2005). Reactive phosphorous compounds, for example, demonstrate a condensed-phase, charring mechanism in polymethyl methacrylate because of their intimate integration, whereas additive phosphorous compounds can volatilise early and react in the gas phase (Lindsay et al., 2000, Price et al., 2001). The activity of phosphorous-based FRs can also change from the condensed phase to the gas phase depending on the polymer substrate (Morgan and Gilman, 2012).

Interference with the standard polymerisation process enables the combination of conventional and FR monomers to create entirely new reactive FR copolymers. Alternately, the FR components can be grafted onto the formed polymer. The high cost associated with the development, manufacture and disposal of these inherently flame retardant or flame-retarded co- or graft polymers limits their use mainly to specialty applications in the military or aerospace industry (Bourbigot and Duquesne, 2007, Morgan and Gilman, 2012). The most pertinent exception to this rule is tetrabromobisphenol A/bisphenol A diglycidyl ether copolymer, which forms the template for printed circuit boards as a flame-retarded epoxy resin (van Esch, 1997, Barontini et al., 2005). Morgan and Gilman (2012) graph the increasing materials cost with decreasing fire hazard for commodity and engineering plastics to research-grade plastics, highlighting the current preference for imparting flame retardancy to otherwise flammable polymers with additives. An additive approach to flame retardancy is also favoured because of the easier adaptation of formulations to different applications (Camino et al., 1991).
2.4 **Standard Tests**

Empirical studies have driven the advancement of FR technology since around 450 BC when humankind first discovered the capacity of alum to reduce the flammability of wood (van Esch, 1997). Over time, methodical research has evolved a number of different measures of fire performance to compare different formulations reliably. These measures include heat release rate, time to ignition, ignition temperature and minimum oxygen concentration required for combustion (Limiting Oxygen Index (LOI)). There is a general consensus that comparing LOIs is less indicative than comparing heat release rates that have a strong relation to real FR performance (Staggs and Nelson, 2001, Price et al., 2005). In fact, Babrauskas and Peacock (1992) state emphatically that heat release rate is the sole dictator of fire hazard in their promotion of cone calorimetry.

Three factors central to combustion must be characterised in order to completely describe a flammable system: Susceptibility to ignition, combustion ferocity and fire propagation rate (Tewarson, 2003). There exist a variety of different standard tests that address these factors. Notwithstanding trivial differences that arise through independent test development, there are a few parameters that are common to at least the three tests outlined here: Prior sample conditioning at 23 ± 2°C and 50 ± 5% relative humidity, a sample size range of 50 – 300 x 10 – 100 x 3 – 50 mm, specifically horizontal or vertical orientation, exposure to radiant heat or a small flame and an environment that is composed of air with additions of either nitrogen or oxygen as required (AS/NZS 3837, 1998, Tewarson, 2003).

Similarly, there are certain observations that are commonly recorded using fire testing apparatus. The following list encompasses the majority of these observations that relate to autoignition or pilot flame ignition stimulated by an applied heat flux (Tewarson, 2003):

- Time to ignition and flame extinguishment
- Whether polymer drops will ignite flammable materials beneath the sample
- Level of light obscuration by smoke
- Rate of flame spread and the min. heat flux/oxygen concentration to achieve a non-zero rate
- Total surface subjected to the flame
- Degree and rate of surface charring
- Heat release rate
- Release rate and characterisation of combustion products (including smoke)
Strict adherence to the guidelines outlined in any standard is clearly necessary for unqualified comparisons to be made with confidence. Significant variation between experimenters is tolerated to an extent by including statistical elements in the standards (Lindholm, 2011).

2.4.1 Limiting Oxygen Index (LOI)

One testing method involves the systematic deduction of LOI, according to the standard ISO 4589-2. For this test, the aim is to find the highest oxygen concentration at which a vertical sample strip does not burn downwards or drip from the point of ignition past a certain mark, or sustain combustion for longer than 180 seconds. LOIs are used to rank materials in order of their resistivity to fire propagation, as a higher oxygen concentration is representative of a higher flame heat flux (Tewarson, 2003). It has also been stated that LOI depends heavily on the kinetic chain length of the polymer (Appendix A2.6) (Tkac and Spilda, 1981).

The ISO standard dictates the values of crucial system parameters to ensure reproducibility; these include a 16 ± 4 mm downwards flame projection from the propane igniter, sets of appropriate sample dimensions and marks for different materials, and very specific instructions regarding the actual ignition and classification procedure. Statistical effects are considered before any LOI is deemed valid (ISO 4589-2, 1996).

Oxidant indices have been determined for nitrous oxide in addition to oxygen to test FR mechanism sensitivity to the oxidant (Savides et al., 1979, Luda di Cortemiglia et al., 1986). Should progressive changes in LOI with FR concentration not be paralleled by the nitrous oxide index, then the oxidant clearly alters the nature of the FR mechanism and gas-phase action is implied (Savides et al., 1979, Bocchini and Camino, 2010). This test seems to be underutilised in mechanistic studies.

2.4.2 Cone Calorimetry

The standard technique of cone calorimetry (currently designated in this region as AS/NZS 3837:1998) was first devised by Babrauskas in the 1980s to provide a practical alternative to LOI testing. At the time, simplifying and better controlling the experimental parameters were considerations made for simulation purposes (Staggs and Nelson, 2001). Irradiance is provided by a cone of heating coils, located above the surface of a horizontal sample face, that delivers anywhere between zero and 100 kW/m². An igniter, if required, is positioned between the cone and the sample; once sufficient flammable volatiles have been expelled, ignition is observed and recorded. The standard setup including all peripheral equipment is given in AS/NZS 3837:1998 and is reproduced in Figure 2-1.
The critical measurements from the cone calorimeter are exhaust gas flow rate and oxygen concentration from an analyser with a better than 12 second response time from 10 – 90%, as these are used to infer instantaneous heat release rate (AS/NZS 3837, 1998) (Nomenclature in Appendix A1):

\[
\dot{q}(t) = \left[ \frac{\Delta h_c}{r_o} \right](1.10)C \frac{\sum \Delta P}{T_c} \frac{X_{O_2}^0 - X_{O_2}(t)}{1.105 - 1.5X_{O_2}(t)}
\]

The calibration constant \(C\) is derived from an initial 5 kW combustion run with methane \((\Delta h_c/r_o = 12.54 \text{ MJ/kg O}_2)\). The value \(\Delta h_c/r_o\) for test samples is assumed to be 13.1 MJ/kg O\(_2\) unless a more accurate value is known. If CO and CO\(_2\) concentrations are analysed, Equation 2-1 must be modified to account for the fact that a portion of the input stream to the oxygen analyser is diverted for this purpose.

A load cell supporting the combusting sample also provides mass loss data, and smoke volume can be derived from the attenuation of a helium-neon laser fitted downstream of a soot filter. A global sampling rate is set for all measurement devices and the mass loss rate is computed using five-point numerical differentiation. Effective heat of combustion can also be inferred from the heat release and mass loss rates (AS/NZS 3837, 1998):
\[ \Delta h_i(t) = \frac{\dot{q}(t)}{m}, \text{ or, as an average, } \Delta \overline{h}_i(t) = \frac{\Delta t \sum \dot{q}_i}{\Delta m} \]

Cone calorimetric data, in particular the reported peak heat release rates, can suffer greatly from experimental setup inconsistencies. Heat output from the cone is not likely to be uniform towards the edges of a standard sample surface area (100 x 100 mm) and the thermal properties of the sample holder dramatically influence thermal feedback from the underside of the sample. While this standard categorises a plaque depth of less than 6 mm as “thermally thin” (AS/NZS 3837, 1998), realistically this quality is highly dependent on whether the sample chars or not. In some cases, a thermally thin sample will not actually be able to form the physical barrier it otherwise would and the result from the test may be unrepresentative of its real fire performance (Schartel et al., 2005). Setup inconsistencies should not impact on the ability to compare between assessments using the same equipment. Provided the results are interpreted carefully, cone calorimetry allows the differentiation of FR mechanisms whereas this is not possible for LOI testing (Price et al., 2001).

Lyon (2000) states that fires that range in size from a match or cigarette through to a building or hydrocarbon pool fire all fall within the irradiance range of 20 – 200 kW/m². Higher heating rates corresponding to irradiances of more than 50 kW/m² are suggested as simulating the response of a test plaque to a well-established fire, and yield more reproducible results. Test outcomes may be significantly different when lower irradiances are used, again due to changes in the FR mechanism (Schartel et al., 2005). As a guide to irradiating power, 2.5 kW/m², essentially equivalent to a radiating source at 200ºC, can be tolerated by the average person for only 30 seconds (Purser, 2000).

2.4.3 UL 94

The most frequently cited standard is the Underwriters Laboratories’ test 94 (UL 94) that was developed in the United States. Conditioned sample materials are distinguished primarily on the bases of extent and rate of flame propagation after exposure to an open Bunsen burner flame at the unsecured end of the sample stick. Each material should pass the horizontal burning test before being subjected to the more demanding vertical test (given the flame impinges from below). As for LOI testing, UL 94 ratings are also a measure of polymer resilience to flame propagation (Tewarson, 2003).

For vertical testing, each of five samples is subjected to two flame applications, both 10 seconds in duration. After the first flame application, an “afterflame” time \(t_1\) is noted and the Bunsen burner flame is reapplied immediately upon the flame extinguishing. After the second flame application, afterflame
and afterglow times \( t_2 \) and \( t_3 \) respectively) are recorded. Materials are rated as V-0, V-1, or V-2, where V-2 corresponds to the least stringent FR criteria. A V-2 rating implies that the five samples do not afterflame for more than 250 seconds in total (25 seconds of afterflaming on average) and that a cotton wad under the sample ignites as a result of incident drops of flaming material. Ignition of the cotton is not allowed for ratings of V-1 and V-0; in addition, the five samples must not afterflame for more than 50 seconds in total to achieve V-0. The quoted time to extinguishment is calculated as the average of the 10 afterflame periods; critically however, any afterflame cannot persist beyond 30 seconds and \( t_2 + t_3 \leq 60 \) seconds for V-1 or V-2, whereas 10 seconds or less of afterflame and \( t_2 + t_3 \leq 30 \) seconds is required for V-0 (UL 94, 1998, Tewarson, 2003). It is possible for a material to not fall into any of the three categories, in which case it remains unclassified.

2.5 Brominated Flame Retardants

Section 2.2 implies that there exist specific chemical elements that are commonly applied in FRs. Inorganic compounds are used more than any other type of FR, approximating half of total usage in recent times (van Esch, 1997, Gann and Gilman, 2003), and attributable mostly to aluminium trihydrate (Market Study, 2011). It is presumed that the assessment of FR usage on a volume basis inflates the perceived dominance of high-loading inorganic FRs. Halogenated and organophosphorus compounds fulfil practically all the remainder of world wide demand (van Esch, 1997), although organophosphorus and newer FR substitutes are implied to be increasing their global market share at the expense of halogenated FRs (Market Study, 2011). Regulatory restrictions imposed on significant brominated FRs in Western Europe and North America are the likely cause of this shift. However, Covaci et al. (2011) and Nnorom and Osibanjo (2008) report increasing relative demand for halogenated FRs (at 25% of total FR volume in 2008) due to heavy use in Asia where the majority of consumer electronics are manufactured. It has been acknowledged that production volume estimates for lesser known brominated FRs are required for a complete picture (Covaci et al., 2011).

Flame retardants containing bromine were first introduced in the 1970s. These organic chemicals were quickly adopted for this role due to their excellent chemical compatibility with polymers, superior performance and cost effectiveness (von der Recke and Vetter, 2007, Xu, 2011, Morgan and Gilman, 2012). Halogenated systems are still the most effective and versatile FR option available today (Bocchini and Camino, 2010). Bromine is the substituent of choice for the vast majority of halogenated FR compounds due to its high efficacy compared with the only other viable halogen, chlorine. Fluoro- and iodo-compounds are impractical as they define the extremes of chemical stability (van Esch, 1997).
In 2003, of the 175 known FR compounds in use, 75 of them were brominated FRs (Salamova and Hites, 2011).

Tetrabromobisphenol A (TBBA; Figure 2-2) exhibits great versatility as either a reactive or additive FR and accounts for 59% of all halogenated FRs in use on a mass basis (Law et al., 2006); 170,000 tonnes of this aromatic compound were produced in 2004 (Font et al., 2012) along with another presumed 18% of this figure as its various functional ether derivatives and oligomers (Letcher and Chu, 2010). Roughly 90% of the total volume of TBBA is used as a reactive intermediate in epoxy and polycarbonate resins (van Esch, 1995, Nnorom and Osibanjo, 2008), which equates to the incorporation of TBBA into 96% of all printed wiring boards (Barontini et al., 2004b). Consequently, TBBA is found within the majority of household electronic devices partnered with the second most prolific halogenated FR, deca-bromodiphenyl ether (Deca-BDE; Figure 2-2), that retards the combustion of electronic unit casings made from high impact polystyrene, as well as polyolefins and latex-based backings on textiles (van Esch, 1997, Nnorom and Osibanjo, 2008). Deca-BDE as an additive in electrical and electronic equipment has been banned in the European Union since July 2008, however, and the intention was to phase it out in other applications by 2013 (Covaci et al., 2011). The 2,3-bisdibromopropyl ether of TBBA (TBBA-BDPE) has already been substituted for Deca-BDE (Haneke, 2002).

![TBBA and Deca-BDE](image)

**Figure 2-2: Tetrabromobisphenol A (TBBA) and deca-bromodiphenyl ether (Deca-BDE)**

### 2.5.1 Environmental and Health Concerns

Of immediate concern in a fire situation is the irritant effect of hydrogen halides on the persons attempting to evacuate a smoke-filled area. The gas-phase action of all halogenated FRs implies that hydrogen halides are present in the smoke generated from materials flame-retarded with halogenated FRs, which may impede egress or even incapacitate. The levels of hydrogen halides required to cause impediment vary for each individual, however the range of severe affliction can be defined roughly as 100 – 500 ppm, where 200 ppm is thought to impair the escape of half the population (Purser, 2000). To put this concentration in context, HCl has been estimated to reach 200 ppm in a 39 m³ room containing...
a single burning polystyrene/polyurethane armchair in roughly four minutes (Purser, 2000). Purser and others, however, point out that carbon monoxide is much more relevant to the incapacitating nature of smoke (Clarke, 1999, Purser, 2000, Gann and Gilman, 2003). While gas-phase flame retardation leads to more incomplete combustion and therefore a higher carbon monoxide/carbon dioxide ratio (Wichman, 2003, Morgan and Gilman, 2012), the overall effect of halogenated FRs on fire safety is unquestionably positive (Clarke, 1999, Gann and Gilman, 2003).

As an aside, the strong acidity of these hydrogen halide fumes can lead to etching and deactivation of electronic equipment that does not suffer from direct flame impingement (Wu et al., 2003, Gann and Gilman, 2003).

Halogenated compounds are typically characterised by relatively high stability, which is desirable in their application but not for their timely removal from the environment. This fact is particularly relevant to additive FRs that can readily leach from the polymer substrate. A number of these FR compounds have been shown to accumulate within biota and abiotic solids alike (Hoh and Hites, 2005, Ward et al., 2008, MacGillivray et al., 2011). The more lipophilic (fat soluble) and resistant to metabolic processes these compounds are, the greater their bioaccumulation potential. High molecular weight compounds (>700 atomic mass units) are generally insoluble in lipids and are not likely to be transported large distances on air currents due to their greater affinity for the particulate phase (Covaci et al., 2011), implying these compounds are more benign. Bioaccumulation and environmental persistence must be considered in concert with toxicity to gain an appreciation of risk.

Polybrominated biphenyls (PBBs) seem to exemplify a high-risk contaminant according to the above criteria. It could be argued that the hyper-exposure caused by the catastrophic mistake of confusing magnesium oxide with PBB for mass distribution in animal feed in Michigan in 1973 did much to damage the public perception of all brominated FRs, given the glut of toxicological studies and knee-jerk ban that followed (Gross et al., 1994, Damerud, 2003, Birnbaum and Staskal, 2004, MacGillivray et al., 2011). Production of PBBs was discontinued despite the reportedly mixed and overall mild effect on human health from this contamination (Damerud, 2003). It appears the main cause for concern is their directly analogous structure to polychlorinated biphenyls (PCBs), and therefore bioaccumulation, formation of highly toxic polybrominated dibenzyl furans (PBDFs) and dioxins (PBDDs) and ultimately interference with the multifunctional aryl hydrocarbon receptor within the human body (Pocar et al., 2005). Only low occurrence coplanar congeners of PBBs (such as 3,3',4,4',5,5'-hexabromobiphenyl) pose a comparable risk to PCBs (Damerud, 2003). Notably, the polybrominated diphenyl ethers
A New Adaptation of The Method of Invariant Kinetic Parameters and its Application to a Flame Retardant System

(PBDEs) that were substituted for PBBs (MacGillivray et al., 2011) also can also form these PBDFs/PBDDs easily through intramolecular elimination of Br₂ or HBr (Weber, Roland and Kuch, 2003). Negative public attention was drawn to PBDEs after an industrial accident that expelled up to a few kilograms of tetrachlorodibenzo-p-dioxin in 1976, which incited much the same reaction as that directed towards PBBs (Bocchini and Camino, 2010). Political pressure in Europe and the United States led to the introduction of regulations to limit the amounts of PBDEs released into the environment, notwithstanding the real risks (Green, 1995, MacGillivray et al., 2011). A major FR production facility in the United States, Great Lakes Chemical Corporation, voluntarily ceased production of penta- and octa-brominated diphenyl ethers in 2004 (Hoh and Hites, 2005), sympathising with the outright ban in the European Union (Möller et al., 2011). These congeners have since decreased to 10% and 30% respectively of 1998/99 importation volumes in Australia (Toms et al., 2008).

The dominance of TBBA is likely to strengthen due to these actions (Ceric and Simon, 1991, Price et al., 2001); in fact, TBBA and its derivatives are considered the most important group of brominated FRs worldwide (Koppen et al., 2006). In 2009, there were no legislated restrictions on the production of TBBA or its derivatives (Covaci et al., 2009). TBBA’s primary use as a reactive flame retardant, with the corollary of negligible environmental contamination compared to the solely additive PBDEs, has no doubt influenced legislators (Covaci et al., 2009). The fundamentally different molecular structure of TBBA compared to PBDEs leads to orders of magnitude lower concentrations of PBDFs/PBDDs following thermal stress that mitigates its toxicological hazard and further contributes to its good favour (Weber, Roland and Kuch, 2003, Barontini et al., 2004a, Covaci et al., 2009). Even successive reprocessing of TBBA does not elevate the levels of PBDFs/PBDDs, whereas the same treatment does for scrap containing PBDEs (Weber, Roland and Kuch, 2003). It is also encouraging that no tri- through hexa-brominated PBDFs/PBDDs are detectable when TBBA is subjected to “abusive” simulated processing conditions (Thies et al., 1990).

Use of the “novel” derivatives of TBBA is likely to increase (Letcher and Chu, 2010) and Koppen et al. (2006) go as far as to say they will ultimately replace TBBA on toxicity grounds. However, the inadequacies of current methods for determination of these compounds, let alone the insufficient data regarding their potential for harm to the environment and humans, are common complaints (Ward et al., 2008, Papachlimitzou et al., 2012). Unbiased information on the derivatives of TBBA is almost non-existent (Darnerud, 2003, Letcher and Chu, 2010). Heath and safety studies pertaining to TBBA-BDPE
commissioned by Great Lakes Chemical Corporation certainly report lower risk levels compared to TBBA, but acknowledge the bioaccumulation potential of this particular derivative (wrt. carp; supported by Letcher and Chu's (2010) findings wrt. Great Lakes herring gulls) (Haneke, 2002). It seems pertinent to reserve judgement on the likely future for TBBA derivatives, particularly in light of burgeoning nanocomposite and other technologies.

2.5.2 Specific Mechanisms of Action

Chemical Scavenging

Flame inhibition due to the presence of halogenated FRs in polyolefins is only satisfactorily described in the gas phase once thermal energy has degraded and volatilised the condensed material to alkyl radicals, halides, halogens and hydrogen halides. It has been determined that gas-phase chemical inhibition is generally independent of which member in a homologous series is combusted, as the scavenging reactions involve the same small decomposition products (Babushok and Tsang, 2000). The following generic mechanism has been proposed and accepted for halide inhibition (Babushok et al., 1998, Kaspersma et al., 2002, Williams and Fleming, 2002). Here, R refers to any length of polymer or other species such as OH, O, RO₂ or H; X is a halogen such as bromine or chlorine, or in the case of suppression, fluorine, and M is an inert molecule:

\[
\begin{align*}
R^\bullet + HX &\rightarrow RH + X^\bullet \\
R^\bullet + X_2 &\rightarrow RX + X^\bullet \\
X^\bullet + X^\bullet + M &\rightarrow X_2 + M \\
\text{Net: } &2R^\bullet + HX \rightarrow RH + RX
\end{align*}
\]

Fire suppression and retardation mechanisms in the gas phase are logically identical. It is clear from the net removal of two radicals that halogens act to reduce the overall reactivity of the combusting gas.

The chemical scavenging action of halogenated FRs cannot be fully appreciated with reference only to this scheme. Obviously the timing of release of these gaseous species and any prior condensed-phase activity will influence the efficacy of the inhibiting effect. It has been observed that a typical single-step decomposition of neat polymer can be transformed by the addition of a brominated FR into two separate steps that both involve the polymer and FR (van Esch, 1997). Although this observation implies non-trivial condensed-phase interactions, these are generally ill-defined and are sometimes overlooked entirely.
Thermal stress will induce the release of molecular fragments above a specific temperature as dictated by the strength of the weakest bond. Chlorine or bromine bonds to carbon are the weakest bonds in a typical hydrocarbon polymer-halogenated FR system and will break first, in the order (Bocchini and Camino, 2010):

\[ C_{\text{benzyl}}-\text{Br} (150^\circ\text{C}) < C_{\text{aliphatic}}-\text{Br} (290^\circ\text{C}) < C_{\text{aromatic}}-\text{Br} (360^\circ\text{C}) < C_{\text{aliphatic}}-\text{Cl} (370 – 380^\circ\text{C}) \]

Alicyclic bromine (e.g. within hexabromocyclododecane (HBCD)) is considered thermally stable to a temperature between that of aliphatic and aromatic bromine (Green, 1996). Aromatic chlorinated compounds are not used for flame retardation because the C-Cl bond strength is too high (van Esch, 1997). Green (1996) implies that it is always best to choose the most thermally labile halogen compound possible; processing temperatures are what limit the selection. Once carbon-halogen bonds begin to break, free halogen radicals or hydrogen halides are availed to either participate in the gas-phase scavenging reactions or interact with the otherwise still chemically stable molten polymer (Mitan et al., 2008).

**Sb\textsubscript{2}O\textsubscript{3} Synergism**

As mentioned in Section 2.2.2, Sb\textsubscript{2}O\textsubscript{3} can be used to generate a heavy, blanketing layer of SbX\textsubscript{3} in preference to HX, and at an earlier moment in the combustion cycle. It has been suggested that the transformation of Sb\textsubscript{2}O\textsubscript{3} is initiated by the earliest emanation of HX; henceforth the deliverance of antimony-halogen compounds to the gas phase is accelerated via the production of progressively more halogenated and thermally labile antimony oxides or directly by the formation of SbX\textsubscript{3}, depending on the availability of halogen (Handa et al., 1979, Bocchini and Camino, 2010). The expected optimal Sb/X atom ratio of one third is only consistently realised for chlorinated paraffins, whereas brominated compounds often exhibit peak performance above or below this ratio (Handa et al., 1979). In some instances, for example when mixed with Deca-BDE (an aromatic source of Br), Sb\textsubscript{2}O\textsubscript{3} must act as a Lewis acid to extract the bromine from the FR compound (Camino et al., 1991).

The multitude of reactions of SbX\textsubscript{3} with gaseous radical fragments (Bocchini and Camino, 2010) can be reduced to the net result:

\[ \text{SbX}_3 + \text{Sb} + 5\text{H}^+ + 2\text{OH}^+ + \text{O}^{••} \rightarrow 2\text{SbO}_3(s) + 3\text{HX} + \text{H}_2 + \text{H}_2\text{O} \]
Hydrogen halide can then scavenge radicals as described previously, while the solid mist of antimony oxide has quenching properties of its own. Finally, Sb$_2$O$_3$ is also attributed the condensed-phase functionality of promoting char formation (van Esch, 1997). Although this mechanism is not as well understood, it seems reasonable to expect the oxidised antimony to reduce and in turn terminate polymer radicals in the condensed phase by abstracting electrons or reforming bonds to halogen atoms (Bocchini and Camino, 2010). If Sb$_2$O$_3$ acts in an analogous manner to that proposed for lanthanum trioxide in an oxygenated environment, aromatisation can result from the elimination of peroxy radicals (HO$_2^•$) and corresponding desaturation of the polymer chains (Shen et al., 2012). Clearly these mechanisms would compete with the acceleration of chain scission expected due to the release of free halogen radicals as raised in Section 2.2.2. Each unique FR system exhibits a different balance between all these effects (Camino et al., 1991, Hornung et al., 2005, Bocchini and Camino, 2010).

**Aliphatic vs. Aromatic Bromine Behaviour**

With reference to the FR systems polystyrene/HBCD/Sb$_2$O$_3$ and polypropylene/TBBA-BDPE/Sb$_2$O$_3$ (the specific system of interest in this study), it has been proposed that bromine behaves differently depending on its functionality within the FR molecule. Kaspersma et al. (2002) assign Sb$_2$O$_3$-assisted aromatic bromine the role of chemical scavenger, and hypothesise that aliphatic/alicyclic bromine enhances chain scission and flow of the polymer. They do not attempt to correlate these different activities to a logical theoretical argument. Moreover, these claims are made despite their admission that the results of their indicative set of tests do not point to the expected optimum Sb/Br atom ratio should these hypotheses apply to the aliphatic and aromatic bromine in TBBA-BDPE (Kaspersma et al., 2002). Kaspersma et al. (2002) refer to the purely antagonistic effect of Sb$_2$O$_3$ on UL 94 tests on the FR system containing HBCD as support for their hypotheses, as HBCD contains only alicyclic bromine. Given HBCD decomposes at temperatures >210ºC (Kaspersma et al., 2002) and the maximum decomposition rate of polystyrene occurs at a temperature up to 90ºC higher than that for polypropylene in air (Gupta and Lilley, 2003), it is possible that Sb$_2$O$_3$ simply forces the emission of bromine too early in the combustion cycle.

The greater strength of the aromatic carbon-bromine bond compared to the aliphatic carbon-bromine bond (Cox, 1962, Tkac and Spilda, 1981, Borojovich and Aizenshtat, 2002, Bocchini and Camino, 2010) undermines the suggestion that “aliphatic bromine stay[s] in the melt for chain scission” (Kaspersma et al., 2002). For this statement to have any validity, the aromatic bromine must leave the condensed phase preferentially, which can only occur if the added Sb$_2$O$_3$ has an overwhelming affinity for aromatic bromine. No literature support can be found for this proposition. In fact, a comprehensive study of the...
effect of Sb$_2$O$_3$ as a synergist for a mixed aliphatic/aromatic FR concludes the opposite (Handa et al., 1979). Lewin and Weil (2001) reiterate that Sb$_2$O$_3$ interacts with halide once it has left the FR molecule as HX, which implies any affinity is irrelevant; however, if Sb$_2$O$_3$ does expressly extract halide as a Lewis acid, aromatic halide would make the better Lewis base. Nevertheless, the combination of aliphatic bromine/Sb$_2$O$_3$ has been evaluated as twice as effective as aromatic bromine/Sb$_2$O$_3$ on the basis of LOI measurements (Lewin and Weil, 2001).

Availability of hydrogen is a relevant factor when considering the thermal decomposition of halogenated FRs. Aliphatic portions of FR molecules generally contain the hydrogen necessary for intramolecular elimination of HX and thus can become unsaturated (Mitan et al., 2008). Halide radicals that evolve from an aromatic environment require hydrogen donors to form HX (Borojovich and Aizenshtat, 2002, Mitan et al., 2008).

When brominated and phosphorous-based compounds are combined, the resulting FR effect is unique and not simply an addition of their respective influences (van Esch, 1997). In fact, it has been found that a synergistic FR formulation of ammonium polyphosphate and HBCD exhibits no gas-phase inhibition at all, as the HBr volatilised from the HBCD simply acts as a blowing agent for the phosphorus-enhanced char (Lewin, 2005). It is important to consider all components of a FR system before predicting which mechanisms will dominate.

**TBBA**

TBBA (a solely aromatic source of bromine) has been thermally analysed without the complication of polymer and descriptive degradation mechanisms have been suggested (Factor, 1973, Borojovich and Aizenshtat, 2002, Luda et al., 2003, Barontini et al., 2004b, Font et al., 2012). There is consensus that evaporation occurs concurrently with degradation, a fifth of the weight of starting material transforms into insoluble, mostly debrominated char and the presence of oxygen in the atmosphere is not at all influential over the initial phase of weight loss. At 10°C/min, the absence of HBr in the volatiles for a 50°C period following the onset of weight loss at 220°C implies that evaporation is the first process to initiate (Luda et al., 2003). Factor (1973) clearly explains why HBr begins to evolve from TBBA above 270°C, well below the cited temperature above which aromatic bromine is expected to homolytically cleave: Phenol-cyclohexadienone tautomerisation (Figure 2-3) significantly lowers the thermal stability of the bonds to bromine para to the hydroxyl groups.
This convincing explanation is compounded with the idea that aromatic bromine initiates ether linkages between the TBBA fragments with the elimination of much greater quantities of HBr at a somewhat higher temperature (Figure 2-4) (Luda et al., 2003). These linkages increase the effective molecular weight of the residue and ultimately trap dioxin-like structures within a stable char (Luda et al., 2003).

Overlayed on these effects is the weight loss above 300ºC due to the scission of the isopropylidene bridge (Figure 2-5) (Luda et al., 2007). As expected, bromophenols of various substitutions in addition to the bromobisphenols already implied to be part of the volatile matter have been found in all studies.

This behaviour is required to conform to the experimental observations of a dramatic 60 – 70% weight reduction followed by a continued but slower weight loss, and sympathetic changes in HBr concentration (Barontini et al., 2004b). Energy required to break bonds exceeds the energy released in forming bonds, as evidenced by the modest endothermic heat flow that corresponds to at least the first stage of weight loss (Luda et al., 2003, Barontini et al., 2004b, Font et al., 2012). Barontini et al. (2004b)
properly put their study into perspective by acknowledging that this behaviour could change if the degradation products are allowed to interact with a pyrolysing polymer, as is the case when TBBA is fulfilling its role as a FR. Other system parameters such as heating rate and pressure also affect the balance between evaporation and condensation (Luda et al., 2003).

### 2.6 Flame Retardant System

While a number of quantitative studies focus on TBBA, there has been comparatively little exploration into the behaviour of its ether derivatives, including TBBA-BDPE (Figure 2-6), which is principally used as an additive FR in the otherwise highly flammable commodity polyolefin, polypropylene (Kaspersma et al., 2002). TBBA-BDPE is also commonly compounded with low and high density polyethylene (LDPE and HDPE) and high impact polystyrene (HIPS) (Koppen et al., 2006). End uses for these plastics include fuse boxes, kitchen hoods, electronic casings, waste water pipes and even paints and textiles (Haneke, 2002, Kaspersma et al., 2002, Covaci et al., 2011).

![Figure 2-6: Tetrabromobisphenol A bis(2,3-dibromopropyl ether) (TBBA-BDPE)](image)

TBBA-BDPE is known commercially as PE-68 [Great Lakes Chemical Corporation], FR-720 [ICL Industrial Products] and Saytex® HP-800 [Albemarle Corporation] and is manufactured in the greatest quantities in China (4000 tonnes in 2006) (Covaci et al., 2011). The melting point of TBBA-BDPE, at 108°C, is lower than the melting points of polypropylene, LDPE, HDPE and HIPS (van Esch, 1995, Koppen et al., 2006) and it is known to degrade at temperatures above 240°C (Kaspersma et al., 2002), marking this additive with the ideal thermal characteristics for processing with these polymers. Bromine in TBBA-BDPE (68 wt%) is distributed evenly in aromatic and aliphatic environments.

Polypropylene itself is a heavily-utilised thermoplastic resin due to its relatively low cost of production (Morgan and Gilman, 2012), its desirable and versatile physical properties and the adaptability of the commercialised polymerisation process to a wide variety of polypropylene grades and copolymers (Andrady, 2003). Its basic chemical structure is that of linear alkyl chains with methyl substituents on each alternate carbon. These methyl groups can either all be orientated on the same side of the chain
(isotactic), or alternate between one side and the other (syndiotactic), causing each chain to twist in a helix (Figure 2-7). These are the commercially significant forms of polypropylene, as their crystalline arrangements give rise to strength and chemical resistivity far superior to amorphous (atactic) polypropylene (Gaur and Wunderlich, 1981, Ballice and Reimert, 2002). Isotactic polypropylene is generally preferred in practical applications and has a weight-average molecular weight of 300,000 – 600,000 amu and a polydispersity index of two to six (Andrady, 2003). This corresponds to a weight-average of 7,000 – 14,000 monomers in each polymer chain but a much greater proportion of shorter chains on a number basis.

Figure 2-7: Isotactic (a) and syndiotactic (b) polypropylene. One chain from the four-chain unit cell of isotactic polypropylene (c) (Gaur and Wunderlich, 1981)

Given polypropylene exhibits a considerable degree of polydispersity, like most polymers, the temperature at which it begins to melt can vary significantly. Importantly, however, polypropylene melts at a higher temperature than HDPE by about 30ºC (163ºC cf. 134ºC) (Bockhorn et al., 1999a), making it suitable for higher temperature applications (e.g. microwave-safe containers). The higher melting temperature of polypropylene constrains the lower limit of thermal stability to about 200ºC for additives such as FRs that must be compounded while the polymer is molten (Kaspersma et al., 2002, Andrady, 2003).

Polypropylene is considered the most flammable in a comprehensive list of common polymers (Morgan and Gilman, 2012). Measured at 700 kW/m² using an oxygen consumption cone calorimeter, it has the highest heat release rate of any of the polymers listed and, along with polyethylene, a gross heat of combustion greater than 45 kJ/g (Lyon, 2000). Polypropylene has a very low LOI of 17.4 (Shen et al., 2012). TBBA-BDPE must be added in excessive loadings (30 – 40%) during polypropylene processing.
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(commonly extrusion) for the plastic product to achieve UL 94 V-0, if this FR is not used in conjunction with Sb₂O₃ (Zhang and Horrocks, 2003). Accordingly, TBBA-BDPE is generally sold in blends with Sb₂O₃ in a Sb/Br atom ratio of 0.27 (Haneke, 2002, Kaspersma et al., 2002) to reduce its loading levels below 10% (Covaci et al., 2009). At these levels, TBBA-BDPE has no discernible effect on the physical properties of polypropylene (Li, X.-M. and Yang, 2006).

As an additive, TBBA-BDPE is present as a dispersed phase within the polypropylene matrix. What appear to be evenly dispersed, small, roughly spherical agglomerations of FR in plaques prepared in a twin-screw extruder have a tendency to bloom on the surface of polypropylene as short filaments over time (Li, X.-M. and Yang, 2006). Li and Yang (2006) note that the average particle size of TBBA-BDPE increases with higher loading. Uniform dispersion is purported to be due to the fact that TBBA-BDPE melts during the compounding process (Chemtura, 2007).

2.6.1 Thermal Decomposition of Polypropylene

Bonds within molten polypropylene will eventually be broken under thermal stress and degradation will initiate. Hydrogen substituents of tertiary carbon atoms are more labile and susceptible to oxygen and radical attack (Frank, 1968). It follows that while polyethylene and polypropylene both have comparatively high decomposition temperatures because of their structural simplicity (Nyden et al., 2004), polypropylene will begin to degrade at a lower temperature than HDPE (Ballice, 2002).

The molecular weight of polypropylene noticeably decreases above 230°C and the loss of volatile material is apparent above 300°C (290°C for atactic polypropylene (Ballice and Reimert, 2002)) under pyrolytic conditions (Frank, 1968, Almeras et al., 2002). In an oxygenated environment, polymer fragments form hydroperoxides (ROOH) or hydroperoxy radicals (RO₂⁺) that catalyse faster pyrolysis at the surface (Tkac and Spilda, 1981). Polypropylene is susceptible to this type of catalysis, particularly before flaming combustion commences and depresses the oxygen concentration (Camino et al., 1991). As such, the loss of volatile material begins at the lower temperature of 250°C in an oxygenated environment at a heating rate of 5°C/min (Almeras et al., 2002). Transition from pyrolysis catalysis to thermal oxidation occurs when the oxygen concentration is 5 – 15% for polypropylene (Mayo, 1976).

Pyrolysis will always drive decomposition in the zone beyond the diffusive reach of oxygen (Camino et al., 1991). This overall endothermic radical process is described by initiation, propagation (via direct monomer elimination or hydrogen rearrangement and β-scission) and termination reactions (Figure 2-8).
Polypropylene thermally decomposes to negligible quantities of monomers (Frank, 1968) and instead to a relatively complex mixture of alkanes, alkenes and dienes without any residue (Bockhorn et al., 1999a, Lyon, 2000). The low monomer yield is explained by the relatively high decomposition temperature disproportionately increasing the rates of termination reactions such that they are more competitive with propagation (Nyden et al., 2004). A high proportion of alkenes (85%) is also identified in this final mix of volatiles, which implies that the intermolecular hydrogen transfer reactions that generate alkanes must be unfavourable (Bockhorn et al., 1999a). Ranzi et al. (1997) highlight the
importance of intramolecular hydrogen transfer to the formation of alkenes, although paradoxically neglect internal isomerisation of large segments with the argument that there is too much steric hindrance imposed by the liquid phase. The inclusion of intramolecular hydrogen transfer, a rearrangement reaction that also readily explains the low monomer yield, is unnecessary for the description of the overall kinetics in any case (Simha and Wall, 1952, Ranzi et al., 1997).

The choice to model termination in polypropylene by combination and/or disproportionation does influence the overall kinetic description (Marongiu et al., 2007), and is inconsistently made in the literature. In general, combination is faster than disproportionation (Appendix A2.6) and Bockhorn et al. (1999a) and Marongiu et al. (2007) cite this reasoning before assuming termination only via combination. Marongiu et al. (2007) actually suggest that the low availability of alkenes reduces the probability of disproportionation. However, alkenes are products of termination, not reactants, and the high proportion of alkenes would seem to imply the opposite. It is unclear why Chan and Balke (1997a) assert that combination is negligible for high temperature processing, particularly when others find an increasing relative rate of combination with temperature (Appendix A2.6). Iedema et al. (2001) actually demonstrate that the best correlation with experimental data is achieved if the theory dictates that radicals from peroxide-initiated polypropylene decomposition only terminate via disproportionation.

Cyclisation and cross-linking are also viable reaction pathways for polymers (Nyden, 2000), but polypropylene does not degrade via these pathways to any significant extent; in fact, the term “degradation” is used synonymously with “chain scission” (Frank, 1968).

Global Kinetic Analysis
Simplistic global $n$-order kinetic models, particularly where $n = 1$, are often used to describe polypropylene pyrolysis to remove the need to make assumptions regarding the specific radical reactions (Ballice and Reimert, 2002). A multitude of apparent reaction orders have been proposed, including $n = 1.1 \pm 0.08$ (Bockhorn et al., 1999a) and $n = 0.35$ (Gao et al., 2003). Kinetic parameters are described as “very dependent” (Vyazovkin et al., 1991a) on experimental conditions and on the grade of polypropylene. MacCallum (1966) warns that the apparent reaction order is likely to change under non-isothermal conditions. Activation energies, which need not rely on the order of the model at least, have been found in the range 210 – 285 kJ/mol for polypropylene pyrolysis (Chan and Balke, 1997b, Ballice and Reimert, 2002) and tend to increase with conversion (Vyazovkin and Sbirrazzuoli, 2006, Gómez-Elvira et al., 2013).
Chan and Balke (1997b) offer an alternative approach and split the degradation into two successive but partially overlapped pseudo first order stages. The first stage is associated with a low activation energy (~98 kJ/mol) to represent the cleavage of weakly bound oxidised groups created through processing and drying, and the second with a high activation energy (~330 kJ/mol) more reminiscent of the aliphatic carbon-carbon bond dissociation energy (Bocchini and Camino, 2010). The concept of “weak links” is also considered plausible by Gomez-Elvira et al. (2013). In air, global activation energy is lowered markedly to 59 – 105 kJ/mol (Vyazovkin et al., 1991a, Almeras et al., 2002).

The method of Invariant Kinetic Parameters (Section 3.4.6) has been applied to polypropylene. Morice et al. (1997) assign the mechanism of nucleation and nucleus growth of order one to its degradation in air with absolute certainty (100% probability). Note that this assignment is consistent with a global $n$-order model with $n = 1$, representing dependence on a single reaction step and not the geometry of the nuclei (Appendix A2.2). Naturally, the gaseous products of oxidative degradation are interpreted as nucleating and growing within the continuous phase of molten polypropylene (Almeras et al., 2002). Mamleev et al. (2000a) suggest the same conceptualisation, and also point out that if a polymer is made to carbonise, then the increased diffusive resistance may precipitate a change in the rate limiting mechanism.

2.6.2 Expected Effect of TBBA-BDPE and Sb$_2$O$_3$

Polypropylene pyrolysis is likely to be influenced by brominated fragments originating from added TBBA-BDPE. This literature survey leads to the conclusion that the thermal decomposition pathways of TBBA-BDPE have not been investigated in any depth, therefore reference must be made to other analogous compounds to guide expectation. From the results of fire tests on this specific FR system, however, it is logical to at least predict the release of large quantities of HBr and radicals from TBBA-BDPE that will remain in the condensed phase and accelerate the chain scission of polypropylene (Kaspersma et al., 2002). The reported optimum Sb/Br atom ratio of 0.27 and little change in performance observed over the ratio range to 0.20 (Kaspersma et al., 2002) must also be consistent with any proposed models.

Since TBBA-BDPE cannot tautomerise in the same way as TBBA (Figure 2-3) or release HBr through condensation (Figure 2-4), it is expected that this ether will begin to degrade at the higher temperature dictated by homolytic cleavage of aliphatic bromine. TBBA-BDPE also contains four more bromine atoms per molecule compared to TBBA; therefore its degradation is less likely to be confounded by evaporation. The isopropylidene bridge is anticipated to be labile above 300ºC as for TBBA.
A higher degradation temperature too close to that of polypropylene is consistent with the practical necessity to add Sb₂O₃ to improve the efficacy of this FR system. It is intriguing to note, however, that while it is stated that aliphatic bromine is often selected for use in polypropylene because of its compatible degradation temperature, improved effectiveness is achieved using blends of aromatic bromine and Sb₂O₃ (Bocchini and Camino, 2010). This statement supports the association of Sb₂O₃ with aromatic bromine, but not the reasoning supplied by Kaspersma et al. (Section 2.5.2). Furthermore, the suggestion from Nyden (2000) that molecular bromine may play a role in char formation seems an ill-considered conclusion from his reactive molecular dynamics simulations: Br₂ was only demonstrated as the major decomposition product from certain FRs in the total absence of hydrogen.

It has been proposed by Handa et al. (1979) that above 280°C Sb₂O₃ converts the HBr evolved from the bromoalkyl groups in 2,3-dibromopropyl pentabromophenyl ether (Figure 2-9) to molten SbOBr, which can then form a strong acid complex with aromatic bromine. This acid has the formula HBr·SbBr₃ and therefore can explain why the Sb/Br atom ratio for best FR performance in this case (0.22) is closer to 0.25 than it is to 0.33. Furthermore, while the maximum SbBr₃ output is realised at the theoretical Sb/Br atom ratio of 0.33, the lower optimum Sb/Br atom ratio coincides with the maximum HBr output. Handa et al. (1979) conclude that if bromine is in excess, then it is possible that the aliphatic bromine will be converted directly to SbBr₃ and sublime before it can react further to release the aromatic bromine, thus reducing overall FR performance and HBr/SbBr₃ concentration. This theory has identical implications for the TBBA-BDPE/Sb₂O₃ system.

![Figure 2-9: 2,3- Dibromopropyl pentabromophenyl ether](image)

The ether linkages between the aliphatic and aromatic components of TBBA-BDPE are analogous to the same linkages in flame-retarded epoxy resins. These polymeric materials are composed of non-brominated or, more commonly, brominated diglycidyl ethers and TBBA residues (Figure 2-10) (Balabanovich et al., 2005, Bocchini and Camino, 2010). Interestingly, both brominated and non-brominated epoxy resins (Figure 2-10 and resins cured/cross-linked with amino groups) exhibit essentially the same thermogravimetric behaviour, which is very similar to that of TBBA: Rapid weight
loss of 40 – 60% between 290 – 400ºC, followed by a gradual weight loss to a residue of about 20 – 30% of the original weight by 600ºC (Balabanovich et al., 2005). Amino-cured brominated epoxy resins are noticeably less thermally stable than their non-brominated analogues; however, this difference appears to be strongly related to the basicity of the amino group (Luda et al., 2007) and is therefore not likely to be indicative of the lability of aromatic bromine in TBBA-BDPE. For brominated resins, small brominated fragments such as alkanes and propenes overwhelm the free HBr concentration initially, which suggests that HBr preferentially reacts to sever the ether linkages (Balabanovich et al., 2005).

![Figure 2-10: Polymerised diglycidyl ether of TBBA](image)

Electronic boards composed mainly of TBBA and non-brominated diglycidyl ether residues pyrolyse at 10ºC/min under 60mL/min nitrogen with an obvious exothermic feature associated with the first stage of rapid weight loss around 300ºC (Barontini et al., 2005). Enthalpy changes subsequent to this event are negligible. When these boards are oxidised, this exothermic feature is still visible but is dwarfed by the heat release from the combustion reactions (Barontini et al., 2005).

Comparison to tetrabromobisphenol S bis(2,3-dibromopropyl ether) (TBBS-BDPE; Figure 2-11) can also be made, although practically no decomposition analyses can be found on this compound either. TBBS-BDPE is a FR found in electronic products worldwide and is manufactured in Japan and most likely China (Letcher and Chu, 2010). Dettmer et al. (1999) determined TBBS-BDPE in the rear of a TV cabinet and found dibromopropene and brominated phenols as major pyrolysis products.

![Figure 2-11: Tetrabromobisphenol S bis(2,3-dibromopropyl ether) (TBBS-BDPE)](image)
TBBA-BDPE is likely to merely accelerate the chain scission of a polypropylene substrate rather than alter the decomposition pathways of the polymer, and thus its thermal decomposition becomes more an issue of timing and volume of HBr release to the gas phase (Bocchini and Camino, 2010).

2.7 Concluding Remarks

Gaps and contradictions exist in the current understanding of the chemical and physical processes occurring within combusting, flame-retarded polymers. This deficiency is broad enough to encompass even the most common FR systems. As a result, the FR industry today relies on dependable halogenated FRs and innovation by trial-and-error. In the closely related field of fire suppression, a detailed kinetic model of Halon 1301 chemistry was only developed well after this chlorofluorocarbon was established as a suppressant. Once Halon 1301 was deemed to be environmentally unsound, this model was used as a “necessary” tool to search for effective replacements (Williams and Fleming, 2002). This study embraces this concept and aims to better articulate the condensed-phase mechanisms of an established, supremely effective, but to-date overlooked FR system that is likely to increase in relevance in the short term, but may eventually be replaced by other technologies.

Non-halogenated intumescent FR systems are gaining in popularity as substitutes for the brominated FRs that are being phased out, particularly for polypropylene (Li, B. and Xu, 2006, Jiao et al., 2008). Bourbigot and Duquesne (2007) report an exponential increase in the number of published articles that deal with intumescence. These FR systems are not ideal substitutes as they can have a tendency to absorb water, are not suitable for polymers of high thermal stability and are not as efficient as brominated FRs (Li, B. and Xu, 2006, Morgan and Gilman, 2012). It may be that new insights into the mechanisms of the perceived benign TBBA-BDPE can either reduce its necessary loading and reliance on Sb₂O₃, increasing its appeal, or perhaps augment the development of new types of FR systems.

TBBA-BDPE has the unique quality of being a mixed aliphatic/aromatic brominated FR. The physical and chemical compatibility of TBBA-BDPE with polypropylene in a fire scenario is apparent, but the reasons why this is so are not as clear. No studies concerning a kinetic analysis of this FR system have been cited, which defines a gap in the literature. This study seeks to analyse conventional thermogravimetric experiments with a new kinetic analysis method, itself arising from a critical study of the available literature (Chapter 3) to inform on the nature of the degradation of TBBA-BDPE in particular. The aim is then to use complementary experiments to develop this analysis into a reasonable scheme for TBBA-BDPE degradation, and finally, verify any hypotheses pertaining to the complete FR system with cone calorimetry, which simulates a real fire scenario.
3 Literature Review: Kinetic Analysis

Kinetic analysis, when considered as a subset of thermal analysis, characterises the variation of a measured property as a function of temperature and time. Solid or liquid samples to be analysed are subjected to a prescribed temperature program in a controlled environment while recording changes in weight, enthalpy or other quantities; often simultaneously. Isothermal conditions were initially preferred for kinetic analyses due to the simplicity of mathematical treatments, but these experiments suffer from lengthy run times and an ever-present induction phase prior to attaining the set constant temperature (Pérez-Maqueda et al., 2002, Weber, Roman, 2008, Vyazovkin et al., 2011, Blanco et al., 2011). Imposing a constant heating rate, on the other hand, decreases experimental run time, reduces the relevance of the induction phase and also introduces the attractive prospect of determining the kinetic model from a single experiment (Pérez-Maqueda et al., 2002, Weber, Roman, 2008). Recently, flexible computational methods and more sophisticated equipment have encouraged interest in complex temperature programs, such as those that give rise to a constant rate of conversion and oscillatory (but otherwise constant or linear with time) programs. The former were introduced to reduce the confounding effects of heat and mass transfer, and the latter to allow the differentiation of reversible and irreversible steps (Pérez-Maqueda et al., 2002, Wunderlich, 2005).

Analysis tools for the traditional temperature programs, isothermal soak and constant heating rate, have been well developed. Notably, the potential of thermogravimetry – measurement of weight change as a function of temperature or time – to reveal kinetic information has been known for more than a century (Wunderlich, 2005). Mathematical methods to extract kinetic parameters from thermogravimetric data obtained at a constant heating rate, however, were first proposed only in the 1950s (Ravindran et al., 1977, Pérez-Maqueda and Criado, 2000, Galwey, 2004). Analysing this type of data using integral methods is inherently more difficult than analysing isothermal data due to the need to numerically solve or approximate the so-called “temperature integral”, which has no analytical solution. This difficulty has led to a lot of different solution algorithms, but also to a lot of uncertainty and incorrect application (Flynn, 1997, Galwey, 2004). Perhaps the grossest examples of this kind of misunderstanding are the application of a kinetic equation clearly derived for isothermal conditions to constant heating rate data (Borah et al., 2005) and the Kennedy–Clark method that combines equations that are incompatible for the same reasons (Ortega, 2009). The kinetic analysis literature can be a baffling minefield for a novice researcher attempting to derive meaning from their results.
The goal of kinetic analysis is to propose equations for use in chemical process plant modelling or to make predictions (Maciejewski, 2000). A rate expression resulting from a suitable kinetic analysis of a plastic, say, can be used to predict its usable lifetime at ambient temperatures, ability to retain certain physical and mechanical properties at elevated temperatures or response to abusive fire conditions (Mamleev et al., 2000a, Vyazovkin et al., 2011, Blanco et al., 2011). As these predictions must rely on a rate expression determined at practical, intermediate heating rates/temperatures, ensuring the general applicability of this expression is a necessity (Mamleev et al., 2000a). Two popular standard methods for determining lifetimes, ASTM E1641 and E698, however, are very restrictive and do not utilise the better algorithms for determining kinetic parameters (Vyazovkin et al., 2011). Kinetic modelling would be more reliable if more general and accurate algorithms were routinely adopted and their use and practical limitations understood. This chapter attempts to provide a thorough and critical presentation of these issues.

3.1 Experimental Considerations

The notion of “garbage in; garbage out” is certainly applicable in the context of kinetic analysis. Sample temperature is the experimental input that is perhaps the most critical and difficult to accurately determine. It can differ from the measured furnace temperature and/or exhibit a gradient from surface to centre due to internal thermal events and/or inadequate sample thermal conductivity (Bockhorn et al., 1999b, Vyazovkin et al., 2011). Thermal inhomogeneity will be minimised if the smallest sample size and lowest furnace temperature or heating rate feasible are selected (Vyazovkin et al., 2011). A compromise may have to be made between material homogeneity, depending on its chemical and physical structure, and thermal homogeneity (Brown et al., 2000).

Isothermal experiments that exhibit negligible decomposition during the induction phase have a clear advantage over non-isothermal experiments in terms of sample thermal homogeneity. The sample and thermocouple will be in thermal equilibrium throughout the decomposition provided any thermal inhomogeneities (caused by reaction) within the sample can be redistributed quickly. Non-isothermal experiments are obviously much more susceptible to thermal lag; for this reason, kinetic parameters determined under isothermal conditions are implicitly deemed the correct ones if there is any dispute (Bockhorn et al., 1999a). This practice has likely been reinforced by the lack of faith in now discounted methods of analysing non-isothermal data (Section 3.4.4).

For non-isothermal experiments, the Biot number can be used to judge whether a significant thermal gradient is likely to exist. It is defined as the ratio of the rate of heat transfer to the sample surface to the
rate of conduction through a characteristic distance $x$ within the sample. Note that this simple measure assumes continuous sample material; discrete solid particles may exhibit a variation in thermal lag with particle size (Van Dooren and Müller, 1982). Biot number is commonly expressed as (Bockhorn et al., 1999c) (Nomenclature in Appendix A1):

$$\text{Bi} = \frac{hx}{k_c} \tag{3-1}$$

The Biot number must be much less than unity, generally $< 0.1$, to guarantee temperature uniformity (Narayan and Antal, 1996). However, the form of Equation 3-1 does seem at odds with real scenarios where radiation is the dominant mode of heat transfer either to or from the sample surface. In these cases, the convective heat transfer coefficient should be appended or replaced with a term that reflects the $T^4$ dependency of radiation, making Biot number a function of the sample and/or bulk temperature (Van Eyk et al., 2011):

$$\text{Bi}(T) = \frac{x}{k_c} \left[ h + (T_\infty + T)(T_\infty^2 + T^2) \right] \tag{3-2}$$

or

$$\text{Bi}(T) = \frac{x}{k_c} \left[ h + \sigma \varepsilon T_\infty^3 \right] \tag{3-3}$$

Bockhorn et al. (1999c) state that radiation is the “main contribution” to heat transfer within a thermogravimetric analyser furnace, but utilise the conventional form of Biot number (Equation 3-1) with a constant heat transfer rate of 20.6 $\text{W/m}^2\text{K}$ based on their furnace geometry.

It is also possible for conduction through a sample crucible to limit the rate of heat transfer to the sample surface, if so, the Biot number should be modified to (Van Eyk, 2011):

$$\text{Bi} = \frac{k_{c,\text{crucible}}x}{k_cx_{\text{crucible}}} \tag{3-4}$$

It may be infeasible to reduce the Biot number below 0.1 through experimental means, say for polymers like polypropylene with low thermal conductivities (Yen et al., 1991). In these instances, the thermal gradient should be estimated conservatively with an energy balance. Then, either “worst case” kinetic parameters may be computed applying lumped heat capacity at the core temperature, or conversion...
may be integrated over the thermal gradient for a rigorous analysis (Bockhorn et al., 1999b, Bockhorn et al., 1999c, Vyazovkin et al., 2011). Bockhorn et al. (1999b) conclude from their rigorous analysis that the effect of simulated thermal lag for polystyrene is not large both in absolute terms and relative to the theoretical errors generated by oversimplifying the degradation process. However, this judgement is made based on sample sizes ranging from 1 – 300 mg and heating rates up to 40°C/min, and possibly understates the importance of the calculated deviations in kinetic parameters.

Care must be taken to design thermogravimetric experiments that can deliver reliable results. One study computes kinetic parameters for polystyrene and polypropylene with no regard for the thermal gradients present in the excessive sample mass of 300 g (Kim and Kim, 2004). These parameters vary dramatically over the range of conversion and the fundamental validity of the reaction order (i.e. model shape) for polypropylene in particular is highly doubtful (0.01 cf. ~1 reported in Section 2.6.1). It should be highlighted that non-isothermal experiments that are carefully controlled and analysed can offer superior results to isothermal experiments that are mired by induction phases (Maciejewski, 2000). One reason for this superiority is the greater range of temperatures able to be assessed with non-isothermal analysis (Roduit, 2000).

The onset of degradation is naturally shifted to higher temperatures as the heating rate is increased due to the reduction in time for the sample to reach a given temperature. This shift, argued by Flynn and Wall to be inversely proportional to activation energy (Chan and Balke, 1997b), will be present notwithstanding the worsening thermal lag. It is imperative for changes in heating rate to generate effects that are consistent with the rate equation only, as a systematic error depending on heating rate of just a few degrees can cause a 10 – 20% error in the kinetic parameters and “enormous” (Vyazovkin et al., 2011) errors in predictions outside the temperature range of the analysis. Temperature calibration across all relevant heating rates is a necessity for this reason (Vyazovkin et al., 2011).

If problems are discovered with reproducibility, it can be said with a high degree of certainty that the source is the sample, not the instrument (Brown et al., 2000). It is advisable for the sample size to be reduced until there is no perceptible difference between the kinetic curves as a first step towards eliminating these problems (Vyazovkin et al., 2011). Experimental parameters not explicitly involved in the subsequent calculations, e.g. instrument pressure or gas flow rate, can also cause unexpected but systematic deviations (coined, “parametric sensitivity of thermal analysis”) and must be held constant and reported or, ideally, varied to assess their effects (Roduit, 2000, Khawam and Flanagan, 2005c).
Non-isothermal thermogravimetric signals also require simple baseline corrections to subtract the buoyancy effect (apparent weight gain with increasing temperature). It is much easier to confidently define conversion with an integral signal, such as a thermogravimetric signal, rather than a differential signal that has an ambiguous baseline. Differential Scanning Calorimetry (DSC) provides such a differential signal (heat flow) that can be used instead to provide critical complementary information to help uniquely elucidate any overlapping processes (Vyazovkin et al., 2011). Model fitting approaches to simple and complex kinetic analysis (Section 3.4.4 and Section 3.4.7) are able to capitalise particularly well on this additional information if a DSC signal is reconstructed from enthalpies assigned to individual processes (Burnham and Dinh, 2007).

3.2 Arrhenius Parameters for Heterogeneous Systems

All analysis methods found in the literature are underpinned by the Arrhenius description of reaction kinetics. In 1889, Arrhenius published his theory based on the collision frequency of activated species in homogeneous systems (Flynn, 1997). Activation energy ($E$ in Equation 3-5) refers to the energy barrier that must be surmounted for the reaction to occur (transition state model). Pre-exponential factor, or frequency factor ($A$ in Equation 3-5), refers to how frequently the configuration of reactant(s) is such that products have the potential to form. There is dissent relating to the extension of this theory to heterogeneous systems, where reactant concentrations raised to specific powers are simply replaced by some function of conversion (Galwey and Brown, 1997, Sanders and Gallagher, 2005):

Homogeneous: 

$$\frac{d[Z]}{dt} = zA \exp\left(-\frac{E}{RT}\right) [X]^x [Y]^y, \text{ for } xX + yY \rightarrow zZ \quad 3-5$$

Heterogeneous: 

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) = k(T) f(\alpha), \text{ where } \alpha = \frac{m_0 - m}{m_0 - m_\infty} \quad 3-6$$

$A$, $E$ and $f(\alpha)$ are known as the “kinetic triplet” (Budrugeac, 2005). Pre-exponential factor and activation energy hold the same mathematical significance in both equations; however, pre-exponential factor in particular must assume a different conceptual meaning in a heterogeneous system because the reaction participants are physically constrained (Galwey and Brown, 1997). Pre-exponential factor will often be a function of the physical dimensions specific to the assumed mechanism (Khawam and Flanagan, 2006), although it has also been ascribed specifically to the vibrational frequency of the activated complex (Vyazovkin et al., 2011). It would seem that prior knowledge of the system must be integrated with the implications of any proposed form of $f(\alpha)$ before deciding upon the meaning of a calculated pre-exponential factor. The conceptual meaning of heterogeneous activation energy is
disputed (Vyazovkin, 2003, Brown, 2005) but is also likely to be correlated to physical properties. Ultimately, the connection of the kinetic parameters to the physical system debases their fundamental implications, unless they are interpreted very carefully (Vyazovkin and Wight, 1997).

It has been clearly shown that to express homogeneous kinetics using any other more complex theory would be futile (Brown, 2005). The only significant alterations to Arrhenius kinetics for heterogeneous systems that have been suggested in the surveyed literature are specifying activation energy as a function of conversion, temperature or time. Malecki and Doumerc (1986), for example, propose a rate of activation energy change that is inversely proportional to time but only loosely link this to a physical meaning for diffusion processes. Adding complexity should always be accompanied by a sound theoretical basis, or else a better correspondence to experimental data is merely achieved because there are more parameters to optimise (Brown et al., 2000, Roduit, 2000). For this particular example, the final model presented is apparently affected by the propagation of errors, as a factor of \( \frac{1}{n} \) (where \( n \) = diffusion order) exists in the expression for \( K \) (rate constant composite) that should not be present.

Some argue that it is against the “phenomenological sense” (Mamleev et al., 2000a) of the Arrhenius activation energy to assign it a dependence on any variable. Furthermore, Mamleev et al. (2000a) implies that if any dependence is assigned, the activation energy cannot be fundamental and is “unacceptable” for predictions. It seems likely that the reason for some observed dependence on other parameters stems from the temperature-dependent errors in approximations employed to solve the temperature integral (Weber, Roman, 2008). Furthermore, pressure variation is usually ignored in kinetic equations, even though it can be very influential on the overall conversion rate of reversible or autocatalytic processes (Vyazovkin et al., 2011). It is also conceivable that the form of the rate equation will change systematically as conversion increases if progressive physical and/or chemical changes (e.g. in atmosphere composition, crystal size, adsorbed/desorbed species, etc.) favour different mechanisms (Vyazovkin and Wight, 1997). Mathematical and computational effects are often overlooked in favour of justifying activation energy variations with physical arguments (Vyazovkin, 2001, Khawam and Flanagan, 2005b), which can be quite superficial (Bourbigot et al., 2002).

Many researchers agree (Maciejewski, 2000, Budrugeac, 2005, Vyazovkin et al., 2011) that it is necessary to determine whether calculated activation energy does remain constant over the whole
conversion range before attempting to describe a process by a single Arrhenius expression. If it does not, the specific dependency may allow certain conclusions to be drawn regarding the nature of the kinetic complexity (Section 3.4.7). The methods used to determine $E(\alpha)$ are deemed isoconversional methods (Section 3.4.2), and should not require any assumptions to be made regarding $f(\alpha)$. Pre-exponential factor, on the other hand, demands knowledge of the function of conversion and is therefore seldom reported or used to determine the constancy of the rate equation (Khawam and Flanagan, 2005b). A perception that activation energy has particular importance for degradation kinetics has been promulgated because of this (Blanco et al., 2011). This is potentially a mistake as the conversion rate is obviously influenced by all three elements of the kinetic triplet (Maciejewski, 2000, Brown, 2005).

It is important to be clear that a rate expression quoted over any range of conversion is not necessarily describing a fundamental process, nor implying that only a single process is active (Vyazovkin et al., 2011). An indirect technique such as thermogravimetry can at best depict global changes brought about by the rate limiting step(s) of a series of sequential processes. Therefore, it is appropriately conservative to interpret any calculated kinetic parameters as composites (Vyazovkin and Wight, 2000). Should overlapping independent processes exist, conventional model fitting or peak deconvolution can be used to reveal the individual steps (Mamleev et al., 2000a, Vyazovkin, 2000, Perejón et al., 2011), but sequential processes of similar rates or competing processes are harder to identify and elucidate (Vyazovkin et al., 2011). In the case of competing reactions, a single rate expression must be replaced with a number of interdependent differential equations that require assumptions to be made regarding the chemical interactions of intermediates (Section 3.4.7) (Bockhorn et al., 1999a, Kandare et al., 2007, Font et al., 2012). Again, the assumption of almost any reasonable set of equations will lead to viable solutions, which means that the multitude of kinetic parameters and overarching model would be difficult to validate.

3.2.1 Compensation Effect

The phenomenological basis for the Arrhenius kinetic parameters would seem to imply that they should be independent. In many heterogeneous processes, however, activation energy and pre-exponential factor are observed to be dependent for the same or similar processes across different studies (Galwey and Brown, 1997). Essentially, if conversion rate is either identical or prescribed as identical across a variation in some quantity that changes the dependence on temperature, the change in activation energy will be almost entirely compensated by the change in pre-exponential factor (Galwey, 1997), since $f(\alpha)$ does not vary significantly with $\alpha$ (Vyazovkin and Wight, 1999). Using the Arrhenius equation (Equation 3-6), this compensation effect is easily shown to take the form $\ln A = bE + c$, where $b$ and $c$
are the compensation parameters. It has been suggested that these compensation parameters should be published instead of the Arrhenius parameters as they are more generally applicable (Somasekharan and Kalpagam, 1987). Flynn (1997) conjectures, however, that because the uncomplicated practice of reporting single pairs of activation energy and pre-exponential factor is ensconced in the literature, any deviation from this convention will simply result in these research articles fading into obscurity.

The compensation effect has been interpreted in a number of different ways; either with reference to mathematical or experimental effects creating “artificial” compensation or to a “real” effect that arises from an effectively linear relationship between activated enthalpy and entropy (Liu, L. and Guo, 2001, Brown and Galwey, 2002). Artificial effects are readily observed if a range of incorrect functions of conversion – that typically can describe any process quite well – are fitted to a single set of data, or data collected at a range of heating rates, and the calculated Arrhenius kinetic parameters are plotted against one another (Pérez-Maqueda et al., 2006, Vyazovkin et al., 2011). Precisely these effects are utilised in the method of Invariant Kinetic Parameters discussed in Section 3.4.6. Other artificial compensations are concerning in that they are meaningless consequences of forcing data with overwhelming uncertainties to conform to the Arrhenius expression. Plotting error bars can allow for easy assessment of whether a compensation effect is a true one or not (Liu, L. and Guo, 2001). It is also possible for meaningless compensations to arise due to poor approximations to the temperature integral (Section 3.4.1) or inaccurate non-linear regression algorithms (Weber, Roman, 2008).

From an experimental perspective, simulations have clearly shown that an unquantified thermal lag will cause the kinetic parameters to deviate from their true, unique values along a compensation effect (Narayan and Antal, 1996). Deviations in the average surface/volume ratio of a solid sample decomposing to a gas may also elicit the same effect (Vyazovkin and Wight, 1997). Reversible processes controlled by Le Chatelier’s Principle, e.g. calcium carbonate decomposition, are likely to exhibit artificial compensation effects should system pressure vary across independent experimental runs; a fact often neglected in analyses (Galwey and Brown, 1997, Vyazovkin et al., 2011). It is therefore somewhat ironic that calcium carbonate decomposition is frequently used to verify experimental and computational methods. Often invalidated kinetic parameters that possibly conform to an unexplored compensation effect are written off to such factors as sample impurities, defects, atmosphere composition and heat and mass transfer (Vyazovkin, 2001, Brown and Galwey, 2002).

Real compensation effects are intrinsic and are characterised in terms of enthalpy and entropy, and in one instance, by the suggestion of a “resonant vibrational energy exchange” (Vyazovkin and Wight,
between sample and environment. Should an activated complex exhibit a compensatory decrease in entropy (disorder) upon the creation of more or stronger bonds for given experimental changes (not including temperature), the free energy of a system will remain essentially constant. It is also possible for the free energy change to be insignificant in comparison to the changes in enthalpy and entropy, which would also lead to a definite linear relationship between enthalpy and entropy (Sharp, 2001). Arrhenius parameters can be readily expressed in terms of activated enthalpy and entropy using transition state theory (Liu, L. and Guo, 2001) and it logically follows that in either of the aforementioned cases, \( \ln A \) and \( E \) will show a linear correlation. Transition state theory has dubious applicability to heterogeneous kinetic analysis, however; if not for the fundamental inappropriateness of the Arrhenius equation, which is a contentious subject, but because different processes are often convolved (Vyazovkin and Wight, 1997, Maciejewski, 2000). This fact, compounded with the higher probability of artificial causes for compensation, diminishes the likelihood that an observed compensation effect for a heterogeneous system will be real (Galwey and Brown, 1997).

If the artificial compensation effects relating to heating rate, mechanism and sample size are not quantified in non-isothermal kinetic analyses, the reported kinetic parameters are not likely to have much general significance or correspond to those of comparable isothermal experiments (Lesnikovich and Levchik, 1983, Vyazovkin et al., 2011). In some cases, the existence but lack of quantification of specific compensation effects is used to justify only cursory comparison with previously reported values (Galwey, 2004). In essence, it is critical to find the coordinates of the centre of all relevant compensation effects before asserting the universal applicability of proposed kinetic parameters and mechanisms.

### 3.3 Mechanisms for Heterogeneous Systems

Supposing the simplistic model for heterogeneous kinetics is valid (Equation 3-6), a function of conversion, \( f(\alpha) \), must be specified and interpreted to complete the description of any process. It is usual to see the integral form of Equation 3-6 presented, as it is commonly required for kinetic analyses:

\[
\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^t A \exp\left(-\frac{E}{RT}\right) dt
\]

\[ \therefore \text{Define:} \quad g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = kt \]

for isothermal experiments \hspace{1cm} 3-7

and

\[ g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^t A \exp\left(-\frac{E}{RT}\right) dt \]

for non-isothermal experiments \hspace{1cm} 3-8
The accepted set of functional forms \( f(\alpha) \) and \( g(\alpha) \) regularly appears in the literature, truncated to various extents. These forms are categorised as acceleratory, deceleratory, sigmoidal and linear depending on the shape of the isothermal conversion versus time curves they give rise to (Galwey and Brown, 1998, Khawam and Flanagan, 2006). When the temperature dependence of the rate constant is factored in for linear heating, they become less distinguishable, as the linear and deceleratory models become acceleratory and sigmoidal respectively (Vyazovkin et al., 2011).

It has recently been acknowledged that it is difficult to find a consolidated discussion of the mathematical and physical bases for these mechanisms (Khawam and Flanagan, 2006), some of which have been in use for more than 70 years (Maciejewski, 2000), and it is suspected that many researchers do not appreciate these functions beyond what meanings can be derived from their names. Innumerable examples where the discussion halts at the selection of the mechanism function can be cited (Richard-Campisi et al., 1996, Liu, J. et al., 1999, Li, D. et al., 2012). Moreover, often assignments of names/equations are incorrect (Dickinson and Heal, 1999). Vlaev et al. (2008) even include functions of conversion that have no physical origin, which is a questionable practice.

Reassessing the validity of these mechanism functions is an “important consideration for the future” (Galwey, 2004). Maciejewski (2000) states that some theoretical postulations, for example the formation of only one growth nucleus per reactant particle (Avrami-Erofe’ev mechanism A1), cannot be confirmed with electron microscopy, and questions the physical significance of the Avrami-Erofe’ev order \( n \). Jacobs (1997), conversely, presents a particularly thoughtful analysis of this theory. He demonstrates that the concept of “one-dimensional nuclei” (Maciejewski, 2000) simply means that growth in the other two dimensions is not rate limiting, which is not too dissimilar to the theoretical treatment of contracting volumes of different orders, and diffusion. Growth in the “inactive” dimensions is either very fast along grain boundaries (Jacobs, 1997) or hindered excessively such that product forms only as lengthening filaments in the slowest case (Galwey and Brown, 1998). In further contrast to Maciejewski’s opinion, the Avrami-Erofe’ev and Prout-Tompkins functions of conversion are also said to have the correct form to describe the thermal decomposition of polymeric materials (Burnham et al., 2004).

In order to encourage their intelligent application and interpretation, each accepted mechanism is illustrated in Table 5-1 with an accompanying summary of the assumptions that have to be made to arrive at \( f(\alpha) \) and \( g(\alpha) \). Comprehensive and critical mechanism derivations are included in Appendix A2 to provide the necessary background for Table 5-1.
Allnatt and Jacobs (1968) make the reasonable observation that while the time independence of the Avrami-Erofe’ev mechanisms is a sound assumption from a statistical point of view, the requirement for spatial homogeneity has dubious validity. This is due to the likely presence of point defects, dislocations and grain boundaries in the crystal structure, and scratches etc. on the macro scale (Allnatt and Jacobs, 1968). A completely uniform substrate is also fundamental to all other mechanisms, which has been cited as a significant flaw in applying these functions to real data that would rarely correspond to such “perfect” material (Appendix A2). Reliance on assumptions of steady-state for reaction intermediates and other physical parameters also makes these mechanisms quite rigid (Michèle et al., 2011).

Adaptations that consider a particle size distribution (Koga, N. and Criado, J.M., 1998), the intimate interaction between nucleation and nucleus growth and diffusion (Pérez-Maqueda et al., 2003) and distributed activation energy (Burnham et al., 2004) have niche applications but do not appear to sway the majority of novice researchers from using none but the simplest approaches.

### 3.3.1 Sestak-Berggren Generalisation

A more flexible equation to account for deviations from the ideal forms listed in Table 5-1 has been popularised (Pérez-Maqueda et al., 2006, Jankovic et al., 2007, Perejón et al., 2011). In 1971, Sestak and Berggren proposed (Brown et al., 2000):

\[
f(\alpha) = \alpha^m (1 - \alpha)^n [-\ln(1 - \alpha)]^p
\]

Equation 3-9

A brief inspection of the conversion functions in Table 5-1 shows that if \( m \), \( n \) and \( p \) take on different values, almost every function can be precisely recreated. Moreover, intermediate, non-integer exponents can represent a particle size distribution and variations in particle morphology (Pérez-Maqueda et al., 2006). In practice, \( p \) is commonly set to zero (Brown et al., 2000); as mentioned in Section 3.2, it is important to keep the number of parameters to fit to a minimum. Sestak himself recommended the use of the truncated form in 1984 (Vyazovkin et al., 1991b):

\[
f(\alpha) = \alpha^m (1 - \alpha)^n
\]

Equation 3-10 is also known as the extended Prout-Tompkins equation. It shifts from the guise of a linear chain branching mechanism (\( m = 1 \) and \( n = 0 \)), through the standard Prout-Tompkins autocatalysis mechanism (\( m = 1 \) and \( n = 1 \)) to a first order reaction mechanism (\( m = 0 \) and \( n = 1 \)) (Burnham and Dinh, 2007). Jankovic et al. (2007) state that it has been demonstrated that \( 0 \leq m \leq 1 \) to...
confer physical meaning. It is notable that this equation has apparently been independently derived multiple times, but only empirically, not by applying rigorous theory (Burnham, 2000a).

A series expansion of Equation 3-10 followed by the regrouping of terms shows that it is basically equivalent to the Avrami-Erofe'ev mechanism equations (Burnham and Braun, 1999), affirming the merit of setting $p$ to zero. Each Avrami-Erofe'ev order $n_A$ corresponds to a unique pair of $m$ and $n$. While the rate equation employing Equation 3-10 can therefore match the Avrami-Erofe'ev models very well (Brown, 1997), the rate constant associated with Equation 3-10 must be scaled up by a factor similar to but slightly greater than $n_A$ (order of the An mechanism) (Vyazovkin et al., 2011). As examples, the truncated Sestak-Berggren representations for A2 and A3 are reported as (Pérez-Maqueda et al., 2006, Vyazovkin et al., 2011):

\begin{align*}
2(1 - \alpha)[-\ln(1 - \alpha)]^{\frac{1}{2}} &\approx 2.079\alpha^{0.515}(1 - \alpha)^{0.806} \quad 3-11 \\
3(1 - \alpha)[-\ln(1 - \alpha)]^{\frac{1}{3}} &\approx 3.192\alpha^{0.693}(1 - \alpha)^{0.748} \quad 3-12
\end{align*}

If conversion is equated at the maxima of the Avrami-Erofe'ev and Sestak-Berggren mechanism equations, it follows that (Jankovic et al., 2007):

\[ n_{ke} = \frac{1}{1 + \ln(n - \ln(n + m))} \quad 3-13 \]

Equation 3-13 can also be expressed as:

\[ n_{ke} = \frac{1}{1 + \ln(1 - \alpha_i)}, \quad \alpha_i = \text{conversion at these maxima (isothermal inflection point)} \quad 3-14 \]

Equation 3-14 illustrates the interdependency of $n$ and $m$. The unique pair must satisfy Equation 3-13 and also cause the Avrami-Erofe'ev equation to overlay with the rescaled Sestak-Berggren equation. Accordingly, the Prout-Tompkins equation is demonstrably distinct from the Avrami-Erofe'ev series because it is not possible to scale the case where $n = m = 1$ to overlay with the Avrami-Erofe'ev mechanism of order 3.26.
Not every function of conversion in existence is guaranteed to conform to the truncated Sestak-Berggren equation, although a recent analysis using the “new” random chain scission mechanism scheme does represent yet another successful application (Sánchez-Jiménez et al., 2010).

This convenient generalisation forms the basis of the Combined Kinetic Analysis technique that is elaborated in Section 3.4.5.

### 3.3.2 Relevance to a Liquid Phase

It is a common oversight to neglect the effects of melting on the nature and relevance of decomposition kinetics. Galwey (2004) surmises that this is because the application of the mechanisms exemplified in Table 5-1 was initially limited to samples known to be solid. Verification of a sample’s physical state therefore did not become habitual. However, if a kinetic triplet is to be used to predict the aging characteristics of a solid, for example, the use of data where degradation has been thermally accelerated past the point of melting is highly dubious (Vyazovkin et al., 2011, Blanco et al., 2011). Most liquid-phase kinetics are expected to be significantly faster than the corresponding solid-phase kinetics due to the increased mobility of the reactant(s) (Galwey, 2004). Blanco et al. (2011) attempt to quantify this difference by comparing the results of high temperature isothermal experiments on polymer melts with three-year long, sub-melting temperature isothermal experiments on the same polymers. Unfortunately, their study suffers from a lack of long-term data and only reports activation energies. Based on their limited evidence, it can be said that, counter-intuitively, the activation energy for degradation is more likely to increase once a polymer melts (Blanco et al., 2011).

The question must be asked whether the mechanisms specifically derived for the solid state can be applied to liquids. Vyazovkin et al. (2011) do not appear to consider this question in much depth before asserting that these mechanisms “may have a very limited (if any) applicability” to the liquid phase. It has been pointed out that mechanisms formulated from specific geometric requirements realistically do not need to be restricted to solid-state kinetics; intracellular liquid-phase chemical reactions can be represented by these equally well (Carr and Galwey, 1986). The standard diffusion equations have also been thought to legitimately apply to a solid dispersed phase in a molten continuous phase (Christie et al., 1978, Dickinson and Heal, 1999). With detailed mechanism derivations such as those supplied in Appendix A2, educated decisions regarding the applicability of the mechanisms in Table 5-1 to specific physical scenarios can be made.
Galwey’s critical review (2004) shows that after almost 20 years in the field he perhaps adopted a more conservative attitude towards expanding the use of equations derived for the solid state. He emphasises the need to consider the physical implications of the formation of any kind of liquid phase, being mindful that partial melting may cause the inverse kinetic problem to become intractable (Galwey, 2004). Galwey also mentions that the kinetic data from entirely homogenous reactions or reactions involving liquid intermediate(s) can bear superficial resemblance to an asymmetric sigmoidal $\alpha$-$t$ curve (i.e. an extended Prout-Tompkins mechanism) (Galwey, 2004). This observation reinforces the previously stated general applicability of the Sestak-Berggren equation (Section 3.3.1).

The most common fate of a solid exposed to heating is melting, which can be detected by the formation of bubbles or a froth that ultimately resolidifies (Galwey, 2004). A polymer, such as polypropylene, entirely melts before significant weight loss is observed (Gersten et al., 2000); it decomposes from an initial state that is physically uniform (Galwey, 2004).

### 3.4 Non-Isothermal Data Analysis

Non-isothermal data are a lot more challenging to analyse to meaningful kinetic solutions compared to isothermal data. Both the rate constant and function of conversion vary concurrently when temperature is not constant, which makes not only the unique determination of each a task that demands the utmost care, but causes the models themselves to become harder to differentiate (Table 5-1) (Vyazovkin et al., 2011). Some of the more reliable methods are at least not reliant on knowing the form of the function of conversion to evaluate activation energy, but an entire kinetic triplet must be proposed before a model can be properly evaluated for its goodness of fit to experimental data (Section 3.4.4). Vyazovkin et al. (2011) state that, “Only those kinetic methods that are capable of treating all three types of the conversion dependencies [i.e. acceleratory, deceleratory and sigmoidal; linear dependency is not mentioned] can be recommended as reliable methods”, which is worth keeping in mind.

It has been suggested that the accuracy and reliability of non-isothermal kinetic analysis methods are in need of reappraisal (Galwey, 2004). Since the impact of even the slightest theoretical or computational error can be enormous, it is “distressing” (Flynn, 1997) to see unexplained contradictions that result from the use of a number of poor analysis techniques published. This section dissects the more common methods and in so doing reveals where some of these contradictions may arise.
Given that the analysis methods that maintain a general temperature-time relationship are equally applicable to isothermal data, only those that can treat non-isothermal data are considered here. Non-isothermal data most frequently refers to data collected at a constant heating rate.

### 3.4.1 Approximating the Temperature Integral

The poor performance of certain analysis methods specifically derived for application to constant heating rate data has been blamed on inaccurate approximations to the temperature integral. Most approximations currently in use were proposed at times when computing power was nowhere near what it is today (Flynn, 1997, Vyazovkin et al., 2011). Beginning from Equation 3-8 and substituting in a constant heating rate \( \beta \) (Ravindran et al., 1977):

\[
g(\alpha) = \int_{t_0}^{t} \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT = \int_{0}^{T} \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT - \int_{0}^{T_0} \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT
\]

\[
∴ g(\alpha) \approx \int_{0}^{T} \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT
\]  

Equation 3-15 neglects the low temperature end of the integral. The significance of the error this induces has been demonstrated with limited evidence for a specific approximation (Cai and Bi, 2008). Orfao (2007) states that the consequence is obviously greater the closer the onset temperature is to the temperature at time \( t = 0 \), and actually shows how those methods that utilise a temperature integral approximation can be modified to reinstate the low temperature end of the integral (Section 3.4.2).

Now, if \( x = \frac{E}{RT} \), \( dT = -\frac{dx}{x^2} \frac{E}{R} \) and thus:

\[
g(\alpha) \approx \frac{AE}{\beta R} \int_{x}^{\infty} \frac{\exp(-x)}{x^2} dx = \frac{AE}{\beta R} p(x), \text{ where } p(x) = \int_{x}^{\infty} \frac{\exp(-x)}{x^2} dx
\]  

The integral \( p(x) \) has no closed-form analytical solution (Burnham and Dinh, 2007). Coats and Redfern applied a series approximation of \( p(x) \) in 1964, truncated to the first two terms (Coats and Redfern, 1964, Quanyin and Su, 1995):

\[
p(x) \approx \exp(-x) \sum_{n=0}^{\infty} \frac{(-1)^n (n+1)!}{x^{n+1}}
\]  

---

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\[ p(x) \approx \frac{\exp(-x)}{x^2} \left(1 - \frac{2}{x}\right) \]  

However, in order to facilitate the easy graphical determination of the Arrhenius parameters (Section 3.4.4), they ultimately drop the second term:

\[ p(x) \approx \frac{\exp(-x)}{x^2} \]

It is suspected that some confusion may exist in the literature regarding which of Equation 3-18 or Equation 3-19 should be labelled the Coats and Redfern approximation, particularly since Murray and White are also credited with Equation 3-19 (Weber, Roman, 2008, Vyazovkin et al., 2011), and, apparently, Doyle (Pérez-Maqueda and Criado, 2000, Orfao, 2007). Only Equation 3-18 appears to be uniquely labelled for Coats and Redfern. It is likely that Equation 3-19’s accuracy has been frequently overestimated because of this ambiguity. Furthermore, the common practice of retaining the second series term in Equation 3-18 but setting the temperature within that term to the mean temperature of the process adds another point of confusion (Vyazovkin and Wight, 1999, Khawam and Flanagan, 2005c, Ebrahimi-Kahrizsangi and Abbasi, 2008, Han et al., 2012). This simplification merely weights \( p(x) \) and still allows the easy graphical determination of the Arrhenius parameters as desired.

Pérez-Maqueda and Criado (2000) are sufficiently clear with their designations and report that Equation 3-19 has an associated error of less than 5% for \( x > 40 \), but suffers from enormous errors as \( x \) approaches 1. In fact, the accuracies of all \( p(x) \) approximations are dependent on \( x \) and generally follow the same trend (Figure 3-1), since they most frequently stem from truncated infinite series that require \( x >> 1 \) to be valid (Starink, 2003, Orfao, 2007). The exception to this rule is the Doyle approximation proposed in 1962 (Ravindran et al., 1977, Burnham and Dinh, 2007) that derives from a linear regression:

\[ \log p(x) \approx -2.315 - 0.4567x \quad \text{or} \quad p(x) \approx \exp(-5.33 - 1.052x) \]  

In this case, \( 28 < x < 50 \) for the error to be within 5%, when evaluated against numerical integration using Simpson’s 1/3 rule (Quanyin and Su, 1995). At least one other pair of researchers, MacCallum and Tanner, chose to use a linear regression to approximate \( p(x) \) (Ravindran et al., 1977).
All approximations where the error consistently reduces with increasing $x$ have the structure:

$$p(x) \approx \frac{\exp(-x)}{x^2} Q(x)$$  \hspace{1cm} 3-21

$Q(x)$ can take on the multitude of forms tabulated by Orfao (2007) in his comprehensive review. In the interests of brevity, only a further two clearly superior approximations are presented here (Equation 3-23 and Equation 3-24).

In 1977, Senum and Yang proposed the use of up to fourth degree rational approximations that originate from the infinite series previously published by Patterson (Pérez-Maqueda and Criado, 2000):

$$p(x) = \frac{\exp(-x)}{x} \left( \frac{1}{x+2} - \frac{2}{x+4} - \frac{6}{x+6} - \ldots - \frac{n(n+1)}{(x+2(n+1))} \right)$$  \hspace{1cm} 3-22

The fourth degree approximation (Equation 3-23) is highly accurate and incurs less than 0.0001% error once $x > 10$, and only 0.6% error at $x = 1$ (Pérez-Maqueda and Criado, 2000, Weber, Roman, 2008).
Solutions are known to quickly converge if Equation 3-23 is used in an implicit equation and thus it is well suited to computational algorithms (Flynn, 1997).

\[ p(x) \approx \frac{\exp(-x)}{x^2} \left( \frac{x^4 + 18x^3 + 86x^2 + 96x}{x^3 + 20x^3 + 120x^3 + 240x^2 + 120} \right) \]  

Even while deriving a new inferior approximation himself, Starink (2003) comments that there is little need or opportunity to further develop this area. Orfao (2007) essentially agrees with this statement after strongly recommending the use of his own fourth degree rational approximation, which he reports has an absolute maximum error of 0.0005%, also by comparison to Simpson’s rule:

\[ p(x) \approx \frac{\exp(-x)}{x^2} \left( \frac{0.9999936x^4 + 7.5739391x^3 + 12.4648922x^2 + 3.6907232x}{x^3 + 9.5733223x^3 + 25.6329561x^3 + 21.0996531x^2 + 3.5984969} \right) \]

This approximation differs subtly from Equation 3-23 because a well-documented approximation to the exponential integral is applied, rather than Equation 3-22, following the integration by parts of \( p(x) \) (Orfao, 2007).

Cai and Bi (2008) have examined literature concerned with kinetic analyses of coal and biomass decomposition and conclude that the Coats and Redfern approximation (implied as Equation 3-18) is still the most commonly applied approximation, and others agree (Vyazovkin and Wight, 1999, Orfao, 2007, Han et al., 2012). In light of the availability of approximations that are highly accurate for any value of \( x \), it is not acceptable to continue to use substandard approximations such as Coats and Redfern’s (Orfao, 2007, Ebrahimi-Kahrizsangi and Abbasi, 2008). This practice has been justified previously on the basis that most solid-state processes exhibit \( 15 < x < 60 \) (Starink, 2003), and \( x < 10 \) is practically unheard of (Pérez-Maqueda and Criado, 2000). However, a recent simulation of biomass pyrolysis kinetics uses a low enough activation energy in relation to the onset temperature to give \( x < 3 \) (Weber, Roman, 2008).

Flynn (1997) says there is “no valid reason not to use precise values for the temperature integral when calculating kinetic parameters”, which is strongly endorsed by Galwey (2004) who also quotes this statement. While Vyazovkin et al. (2011) acknowledge that the Doyle linear approximation is “very crude”, they actually recommend the use of the most basic Murray and White approximation (via the
Kissinger–Akahira–Sunose isoconversional method) and promote their own numerical isoconversional method in lieu of even mentioning rational approximations.

3.4.2 Isoconversional Methods

Due to the often complex nature of solid-state kinetics and issues associated with separating the effects of $k(T)$ and $f(\alpha)$, only isoconversional methods (i.e. that fix conversion) and a few other techniques have withstood the “pessimistic attitude” (Brown et al., 2000) towards non-isothermal data analysis. Isoconversional methods can be used to define $E(\alpha)$, or at least $E_\alpha (E$ at a specific conversion, $\alpha$) to help interpret these complexities if they exist (Section 3.4.7) rather than relegate them to a mere inconvenience for methods that assume a single step (Vyazovkin and Sbirrazzuoli, 2006). The nature of the Arrhenius equation dictates that activation energy is the principal result from an isoconversional analysis (Burnham and Dinh, 2007).

It must be appreciated that the validity of all isoconversional methods is critically dependent on the isoconversional principle; i.e. the theory that the conversion rate is a function only of temperature at a set conversion (Vyazovkin, 2002). If a dependence on heating rate also exists, normally as a result of kinetic complexity (Section 3.4.7), then “serious errors” (Han et al., 2012) can manifest. The isoconversional principle is only guaranteed to hold if the entire conversion range is constructed from non-overlapped steps that are themselves described simply by Equation 3-15. This is called “multi-step” character (Vyazovkin and Sbirrazzuoli, 2006).

Friedman Method

Direct application of the differential rate equation (Equation 3-6) is the easiest and most general approach to obtain $E(\alpha)$, which is named after Friedman (Friedman, 1964). In practice, the left-hand side of Equation 3-25 is computed at a specific conversion across multiple data sets and plotted against $T_\alpha^{-1}$; $E$ at that specific conversion can be evaluated from the slope of a linear regression. This process is repeated to develop $E(\alpha)$ (Sánchez-Jiménez et al., 2010).

$$\ln\left(\frac{d\alpha}{dt}_{\alpha}\right) = \ln(Af(\alpha))_{\alpha} - \frac{E_\alpha}{RT_\alpha}$$

Equation 3-25

The product $Af(\alpha)$ does not need to be separated in order to reconstruct the predicted kinetic curve from the differential rate equation (Burnham and Dinh, 2007).
Conversion data are often collected in integral form (e.g. thermogravimetry) and must be parsed by some kind of differentiation algorithm before use in Equation 3-25 (Vyazovkin et al., 2011). Provided data are smoothed appropriately, the Friedman method can be recommended as a reliable technique (Burnham and Dinh, 2007). Differential data direct from experiment (e.g. heat flow) suffer heavily from indeterminate, possibly uneven baselines (Vyazovkin et al., 2011). In 1977, Ravindran et al. believed that the “precise” Friedman method was still inferior to approximate integral methods (Ravindran et al., 1977). Improvements in differentiation techniques and data logging may justify a reversal of this opinion, particularly considering some of the oldest and most inaccurate approximations are still the most popular (Vyazovkin and Sbirrazzuoli, 2006). Starink (2003) suggests that if the rate of conversion and sample heating rate can be measured/estimated to a precision better than 0.1%, the Friedman method will lead to more accurate kinetic parameters.

**Methods Utilising Temperature Integral Approximations**

Isoconversional methods that result from the temperature integral approximations mentioned in the previous section can be conveniently generalised by substituting Equation 3-21 into Equation 3-16 (Orfao, 2007):

\[
g(\alpha) \approx \frac{AR}{\beta E} T^2 \exp \left(-\frac{E}{RT} \right) Q \left( \frac{E}{RT} \right)
\]

\[
\Rightarrow \ln \left( \frac{\beta}{T^2 \alpha^2 \cdot \frac{E}{RT}} \right) \approx \ln \left( \frac{AR}{g(\alpha)E} \right) - \frac{E}{RT}\alpha
\]

i.e. \[
\ln \left( \frac{\beta}{T^2 \alpha^2 \cdot \frac{E}{RT}} \right) \approx \text{Constant} - \frac{E}{RT}\alpha
\]

An iterative solution must be sought if \( Q \left( \frac{E}{RT} \right) \) is a function of \( E(\alpha) \). A series of linear regressions are used to develop \( E(\alpha) \) from Equation 3-26 in the same manner as the differential Friedman method. Despite this similarity, the integral nature of Equation 3-26 should not be overlooked: Given that \( \rho \left( \frac{E}{RT} \right) \) and thus \( Q \left( \frac{E}{RT} \right) \) are derived assuming constant kinetic parameters over the range of conversion 0 to \( \alpha \), the \( E(\alpha) \) function that results does not strictly supply the specific value of activation energy at the indicated conversion \( (E_{\alpha}) \). Integration will also cause real fluctuations, not just those that might be due to noisy data, to be smoothed progressively more as conversion increases (Vyazovkin, 2002, Burnham and Dinh, 2007). Ultimately, integration errors as large as 20 – 30% can be induced in isoconversional activation energies (Vyazovkin and Sbirrazzuoli, 2006).
The low temperature end of the temperature integral can be effectively reinserted by multiplying \( Q_{T_{\infty}} \) in Equation 3-26 by the term (Orfao, 2007):

\[
1 - \left( \frac{T_\alpha}{T_0} \right) ^ 2 \frac{Q_{E a}(R/T_0)}{Q_{E a}(R/T_\alpha)} \exp\left( - \frac{E_a}{R} \left( \frac{1}{T_0} - \frac{1}{T_\alpha} \right) \right) \]

Equation 3-27

Given modifying Equation 3-26 will introduce more integration error if \( E(\alpha) \) varies substantially, the expression labelled 3-27 is more relevant to linear model fitting (Section 3.4.4). Inclusion of this term does not change the order of magnitude of the error in activation energy in any scenario (Orfao, 2007) and can be neglected in any case.

It appears that the only example of a popularised generalisation of Equation 3-26 for isoconversional analyses substitutes \( Q_{E a}(R/T_\alpha) = 1 \) (Murray and White approximation) to lead to the Kissinger–Akahira–Sunose equation:

\[
\ln \left( \frac{\beta}{T_\alpha ^ 2} \right) \approx \ln \left( \frac{AR}{g(\alpha)E} \right)_{\alpha} - \frac{E_a}{RT_\alpha} \]

Equation 3-28

The reason for Equation 3-28’s popularity is no doubt because the need to iterate is avoided. This method should not be confused with the Kissinger method discussed in Section 3.4.3. Substitution of the truncated series in Equation 3-18 for \( Q_{E a}(R/T_\alpha) \) to give the so-called Modified Coats and Redfern method has been cited in this context as well (Brown et al., 2000), but does not seem to be popular. In a few instances (Chen and Wang, 2007, Weber, Roman, 2008), an \( n \)-order reaction mechanism is also assumed, making the method overly specific.

The Ozawa–Flynn–Wall method cannot be generalised as above as it incorporates the Doyle approximation (Equation 3-20) that does not conform to Equation 3-21 (Budrugeac et al., 2004). It can be derived from Equation 3-16 as:

\[
\ln \beta \approx \ln \left( \frac{AE}{Rg(\alpha)} \right)_{\alpha} - 5.33 - 1.052 \frac{E_a}{RT_\alpha} \]

Equation 3-29
This clearly inaccurate method, again employing an identical solution procedure to the Friedman method, is the most often used for integral isoconversional analysis (Vyazovkin and Sbirrazzuoli, 2006). Arora et al. (2009) suggest that pre-exponential factor can be computed in this particular case as:

\[
A_\alpha = \frac{\beta}{RT_\alpha^2} \exp\left(\frac{E_\alpha}{RT_\alpha}\right)
\]

No qualification accompanies Equation 3-30. Ravindran (1977) provides the insight that this relationship can be derived only for deceleratory and sigmoidal mechanisms with \( \frac{d^{\prime} (\alpha)}{d\alpha} \bigg|_{\alpha_{\text{max}}} = -1 \), e.g. a first order mechanism, where \( T_\alpha = T_{\text{max}} \) ("max" refers to conditions at the maximum rate of conversion). Thus, in general Equation 3-30 is inadmissible. The inability to calculate pre-exponential factor without knowledge of the function of conversion is a known limitation of isoconversional methods (Khawam and Flanagan, 2005a).

For these approximate integral methods, the computational error in \( E_\alpha \) is obviously a function of the error in the approximation employed, and thus the dimensionless ratio \( \frac{E_\alpha}{RT_\alpha} \). The relative error in activation energy that originates from the approximation, neglecting the not insignificant contribution from the omitted low temperature end of the temperature integral (Cai and Bi, 2008), is roughly:

\[
\frac{\partial E_\alpha}{E_\alpha} = \frac{Q'(\frac{E_\alpha}{RT_\alpha})}{Q'(\frac{E_\text{exact}}{RT_\alpha})} - \frac{Q'(\frac{E_\text{exact}}{RT_\alpha})}{Q(\frac{E_\text{exact}}{RT_\alpha})}
\]

where \( Q'(\frac{E_\text{exact}}{RT_\alpha}) \) is defined from Equation 3-24 (Orfao, 2007).

This functional relationship transforms the relative error in the approximation to a much smaller value \( (\frac{\partial E_\alpha}{E_\alpha} > 5\% \text{ only if } \frac{E_\alpha}{RT_\alpha} < 5 \text{ when the Murray and White approximation is used}) \), which is reinforced by Starink (2003) who contrasts this performance to the gross errors expected from the Ozawa–Flynn–Wall method. These estimates of course do not incorporate any cumulative integration errors.

It is argued that even an error greater than 0.05% in activation energy is unacceptable (Orfao, 2007). This error is trivial in comparison to Vyazovkin and Wight’s (2000) estimate of realistic statistical uncertainties ranging from 26% to 17% for three to five heating rates respectively, and even to the common practice of quoting activation energies to a precision of 5 – 10% (Vyazovkin, 2002). Brown et
al. (2000) also agree that reporting an uncertainty in activation energy in the realms of, say, ±0.01 kJ/mol is often unrealistic.

To minimise the chance of computational errors becoming comparable to the uncertainties in $E(\alpha)$, it would appear wise to avoid using these approximate integral methods, despite their popularity.

**Advanced Isoconversional Method**

Vyazovkin et al. (2011) advocate the use of the Advanced Isoconversional method that minimises the sum of the ratios of the temperature integrals evaluated at specific conversions across $V$ different data sets by varying $E_\alpha$ until convergence:

$$\text{min}_{\text{etc}} = \sum_{i=1}^{V} \sum_{j=1}^{V} \frac{J(E_\alpha, T_{\alpha,i})}{J(E_\alpha, T_{\alpha,j})}$$

where $J(E_\alpha, T_\alpha) = \int_{\alpha-\Delta\alpha}^{\alpha} \exp\left(-\frac{E_\alpha}{RT(t)}\right) dt$

Clearly the optimum solution to Equation 3-32 occurs when each term in the summation is unity (Vyazovkin and Wight, 2000). Vyazovkin recommends supplanting analytical approximations to the temperature integral with rigorous numerical integration (e.g. trapezoidal rule) that can cope with more than just constant heating rate data (Vyazovkin and Wight, 2000, Khawam and Flanagan, 2005c). Furthermore, it is recommended to perform the integration over which $E_\alpha$ is assumed constant for small intervals $\Delta\alpha$ (e.g. $\Delta\alpha = 5\%$ (Khawam and Flanagan, 2005c)) to avoid the aforementioned systematic integration errors (Vyazovkin et al., 2011).

It is worth noting that Vyazovkin initially proposed this algorithm before deciding to abide by these two recommendations (Vyazovkin, 2000, Khawam and Flanagan, 2005c), which compelled him to respond (Vyazovkin, 2002) to dated criticisms regarding the method’s worth (Budrugeac and Segal, 2001). Realistically, if the heating rate is constant, there is nothing to be gained by numerically integrating Equation 3-32 rather than applying a highly accurate approximation (Starink, 2003), provided the piecewise nature of the integral is retained. Activation energies from the Advanced Isoconversional method converge to Friedman solutions as $\Delta\alpha$ approaches zero (Burnham and Dinh, 2007), thus $\Delta\alpha$ is a measure of the compromise between instantaneous accuracy and noise handling. If noise is minimal, then there is no reason not to employ the simpler Friedman method.
Khawam and Flanagan (2005c) studied the impact of simulated experimental errors on activation energies calculated by isoconversional methods for a hypothetical single-step first order reaction. They report that a translation along the temperature axis creates both an artefactual variation in activation energy (perceptibly more at low conversions) and significantly affects its calculated value, while a misrepresentation of the heating rate only alters its value. If $E(\alpha)$ is deemed constant over a range of conversion within the bounds of experimental and method uncertainty, then it is reasonable to assume activation energy as its mean value and consider any subsequent single-step analysis over this range as validated (Vyazovkin, 2001).

### 3.4.3 Kissinger Method

The Kissinger method is sometimes erroneously grouped with isoconversional methods due to its superficial similarity to the Kissinger–Akahira–Sunose method (Equation 3-28) (Vyazovkin and Sbirrazzuoli, 2006, Chrissafis, 2009). It is actually derived from the second derivative of the differential rate equation for a constant heating rate $\beta$ (Criado and Ortega, 1986):

$$\frac{d^2 \alpha}{dt^2} = \left(\frac{E \beta}{RT^2} + A \frac{df(\alpha)}{d\alpha} \exp\left(-\frac{E}{RT}\right)\right) \frac{d\alpha}{dt}$$ \hspace{1cm} \text{(3-33)}$$

For a calculable maximum on the $\alpha$-$t$ curve at $(T_{\text{max}}, \alpha_{\text{max}})$:

$$\ln\left(\frac{\beta}{T_{\text{max}}^2}\right) = \ln\left(-\frac{AR}{E} \frac{df(\alpha)}{d\alpha}_{\text{max}}\right) - \frac{E}{RT_{\text{max}}}$$ \hspace{1cm} \text{(3-34)}$$

The left-hand side of Equation 3-34 is evaluated for different data sets and plotted against $T_{\text{max}}^{-1}$. A linear regression supplies a constant value of activation energy for the assumed single-step process. Kissinger originally derived this method for a first order mechanism, i.e. $f(\alpha) = 1 - \alpha$ (Ravindran et al., 1977), which is required for constant $\frac{df(\alpha)}{d\alpha}_{\text{max}}$ across different heating rates (Vyazovkin et al., 2011). Clearly, this requirement is not met for all other mechanisms and the linear regressions degrade; however, this effect is counterbalanced as $\frac{E}{RT_{\text{max}}}$ increases such that the error in activation energy will always be less than 5% for $\frac{E}{RT_{\text{max}}}>10$ (Criado and Ortega, 1986, Budrugeac et al., 2007). To adopt this method where it is rigorously correct for only one standard mechanism form does not seem wise.
Equation 3-33 also restricts application of the Kissinger method to sigmoidal and deceleratory mechanisms, violating the previously quoted definition of a reliable method (Section 3.4). Even so, the Kissinger method is the most frequently applied multiple heating rate method due to its simplicity (Vyazovkin et al., 2011). In its favour, any uncertainty in the baseline will be at its least influential at the maximum rate of conversion (Starink, 2003).

3.4.4 Model Fitting

Model fitting refers to the practice of assuming the mathematical form of the kinetic model and approximating or force fitting its parameters based on that assumption. In this respect it has somewhat similar demands to the Kissinger method, only model fitting generally fits parameters by reference to the entire range of conversion rather than just the point of maximum rate. Specifying the correct function of conversion is absolutely critical and allows both activation energy and pre-exponential factor to be determined simultaneously. If this method is applied to insufficient data or a low standard of correlation is accepted, then the erroneous mechanism selection that is almost certain to result will lead to meaningless kinetic parameters (Vyazovkin et al., 2011).

Consolidating certain cross-disciplinary concepts relevant to kinetic analysis has been cited as a problem (Liu, L. and Guo, 2001). The thermal analysis community took a decade longer than other disciplines to realise that a kinetic triplet cannot be reliably determined from a single heating rate experiment (Burnham and Dinh, 2007). This delay is implied as responsible for the antagonism towards non-isothermal kinetic analysis (Vyazovkin and Wight, 1997). Even recently, examples can be found where single heating rate model fitting methods are mentioned without heavy criticism (Vlaev et al., 2008, Grause et al., 2010), despite the presence in the literature of strong reminders such as, “No papers with kinetic analyses based on experiments done at a single heating rate should be accepted for publication” (Brown, 2005).

Published statements such as, “For simple reactions, \( f(\alpha) \) usually has the form \( f(\alpha) = (1 - \alpha)^n \)” (Petrovic and Zavargo, 1986) permit researchers who are ignorant of the inherent difficulty of the inverse kinetic problem to make assumptions that simplify but may invalidate their kinetic analyses (Budrugeac, 2005). It is suspected that articles that downplay the assumption of \( n \)-order kinetics or similar can be published in their application-specific journals with relative impunity (e.g. Borah et al. (2005)), making these analyses difficult to eliminate from the literature. Methods that expressly include only certain mechanism forms (e.g. Freeman and Carroll (Galwey and Brown, 1998)) and, realistically, the Kissinger method) should also be eliminated because they create an unrealistic impression of the
determinism of the kinetic problem and may be used (Arora et al., 2009) to compute clearly unreasonable parameters. Vyazovkin and Wight (1997) state that even negative activation energies and negative estimated number of collisions have been reported. It must be accepted that while sometimes kinetic parameters can agree with expectation after indifferently selecting a model (Sánchez-Jiménez et al., 2010), it does not mean that this practice is reliable.

**Linear Methods**

In 2000, Vyazovkin lamented that model fitting to a single heating rate experiment had been adopted more often than any other non-isothermal method (Vyazovkin, 2000). This is a practice that, while not as common as it once was, still sets back the integrity of the literature (e.g. Yorulmaz and Atimtay (2009)). Again, this resistance to change seems to stem from the ease of use of the simpler linear methods that Galwey disconsolately accepts as “permanent” (Galwey, 2004). They can be generalised as for isoconversional analysis:

$$
\ln \left( \frac{g_j(\alpha_v)}{T_v^2} \right) \approx \ln \left( \frac{A_j R}{\beta_j E_{jv}} \right) - \frac{E_{jv}}{RT_v} \quad \text{or} \quad \ln \left( \frac{g_j(\alpha_v)}{T_v^2} \right) \approx \ln \left( \frac{A_j R}{\beta_j E_{jv}} \right) - \frac{E_{jv}}{RT_v}
$$

The subscripts denote that the attached term is specific to either the mechanism counter \((j)\) or the experiment counter \((v)\), or both. In this context, the integral form of the conversion function is included in the left-hand term that is plotted against \(T_v^{-1}\) for a single constant heating rate \(\beta_v\). Both apparent kinetic parameters can be extracted as constants from the slope and intercept. The popular Coats and Redfern method normally cited inserts the approximation of Equation 3-18 (Vyazovkin, 2001, Khawam and Flanagan, 2005a, Han et al., 2012):

$$
\ln \left( \frac{g_j(\alpha_v)}{T_v^2} \right) \approx \ln \left( \frac{A_j R}{\beta_j E_{jv}} \right) \left( 1 - \frac{2RT}{E_{jv}} \right) - \frac{E_{jv}}{RT_v} \quad \text{for} \quad T = \text{mean experimental temperature}
$$

However, the grosser simplification of \(O_{\frac{E_{jv}}{RT}} = 1\) is also named for Coats and Redfern (Galwey, 2003b) and has been applied recently (Jankovic et al., 2007):

$$
\ln \left( \frac{g_j(\alpha_v)}{T_v^2} \right) \approx \ln \left( \frac{A_j R}{\beta_j E_{jv}} \right) - \frac{E_{jv}}{RT_v}
$$
Frequent mention is made of the readily apparent fact that almost any function of conversion will generate a linear relationship from Equation 3-37 with a respectably high correlation coefficient. Thus, the practice of choosing a mechanism because it happens to be associated with the highest of a range of statistically equivalent correlation coefficients is seriously flawed (Vyazovkin and Wight, 1999, Budrugeac et al., 2007). This indeterminacy has been discussed in Section 3.2.1 as the manifestation of an artificial compensation effect, and arises from the inadmissible correlation between the ordinate and abscissa (Khawam and Flanagan, 2005a). Certain subsets of mechanisms are by definition indistinguishable on the basis of correlation coefficient if substituted into either Equation 3-36 or Equation 3-37, such as the An (Khawam and Flanagan, 2005a) and Pn mechanisms that can be shown mathematically to simply scale the apparent kinetic parameters with \( n \) (Galwey, 2003b). Moreover, mechanisms that fall within the uncertainty limits of the best correlated mechanism can give rise to vastly different kinetic parameters (Vyazovkin and Wight, 2000). The methods of Invariant Kinetic Parameters and Combined Kinetic Analysis demonstrate that this artificial compensation effect precludes any simultaneous conclusions regarding kinetic parameters and mechanism from a single heating rate experiment.

Less ambiguous mechanism selection can be achieved by comparing the much more sensitive \( F \)-statistic from individual linear regression analyses (Urbanovici et al., 1999). In this context, each \( F \)-statistic is calculated as the ratio of the data variation from their average values to the residual sum of squares (Phipps and Quine, 1998, Urbanovici et al., 1999):

\[
F_{j,1,v-2} = \frac{a}{I_v - 2} \sum_{i=1}^{k_v} \left( \ln \left( \frac{g_f(\alpha_{vi})}{T_{vi}^2} \right) - y_i \right) - \bar{y} \left( \frac{1}{T_{vi}^2} - \bar{x} \right), \quad \text{for the linear regression } \ y = ax + b
\]

The greater the \( F \)-statistic, the higher the probability that the regression equation must be more complex than \( y = \bar{y} \) and the more appropriate the specified linear relationship between \( x \) and \( y \). \( F_{j,1,v-2} \) will be statistically significant for any Arrhenius model but its highest value should correspond to the best mechanism with more reliability than the highest correlation coefficient or smallest residual sum of squares (Urbanovici et al., 1999).
A New Adaptation of The Method of Invariant Kinetic Parameters and its Application to a Flame Retardant System

Even if the mechanism is correctly assigned, the error associated with the temperature integral approximation seems to introduce a much greater error into the apparent kinetic parameters compared to the isoconversional activation energies. Ebrahimi-Kahrizsangi and Abbasi (2008) report an overestimation of activation energy by up to 25% when applying Equation 3-36 to a single heating rate, and a pre-exponential factor that differs from its set value by six orders of magnitude. Over a wide range of heating rates (5 – 50°C/min) the error in activation energy is shown to be almost as bad (+23%) when \( 2.7 < \frac{E_{jv}}{RT} < 9.7 \) (Table 4 in Weber (2008)). Contrary to these results, Khawam and Flanagan (2005c) report much smaller errors in activation energy (< 0.5%) and pre-exponential factor (< 10%) averaged over five heating rates even when systematic temperature and heating rate errors are deliberately introduced. However, in this instance \( \frac{E_{jv}}{RT} \approx 20 \), and their observations are essentially in agreement with Table 3 in Weber (2008) where \( 11.6 < \frac{E_{jv}}{RT} < 22.1 \). This corroborates the idea that a slightly higher value of \( \frac{E_{jv}}{RT} \) practically eliminates the approximation error (Figure 3-1). It is also recommended to use as wide a range of heating rates as possible to minimise uncertainty (Vyazovkin et al., 2011).

**Non-Linear Methods and Mamleev’s Approach**

An obvious alternate approach to linear model fitting is to optimise the kinetic parameters by minimising the residual sum of squares between experimental and reconstructed curves (Perejón et al., 2011), which at least provides an in situ check of whether a kinetic triplet is valid (Sánchez-Jiménez et al., 2009, Vyazovkin et al., 2011):

\[
\sum (x_{\text{experimental}} - x_{\text{model}})^2 = \min
\]

Comparisons can be made based on rate, conversion or both (dictating \( x \) in Equation 3-39) (Vyazovkin et al., 2011). While linear methods disproportionately weight points at lower conversions due to the presence of logarithms in Equation 3-35, non-linear optimisation naturally weights data points evenly. There is also scope to tailor the weighting to match mechanism characteristics beyond simply restricting the range of calculation (Mamleev et al., 2000a, Vyazovkin et al., 2011). Culling the number of mechanisms before performing rigorous optimisations can be achieved through visual inspection (Dollimore et al., 1992, Vyazovkin et al., 2011). Vyazovkin et al. (2011) state that, “If the reaction rate continues to accelerate to the end of the reaction, a power law model should be considered”. However, this advice could be misleading as it is shown in Appendix A2.1 that the power law is incapable of representing the end of a reaction.
A New Adaptation of The Method of Invariant Kinetic Parameters and its Application to a Flame Retardant System

Unfortunately for those who wish to avoid the problems inherent in linear methods, detailed descriptions for more involved non-linear optimisations are generally not available (Mamleev et al., 2000a). Mamleev et al. (2000a) attempt to rectify this by describing their approach to modelling non-isothermal data, but disrupt their article with typographical errors in equations and unconventional symbols. A brief interpretation of their approach is supplied here.

Mamleev et al. (2000a) generate an approximate experimental curve with what they call an "auxiliary function" (Bourbigot et al., 2002):

\[ \int_0^{\alpha_v} \frac{d\alpha}{f_j(\alpha)} \approx g_j(\alpha_v) \]  

This is the merely the same function used in linear model fitting. Depending on the mechanism form, Equation 3-40 should be comparable to the curve reconstructed from the temperature integral:

\[ A_j \int_0^{\alpha_v} \exp \left( \frac{-E_j}{RT_i} \right) dt_v = g_j(\alpha(t_v)) \]

To derive an equation for the temperature integral that can be applied to each discrete temperature-time data set, first the term \( \frac{E_j}{RT} \) is linearised from the upper datum (Bourbigot et al., 2002):

\[ \frac{E_j}{RT} \approx \frac{E_j}{RT_i} - \frac{E_j(T - T_i)}{RT_i^2} ; \quad T_{i-1} \leq T \leq T_i \]

Note that the subscript \( v \) is dropped in Equation 3-42 and Equation 3-43 for clarity. Equation 3-42 and the temperature and time differences can be substituted into the integral equation for one time step and integrated analytically to an expression for each element in the sum:

\[ g_j(\alpha(t_i)) \approx A_j \sum_{i=1}^{Lj} \frac{RT_i^2}{E_j} \exp \left( \frac{-E_j}{RT_i} \right) \left( 1 - \exp \left( \frac{E_j(T_{i-1} - T_i)}{RT_i^2} \right) \right) \left( \frac{t_i - t_{i-1}}{T_i - T_{i-1}} \right) \]

\[ \int_{t_{i-1}}^{t_i} \exp \left( \frac{-E_j}{RT} \right) \frac{dt}{dT} dT \approx \int_{t_{i-1}}^{t_i} \exp \left( \frac{-E_j}{RT_i} \right) \exp \left( \frac{E_j(T - T_i)}{RT_i^2} \right) \left( \frac{t_i - t_{i-1}}{T_i - T_{i-1}} \right) dT \]

\[ \Rightarrow g_j(\alpha(t_i)) \approx A_j \sum_{i=1}^{Lj} \frac{RT_i^2}{E_j} \exp \left( \frac{-E_j}{RT_i} \right) \left( 1 - \exp \left( \frac{E_j(T_{i-1} - T_i)}{RT_i^2} \right) \right) \left( \frac{t_i - t_{i-1}}{T_i - T_{i-1}} \right) \]
Equation 3-43 exemplifies the fact that a vast number of data points will successfully integrate the temperature integral for any relationship between temperature and time; thus it is accepted that \( g_j(\alpha(t_{vi})) \) can be computed with the “high accuracy” claimed (Mamleev et al., 2000a).

The best estimate for each pair of kinetic parameters is calculable by minimising the residual sum of squares between the logarithms of the auxiliary function and Equation 3-43 (Mamleev et al., 2000a):

\[
\sum_{i=1}^{V} \sum_{j=1}^{I_{v_i}} \left( \psi_j \left[ \ln[g_j(\alpha(t_{vi}))] - \ln[g_j(\alpha(t_{vi}))] \right]^2 = \min; \quad \psi_j = \text{weighting function} = 1 \tag{3-44}
\]

Logarithms are introduced into the objective function (Equation 3-39) with even weighting purportedly because the residuals then contribute approximately evenly over the full range of conversion. While this is true when activation energy is set close to its correct value, it is suspected that this choice has more to do with allowing a three parameter optimisation problem to be simplified to three successive single parameter optimisations (mechanism form \(\rightarrow\) activation energy \(\rightarrow\) pre-exponential factor) (Mamleev et al., 2000a).

It is shown that the even weighting of logarithms leads to residual sums that reliably increase with the increasing activation energy uncertainty associated with progressively poorer mechanism selection. Conventional residual sums based on conversion appear to be much more erratic. Only by transforming these to the same logarithmic scale with an approximate weighting function can a similar reliability be observed (Mamleev et al., 2000a):

\[
\sum_{i=1}^{V} \sum_{j=1}^{I_{v_i}} \left( \phi_j \left[ \alpha_{vi} - \alpha(t_{vi}) \right] \right)^2 = \min \tag{3-45}
\]

where

\[
\phi_j = \psi_j \frac{d\left[\ln(g_j(\alpha))\right]}{d\alpha} \bigg|_{\alpha(t_{vi})} = \psi_j \frac{1}{g_j(\alpha)} \frac{dg_j(\alpha)}{d\alpha} \bigg|_{\alpha(t_{vi})} \tag{3-46}
\]

The derivative in Equation 3-46 is easy to deduce analytically for each mechanism function (Table 5-1). Furthermore, once below a certain critical value, a smaller value for the objective function (Equation 3-45) appears to always correspond to a better estimate for activation energy, regardless of mechanism (Mamleev et al., 2000a). This behaviour is at odds with the known outcome of linear methods where the objective function is the linear correlation coefficient.
The unique approach of Mamleev et al. (2000a) may not handle imperfect experimental data well. A modest simulated random error in sample weight of 5% causes the order of reaction to shift from the exact value of 2 to 2.25 (incremented manually in steps of 0.05), and introduces a 9% error in activation energy and almost an order of magnitude change in pre-exponential factor. It is possible that this response is partially attributable to the fact that only seven points are used for the minimisation (but, importantly, not for the temperature integral) (Mamleev et al., 2000a).

Regardless of the algorithm form, both an initial guess and the expected outcome for activation energy are best matched to an isoconversional analysis (Khawam and Flanagan, 2005a, Vyazovkin et al., 2011). It is recommended that the uniqueness of the solution obtained through multi-parametric optimisation is also tested by checking the response to an approach from well above and below the optimised activation energy (Vyazovkin et al., 2011). If basically the same solution is confirmed, an estimate of the uncertainty in the method can at least be quoted (Weber, Roman, 2008). Model fitting can describe heterogeneous kinetics well, so long as it is conscientiously applied to a set of multiple heating rate experiments and has the ability to describe complex processes when necessary (Section 3.4.7) (Maciejewski, 2000).

Relative F-Testing

$F$-testing can also be used to judge the goodness of fit of alternate models relative to the prescribed “correct” model across a number of experiments where one independent parameter is varied (e.g. heating rate). It has been applied to variances derived for the Advanced Isoconversional method (Vyazovkin and Wight, 2000) and the residual sum of squares between experiment and prediction, either in terms of non-isothermal rate (Richard-Campisi et al., 1996) or time to conversion under isothermal conditions (Vyazovkin and Wight, 1999). The correlation coefficients of the Coats and Redfern linear regressions can also be subjected to similar testing (Vyazovkin and Wight, 1999). In all these applications, the $F$-statistic is taken as the ratio of each variance $S_i$ relative to the minimum variance. It is therefore equivalent to the ratio of two chi-squared distributions both with $n - 1$ degrees of freedom, where $n$ is the number of experiments:

$$F_{i,n-1,n-1} = \frac{S_i^2}{S_{\text{min}}^2}$$
The probability that any other randomly selected model \( j \) will not fit as well as model \( j^* \) can be represented by the area under the tail of the \( F \)-distribution from \( F_{j,n-1,n-1} \) (Richard-Campisi et al., 1996):

\[
P(F_{j,n-1,n-1} > F_{j^*,n-1,n-1}) = 1 - \frac{\Gamma(n-1)}{\Gamma^2((n-1)/2)} \int_0^{F_{j^*,n-1,n-1}} z^{(n-1)/2} (1 + z)^{-(n-1)} \, dz
\]

Richard-Campisi et al. (1996) appear to presume that they have considered every possible model and normalise Equation 3-48 with respect to the sum of the 18 probabilities they calculate, creating a very subjective set of “probabilities”. Despite this criticism, these arbitrarily normalised relative probabilities are still indicative of either very successful mechanism discrimination and thus a highly probable kinetic triplet (Siat et al., 1997), or very poor discrimination (Griffin et al., 2005).

As this particular \( F \)-test is reliant on the minimum variance denoting the “correct” model, it makes more sense to instead exclude any model \( j \) outside, say, the 95% confidence interval (i.e. \( F_{j,n-1,n-1} > F_{0.95*,n-1,n-1} \Rightarrow \text{exclusion} \) (Phipps and Quine, 1998, Vyazovkin and Wight, 1999). In the case of its application to the Advanced Isoconversional method, the \( F \)-test can be used in a similar manner to estimate the uncertainty in \( E_\alpha \) (Vyazovkin and Wight, 2000).

### 3.4.5 Combined Kinetic Analysis

A sophisticated example of linear model fitting is the method of Combined Kinetic Analysis (Vyazovkin et al., 2011). It is necessary to correctly represent the Sestak-Berggren equation, Equation 3-10 in Section 3.3.1, multiplied by some factor (\( c \) in Equation 3-49) to account for the fact that the pre-exponential factor may be scaled (Sánchez-Jiménez et al., 2010). As long as this factor is known, such as in the examples for the A2 and A3 mechanisms shown in Section 3.3.1, the “true” pre-exponential factor can be extracted along with the other elements of the kinetic triplet using Combined Kinetic Analysis (Pérez-Maqueda et al., 2006, Vyazovkin et al., 2011). This analysis procedure optimises \( m \) and \( n \) by fitting the left-hand side of Equation 3-49 to the straight line (as a function of \( T^{-1} \)) that maximises the linear correlation coefficient (Pérez-Maqueda et al., 2003):

\[
\ln \left( \frac{d\alpha/dt}{\alpha^m (1-\alpha)^n} \right) = \ln(cA) - \frac{E}{RT}
\]
Activation energy and the product $c A$ are the outputs from this optimisation procedure. If the ultimate values of $m$ and $n$ do not allow the function of conversion to be equated to a specific mechanism type, then $c$ remains unknown, but close to unity and therefore relatively inconsequential to the usually large pre-exponential factor (Vyazovkin et al., 2011).

Combined Kinetic Analysis can be applied to any temperature program as no assumptions are made other than the ability to conform the true mechanism equation to the Sestak-Berggren generalisation and single-step Arrhenius kinetics. The futility of attempting to calculate reliable kinetic parameters by model fitting a single constant heating rate experiment is underscored by this method; a large range of $m$ and $n$ will yield perfect, parallel straight lines for a range of heating rates, but only one pairing of $m$ and $n$ will cause these parallel lines to overlay (Pérez-Maqueda et al., 2006).

While the physical meaning of $m$ and $n$ remains ambiguous without additional supporting information, it has been confirmed that this analysis method will yield the input activation energy and pre-exponential factor when simulated data is confounded with a particle size distribution or constructed from a mixture of cylindrical and spherical particles undergoing idealised contraction (Pérez-Maqueda et al., 2006). The success of these tests convincingly demonstrates both the merit of optimising the function of conversion primarily and also the validity of the Maximise function within the Mathcad software used by these researchers. Pérez-Maqueda et al. (2003) do assure that any other optimisation program, such as Solver in Microsoft Excel, would also suffice.

In all instances where this technique is presented (Pérez-Maqueda et al., 2006, Sánchez-Jiménez et al., 2009, 2010, Perejón et al., 2011), certain mechanisms from Table 5-1 are glaringly omitted: $Pn$ (and therefore $R1$ and $F0$) and $D1$. This raises doubts as to the ability of the Mathcad Maximise function to find a solution for all mechanistic forms, particularly given Pérez-Maqueda et al. (2006) state that the Sestak-Berggren equation can be replaced by an equally representative equation with no penalty (i.e. the Sestak-Berggren equation itself is implied not to be limiting in this regard). Reference to Table 5-1 suggests that optimisation may be impossible when $n = 0$ in Equation 3-49. The quote from Vyazovkin et al. (2011) questioning the reliability of methods that cannot treat all mechanism shapes (Section 3.4) may be relevant in this case.

3.4.6 The Method of Invariant Kinetic Parameters

The method of Invariant Kinetic Parameters (IKP) is a multiple heating rate method that has the unique quality of being able to supply not only activation energy, but pre-exponential factor as distinct from an
unspecified function of conversion. Accordingly, this method can be categorised as “model-free” (Vyazovkin et al., 2011). Each artificial compensation effect induced by deliberately assigning a range of incorrect mechanisms is plotted to determine the heating rate-dependent compensation parameters, $b_v$ and $c_v$:

$$\ln A_{jv} = b_v E_{jv} + c_v$$  \hspace{1cm} 3-50

This compensation effect, which is only a feature of non-isothermal data (Budrugeac et al., 2007), highlights the profound uncertainty in the “true” values for activation energy and pre-exponential factor if only one heating rate is considered. By plotting at least three sets of compensation parameters against one another, this uncertainty can be dramatically reduced:

$$c_v = \ln A_{inv} - b_v E_{inv}$$  \hspace{1cm} 3-51

If this “super correlation” is not found, it indicates that the unspecified mechanism is not valid for all the heating rates considered (Lesnikovich and Levchik, 1983) or the kinetics are complex (Han et al., 2012). Invariant pre-exponential factor ($A_{inv}$) and activation energy ($E_{inv}$) found from a positive correlation to Equation 3-51 are so labelled because they are, by definition, invariant with respect to heating rate (and all associated secondary effects defining the bounds of uncertainty) and the function of conversion (Lesnikovich et al., 1986).

Apparent parameters for use in Equation 3-50 are exclusively calculated using linear model fitting methods (Section 3.4.4) (Han et al., 2012), and rarely by any method other than the simpler Coats and Redfern method (Equation 3-37). An implicit association between the two methods seems to have been accepted (Griffin et al., 2005, Grause et al., 2010). Based on the original proposal of the IKP method by Lesnikovich and Levchik (1983), there should be no such association. These pioneers do exemplify the IKP method using the Coats and Redfern method (Lesnikovich et al., 1984), which probably encouraged this connection. High accuracy, widely varied apparent parameters covering a similarly broad range of heating rates are critical to the quality of the linear regressions used to determine $A_{inv}$ and $E_{inv}$ (Lesnikovich and Levchik, 1985, Vyazovkin et al., 2011). It is cautioned that the linearity of the compensation effect will fail as $E \rightarrow 0$ and $\ln A \rightarrow \infty$ (Mamleev et al., 2000a).

The invariant kinetic parameters are computed as constants; therefore a preliminary isoconversional analysis is required to nominally verify that the calculation range covers only a single-step process
Uncertainties in the Kinetic Parameters

Uncertainties in the IKP calculated by the standard method are difficult to calculate rigorously (Lesnikovich et al., 1984, Vyazovkin et al., 2011) but can be depicted as the intersection of $V$ prolonged ellipsoidal confidence intervals (Lesnikovich and Levchik, 1983, Lesnikovich et al., 1984) (Figure 3-2). Standard errors in $A_{\text{inv}}$ and $E_{\text{inv}}$ can at least be estimated from a regression analysis of Equation 3-51 (Lesnikovich et al., 1984).

Consistently high standard errors in the intercept compared to negligible errors in slope for Equation 3-50 propagate to much greater uncertainties in $A_{\text{inv}}$ compared to $E_{\text{inv}}$ (Budrugeac et al., 2004), although not usually in excess of 10% for $\ln A_{\text{inv}}$ (Lesnikovich et al., 1984). Invariant activation energies are in agreement with those obtained from isoconversional (Budrugeac et al., 2004, Budrugeac et al., 2007, Jankovic et al., 2007) and isothermal (Lesnikovich and Levchik, 1983) analyses. Equation 3-51 can be compared to the Kissinger method (Equation 3-34) and demonstrated to be technically valid for the
same condition: \( \frac{df(\alpha)}{d\alpha} \bigg|_{\alpha_{\text{max}}} = \text{Constant} \). It follows that the majority of the uncertainty in Equation 3-51 can be traced to the diffusion mechanisms, while almost nil arises from \( n \)-order mechanisms (Budrugeac, 2007). In addition, the poorer fit to the data of any inappropriately-shaped mechanisms will add to the final uncertainty (Budrugeac et al., 2004).

Vyazovkin et al. (2011) suggest that the difficulty in evaluating errors and the relative computational intensity of the IKP method compared to, say, the Kissinger method easily outweigh the advantage of obtaining the kinetic parameters simultaneously. Budrugeac (2007) disagrees and does so within a much more detailed appraisal (cf. Vyazovkin et al. (2011) who also incorrectly state Equation 3-51). Vyazovkin et al. (2011) suggest that the model-free activation energy is better substituted directly into the compensation effect (Equation 3-50) to obtain the model-free pre-exponential factor. This suggestion is of equivalent merit to IKP only if the compensation parameters vary little with heating rate; Vyazovkin et al. (2011) do not acknowledge any dependence in this context nor do they seem to appreciate that the computational intensity of direct substitution is at least equivalent to the IKP method.

**Deducing the Mechanism**

Once \( A_{\text{inv}} \) and \( E_{\text{inv}} \) have been deduced, the rate constant can either be combined with each mechanism function in turn to \( F \)-test the residual sums of squares (Rose et al., 1994, Richard-Campisi et al., 1996, Siat et al., 1997, Griffin et al., 2005, Grause et al., 2010), or factored out of the rate equation to develop a numerical approximation proportional to the “true” function of conversion, provided \( E_{\text{inv}} \) is relatively error free (Budrugeac et al., 2004, Jankovic et al., 2007). In either case, the mechanism that is measured to best represent the experimental data is selected. If no apparent activation energies match the invariant activation energy, then it is unlikely that any of the mechanisms used to generate the compensation effect actually drive conversion (Jankovic et al., 2007).

To move forward from this negative result, a different arrangement of the defining equation for Combined Kinetic Analysis can be used to explicitly calculate the accommodation parameters \( m \) and \( n \). Conversion at the inflection point (\( \alpha_i \)) must be estimated from the numerical representation of \( f(\alpha) \) (Jankovic et al., 2007). As discussed in Appendix A2.3, \( \alpha_i \) must correspond to that for an isothermal experiment, i.e. the conversion at the maximum value of \( f(\alpha) \). The unknown constant of proportionality \( c \) introduced in Equation 3-49 should also be present in Equation 3-52. Since it is not, validating the calculated pre-exponential factor against \( A_{\text{inv}} \) can only be done approximately (within an order of magnitude (Jankovic et al., 2007)).
\[
\ln \left( \frac{d\alpha}{dt} \exp \left( \frac{E_{\text{act}}}{RT} \right) \right) = \ln A + n \ln \left[ \alpha^i (1 - \alpha) \right], \quad \text{where} \quad s = \frac{m}{n} = \frac{\alpha_i}{1 - \alpha_i}
\]

### Method Variants

Isoconversional analysis is actually intimately incorporated into a recent modification to the IKP method (Grause et al., 2010). Using a small conversion increment of 1%, \( E(\alpha) \) is computed along with apparent pre-exponential factors by assuming a mechanism. The compensation effect of Equation 3-50 is redefined as the straight line between a pair of adjacent points \( (E_{\alpha}, \ln A_{\alpha}) \) and \( (E_{\alpha} + 1\%, \ln A_{\alpha} + 1\%) \) (Grause et al., 2010). It follows that the kinetic parameters found from the super correlation (Equation 3-51) are invariant with respect to heating rate and the conversion range from which the selected straight lines correspond. \( E_{\text{inv}} \) is also invariant with respect to mechanism, but \( A_{\text{inv}} \) is not in this case.

Conversion ranges that abide by the same super correlation can be readily discerned in the \( (E(\alpha), \ln A(\alpha)) \) space (Grause et al., 2010), but are no more apparent than these ranges when plotted more intuitively as \( E(\alpha) \).

Kinetic parameters that are invariant with respect to other experimental factors can be evaluated by modifying the sense of the compensation effect (Lesnikovich et al., 1986). Lesnikovich et al. (1986) seem to suggest that the type of flame retardant added to a polymer, polyethylene terephthalate (PET) in their example, can be varied with the experiment counter \( \nu \) while relegating heating rate to a mere secondary effect. It appears that the mechanism counter is also replaced with incremental conversion in an identical manner to that described by Grause et al. (2010). Three separate stages are identified for the oxidative degradation of flame-retarded PET. Flame retardants are said to influence the first and last stages as only these super correlations arrive at different sets of \( A_{\text{inv}} \) and \( E_{\text{inv}} \) to those for no flame retardant. The second stage is presumed to correspond to unaffected polyester radical decomposition (Lesnikovich et al., 1986).

### 3.4.7 Complex Kinetics

It is an unavoidable and inconvenient reality that solid-state degradation kinetics generally exhibit complex character (i.e. overlapping processes) that cannot be treated using the methods as they have been outlined in the preceding sections. Complex character can be detected in the form of disagreement between kinetic triplets obtained from single-step analyses of corresponding isothermal and non-isothermal data, but not always (Vyazovkin, 2000). It has been convincingly demonstrated that the best way to identify any form of complex kinetics is to perform an isoconversional analysis (Vyazovkin and Lesnikovich, 1990, Brown et al., 2000, Vyazovkin, 2000), however even this will fail if...
the task is to differentiate between a number of processes with very similar activation energies (Maciejewski, 2000) or the isoconversional principle (Section 3.4.2) does not hold (Han et al., 2012). Because of the difficulty in modelling any type of process complexity, there is a need to develop reliable methods to treat convoluted kinetic data (Brown, 2005, Perejón et al., 2011).

Recently, an extension to the IKP method, named the Incremental IKP (IIKP) method, was proposed as a means to first judge the validity of the isoconversional principle stepwise over the whole conversion range (Han et al., 2012). Apparent parameters for a range of mechanisms are computed at each 10% conversion increment using a model fitting method for an interval of \( \Delta \alpha = 0.05 \) (Han et al., 2012). If the compensation effects computed for different heating rates do not lead to a point or at least a small zone of intersection (\( \Delta E_\alpha < 20 \text{ kJ/mol} \)), \( E_\alpha \) is proven erroneous; i.e. a significant dependence on heating rate must also exist. If this is the case, overlapped, relatively evenly-weighted processes are likely to be invalidating the isoconversional principle at this conversion (Vyazovkin, 2000, Han et al., 2012). The surface plot of Figure 3-3 illustrates the potential for an isoconversional analysis to give the appearance of a definite trend in \( E(\alpha) \) when there is in fact considerable ambiguity, even for perfect simulated data. IIKP cannot supplant the differential or piecewise integral isoconversional methods for the actual evaluation of \( E_\alpha \) at those conversions deemed valid because it is much too sensitive to changes in the relative contributions of the overlapping processes (Han et al., 2012).

![Figure 3-3: Representation of the actual \( E(\alpha, \beta) \) surface and the projection \( E(\alpha) \) for two overlapping first order reactions with activation energies 80 kJ/mol and 120 kJ/mol (Copyright © 2000 Elsevier. Used with permission from Vyazovkin (2000))](image-url)
Independent processes and the more challenging to model competing/sequential processes can be generalised as (Burnham and Braun, 1999):

\[
\frac{dx}{dt} = -k_1 f_1(x) - k_2 f_2(x) \quad \text{Reactant} \tag{3-53}
\]

\[
\frac{dy}{dt} = k_1 f_1(x) - k_3 f_3(y) \quad \text{Intermediate} \tag{3-54}
\]

\[
\frac{dz}{dt} = k_2 f_2(x) + k_3 f_3(y) \quad \text{Product} \tag{3-55}
\]

Independent and sequential processes require \(k_1 = 0\) and \(k_2 = 0\) respectively (Burnham and Braun, 1999). This general complex kinetics scheme can be extended to any number of reactants and intermediates, and the product rate of change (Equation 3-55) normalised to that for dimensionless conversion. Thus for \(P\) independent processes (Vyazovkin et al., 2011, Han et al., 2012):

\[
\frac{d\alpha}{dt} = \sum_{p=1}^{P} a_p k_p f_p(\alpha_p) ; \quad a_p = \text{fraction converted via process } p, \Rightarrow \sum_{p=1}^{P} a_p = 1 \tag{3-56}
\]

Also, if just the intermediate rate equation (Equation 3-54) is paired with an equal but opposite rate equation for \(x\), then these two equations would represent a reversible process (Han et al., 2012).

**Activation Energy Variation**

Vyazovkin and Wight (1997) propose that competing and some independent and sequential processes will manifest increasing but decelerating trends of activation energy with conversion, citing oxidative and pyrolytic polypropylene decomposition as examples. Gao et al. (2003) calculate the same increasing but somewhat acceleratory function of conversion for non-isothermal polypropylene pyrolysis. In this case, the activation energy variation is attributed to the systematic deviation from the steady-state assumption as heating rate increases, a general issue for non-isothermal kinetics, as well as the fact that the size range of volatile degradation products increases with increasing temperature (Gao et al., 2003).

Computations by Chan and Balke (1997b) and Gómez-Elvira (2013) fully support Vyazovkin and Wight’s qualitative description of \(E(\alpha)\) for polypropylene decomposition, but Chen and Wang (2007) report a subtle decreasing function. Insufficient information is available to reconcile these contradictions; although the different methods used to evaluate \(E(\alpha)\) (Friedman/Kissinger–Akahira–Sunose and Ozawa–Flynn–Wall respectively) are known to yield different results when activation energy is not constant (Budrugeac et al., 2004). Application of the more trustworthy Advanced Isoconversional
method to polypropylene pyrolysis data shows $E(\alpha)$ as a monotonically increasing function, with a rapid deceleration up to 10% conversion followed by a gradual acceleration; i.e. sigmoidal overall (Vyazovkin and Sbirrazzuoli, 2006). Figure 3-3 suggests that it may be unwise to place much significance on the curvature of $E(\alpha)$.

If polymers or other organic substances become increasingly refractory in nature as decomposition progresses, activation energy will increase (Vyazovkin et al., 2011). Alternately, if diffusion of one reactant through a growing product layer (Appendix A2.7) eventually becomes rate limiting, activation energy will decrease (Vyazovkin and Wight, 1997). Reversible endothermic reactions where an irreversible reaction follows are likely to induce much more dramatic decreases in activation energy as conversion increases. Conversely, an uncomplicated reversible reaction such as calcium carbonate decomposition is likely to show increasing activation energy with conversion, particularly if the pressure dependence is not explicitly accounted for (Vyazovkin and Wight, 1997). These are examples that can be generalised with a decision tree, such as that proposed by Vyazovkin and Lesnikovich in 1990 (Figure 3-4). However, it is noted that Vyazovkin omits such a definitive schematic and appears to downgrade the certainty of his conclusions from $E(\alpha)$ in articles that follow (Vyazovkin and Wight, 1997, Vyazovkin and Sbirrazzuoli, 2006, Vyazovkin et al., 2011). Deciding upon an underlying complex kinetics scheme for further analysis can be guided by both the shape of the $E(\alpha)$ dependence and its physical interpretation.

![Figure 3-4: Decision tree for activation energy dependence on conversion (Copyright © 1990 Elsevier. Used with permission from Vyazovkin and Lesnikovich (1990))](image-url)
If a valid isoconversional analysis produces an increasing sigmoidal $E(\alpha)$, the nature of the complexity can be confidently narrowed down to a set of overlapping independent processes (Vyazovkin et al., 1992). It has been suggested that the degradation kinetics of some materials known to contain a range of components (e.g. biomass and fossil fuels) conform to Equation 3-56 with large $P$, also known as a distributed reactivity model (Burnham et al., 2004, Vyazovkin et al., 2011). Activation energies are commonly matched to a Gaussian, Weibull or Gamma distribution about a mean value for activation energy initially estimated from a single-step calculation method (Burnham and Braun, 1999, Vyazovkin et al., 2011). Pre-exponential factors are either simplified to a constant value or specified as some function of activation energy that best suits the empirical data (e.g. the typical compensation relationship $\ln A = \ln A_0 + bE$) (Burnham and Braun, 1999, Burnham and Dinh, 2007). It is implied that a first order mechanism ($f(\alpha) = 1 - \alpha$) is frequently selected for the constituent processes (Vyazovkin et al., 2011), but regardless of the choice, any flexibility in the function of conversion is not allowed (Burnham and Braun, 1999). One should be mindful that a distributed reactivity model may not be mathematically distinct from a number of alternatives conforming to Equation 3-56 (Burnham and Braun, 1999, Vyazovkin et al., 2011).

**Overlapped Independent Processes**

If there is no cause to sum a large number of processes but $E$ exhibits a definite increasing dependence on conversion, it may be valid to simply assign two overlapping independent processes (Vyazovkin and Lesnikovich, 1990, Vyazovkin et al., 2011). A shoulder, or “separation point”, in a thermogravimetric signal that consistently appears at the same conversion for a number of heating rates is indicative of this type of complexity (Mamleev et al., 2000b). The maximum and minimum values of $E(\alpha)$ are theoretically sound initial guesses for the required two activation energies (Vyazovkin, 2000, Vyazovkin et al., 2011) (Figure 3-3). The most common approach to deducing the complete kinetic description is to introduce these activation energies into a non-linear regression optimisation algorithm for each of a wide range of different mechanism permutations (Perejón et al., 2011). As for single-step model fitting methods, the minimum variance between theory and experiment dictates the most appropriate permutation. Pairs of kinetic triplets that accurately describe simulated data have been successfully extracted in this manner (Vyazovkin, 2000).

The extension of the unique algorithm presented by Mamleev et al. (2000a) to this style of problem has been elaborated in similar detail, and, regrettably, with similar typographical errors (Mamleev et al., 2000b). It is noted that the “separation point”, labelled $x$, is inserted into the optimisation and is taken literally as an estimator of “the end of the first stage and the beginning of the second one” (Mamleev et
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al., 2000b). Conceptually this is flawed; mathematically, $x$ clearly corresponds to the weight transformed via the second process, plus any inert weight, as can be observed from the reported equation for predicted weight (Bourbigot et al., 2002):

$$m(t_{vi}) = (m_{v0} - x)(1 - \alpha_1(t_{vi})) + (x - m_{v0})(1 - \alpha_2(t_{vi})) + m_{v0}$$  \hspace{1cm} (3-57)

Their misleading terminology persists in subsequent articles (Bourbigot et al., 2002, Lefebvre et al., 2005). Thinking of $x$ as a point on the weight loss curve is technically correct for the first iteration, as the two processes are defined to end and start at this point and can be treated entirely separately. Once the two pairs of kinetic parameters have been optimised for this scenario for each process/mechanism permutation using relatively unconvolved, narrow conversion ranges (e.g. spanning 10%), corresponding estimates for $x$ can be calculated that minimise the difference between Equation 3-57 and the measured weight across multiple experiments (Bourbigot et al., 2002):

$$x = \frac{\sum_{i=1}^{I_v} \sum_{j=1}^{I} \left[ \alpha_2(t_{vi}) - \alpha_1(t_{vi}) \right] \left[ m_{v0}(1 - \alpha_1(t_{vi})) - m_{v0}(1 - \alpha_2(t_{vi})) + m_{v0} - m_{vi} \right]}{\sum_{i=1}^{I_v} \sum_{j=1}^{I} \left( \alpha_2(t_{vi}) - \alpha_1(t_{vi}) \right)^2}$$  \hspace{1cm} (3-58)

Strict adherence to the reaction scheme and the lack of any other systematic variations are therefore critical. Component conversions are recalculated for each datum $i$ by equating the right-hand side of Equation 3-57 to the measured weight using these updated $x$. All component conversions in Equation 3-57 that are not the subject of the calculation assume their values from the previous iteration. The entire procedure is repeated as many times as necessary, expanding the conversion ranges used for computation as the deconvolution improves. Overall convergence is said to be realised in about 10 – 15 iterations for most models (Mamleev et al., 2000b).

Similar exceptional results to those claimed for single-step model fitting are reported for the method’s application to perfect simulated data, but not for real data. Predicted conversion rate maxima do not align with those in the real data (Lefebvre et al., 2005), an incorrectly-shaped mechanism is selected (Bourbigot et al., 2002) and in one instance only the integral signal of conversion is presented such that the quality of the fit cannot be fairly judged (Mamleev et al., 2000b). Bourbigot et al. (2002) acknowledge the poor correlation to real thermal degradation data for cotton but draw strong conclusions regardless; in fact, the inconvenient geometry for diffusion implied by their optimisation
procedure is simply replaced by that deemed physically more likely (Bourbigot et al., 2002). These less than impressive results do raise questions regarding the stability and general applicability of the algorithm.

Deconvoluting peaks in the real conversion rate data using statistical functions before kinetic analysis can avoid many of these problems. Provided these functions precisely match the curvature of the data and do not smooth anything but noise (Vyazovkin et al., 2011), they effectively allow the treatment for overlapping independent processes to become as simple as that for multiple simulated single-step processes. Perejón et al. (2011) find that it is imperative to employ statistical functions capable of modelling asymmetry (e.g. Fraser-Suzuki) rather than the relatively inflexible symmetrical Lorentzian and Gaussian functions commonly used in this context (Burnham et al., 2004, Perejón et al., 2011). These researchers favour the use of Combined Kinetic Analysis, which means the apparent inability of this method to accommodate linear or acceleratory Pn mechanisms becomes moot since these statistical functions cannot either. While the residuals are very small following the deconvolution of rate data for the thermal dehydrochlorination of PVC (Perejón et al., 2011), it is noted that the curvature is not a precise match.

Ensuring the uniqueness and authenticity of the final solution is of mounting concern as the number of processes in the scheme increases. It is pertinent to question whether the reduction in residual sum of squares and the precision of the data justifies increasing the mutual correlation between model parameters before confirming an additional process (Vyazovkin et al., 2011). If J mechanisms are considered for P independent processes, there are J^P different permutations to consider, notwithstanding the variations that could arise by weighting the individual processes differently. Mamleev et al. (2000b) reduce the number of permutations to J^2 + (P – 2)J by optimising the first two overlapped processes before calculating the impact of the third, and so on (Mamleev et al., 2000b, Lefebvre et al., 2005). A process that overlaps with more than one process on either side would not be discriminated using this simplified approach. In the case of peak deconvolution followed by Combined Kinetic Analysis, there are no permutations for the P independent processes as such; correlation back to the real data is of more concern.

It is concerning to see how easily independent processes may be fitted to complex schemes that are actually constructed from sequential or competing processes. Anomalies can be hard to identify without knowing the underlying mechanism, e.g. an invalid isoconversional principle may only be identifiable from a subtle low frequency oscillation in E(α) (Burnham and Dinh, 2007). The indeterminate nature of
complex kinetics perhaps explains how an interpretive error has been promulgated in the literature by
the same research group who do not validate single-step kinetics before applying the IKP method
(Section 3.4.6). They have the impression that since $A_{inv}$ and $E_{inv}$ are invariant with respect to
mechanism, multiple mechanisms can be associated with these parameters at the same time to create
a complex system of independent processes (Richard-Campisi et al., 1996, Siat et al., 1997, Almeras et
al., 2002). Richard-Campisi et al. (1996) further consolidate this error by weighting mechanisms
according to their arbitrarily normalised probabilities (Section 3.4.4). That is, they assert that a
probability ($P(F_{i,n-1,n-1} > F_{j,n-1,n-1})$ of 80% for mechanism A2, say, means that there is 100%
probability of mechanism A2 contributing 80% to the overall rate of conversion, which is clearly at odds
with the mathematical meaning of Equation 3-48.

3.5 Concluding Remarks

It is a challenge to develop unbiased opinions of the literature, which is “often contradictory” (Burnham,
2000a) and does not generally elaborate on the precise manner of computation (Mamleev et al.,
2000a). Unfortunately, these issues lead to the preferential adoption of simple methods, and the harder
methods that are elaborated, regardless of merit.

Galwey has a somewhat cynical attitude towards the kinetic analysis field. He answers his own
question, “Is the science of thermal analysis kinetics based on solid foundations?” with a lengthy review
that he summarises as, “No” (Galwey, 2004). Vyazovkin is more forgiving and has a favourable attitude
towards isoconversional analysis in particular, which he has played a major part in progressing. The
conflict between Galwey and Vyazovkin is clear: Galwey incites a particularly vicious response from
Vyazovkin (Vyazovkin, 2003) after voicing his opinion that the introduction of the variable activation
energy concept is a “retrograde step” (Galwey, 2003a). Regardless, it is at least true that any method
applied to kinetic data should be understood in its entirety (Galwey, 2003b) and multiple calculation
methods should be used, if at all, in a complementary fashion rather than competitively (Brown et al.,
2000, Vyazovkin et al., 2011). The goal of kinetic analysis should be to correlate the computed
predictions to measurable or realistic attributes of the sample in question.

It is noted that Mamleev et al. (2000a) do not believe that it is possible to distinguish between three-
dimensional contraction and first order reaction mechanisms based on the output of their model fitting
algorithm to data synthesised from a first order model. Reference to Figure 5 in their article in fact
shows a clear difference between the two models. The philosophy that should be applied to any final
optimised solution is captured in Burnham’s article (Burnham, 2000b) where he describes a fit that is
“great, but not perfect”. Because the inverse kinetic problem is so ill-defined, any deviation indicates that the decomposition is more complex or follows a course not considered in the analysis. This philosophy is adopted for the new kinetic analysis method described in Chapter 5, in part because $F$-tests are included to judge the quality and uniqueness of the model fits with more reliability than that achievable by eye.

The necessity to carefully control thermal analysis experiments is highlighted with reference to compensation effects that commonly add to the uncertainty of computed kinetic triplets. Experimental methods described in the following chapter provide data input of sufficient quality. The IKP method is perceived as a reliable, “entirely adequate” (Vyazovkin et al., 2011) method to elucidate single-step kinetic parameters, and is therefore selected as the basis for the new kinetic analysis method. Revision of the relatively uncertain invariant pre-exponential factor can be achieved through model fitting and inclusive but careful selection of the function of conversion, also exemplified in the new method. The powers and limitations of isoconversional analysis are appreciated with respect to validating single-step kinetics and complex kinetic analysis. The simple approach of Friedman is deemed the most suitable isoconversional method to apply to the well-resolved data that are obtained from the thermogravimetric experiments on the flame retardant system investigated in this study.
4 Experimental Methodology

In order to utilise the new kinetic analysis method described in the following chapter, data sets comprising at least three different constant heating rate thermogravimetric (TG) experiments were required for the evaporation of water (method validation) and the components of the flame retardant (FR) system and plastic formulations. Complementary differential scanning calorimetric (DSC) and Fourier transform infrared spectroscopic (FTIR) data were collected simultaneously, as well as TG/DSC data for available molecular analogues of tetrabromobisphenol A bis(2,3-dibromopropyl ether) (TBBA-BDPE), to support the results of the kinetic analyses. Cone calorimetry was also used to acquire data characterising the fire performance of the commercial formulations for commentary in Section 7.4.2.

This chapter describes the samples themselves and the methods followed for the two simultaneous thermal analysers and the cone calorimeter used in this study. Section 3.1 identifies certain experimental considerations specific to simultaneous thermal analysis that are also addressed here.

4.1 Sample Formulations

4.1.1 PolyPacific Formulations

Formulations of flame-retarded polypropylene from PolyPacific were provided by the CSIRO Division of Manufacturing and Infrastructure Technology (Table 4-1). These formulations had been prepared by a large-scale extrusion process and were supplied as pellets, sticks and square plaques. Common additives for processing and UV stabilisation were present. TBBA-BDPE originated from Great Lakes Chemical Corporation, nominally 100%, and is referred to by its commercial name “PE-68”. The antimony trioxide (Sb₂O₃) synergist was included as an 80:20 w/w mixture with low density polyethylene (LDPE). All formulations were opaque off-white, brittle solids where opacity increased with FR concentration; Sb₂O₃ added brilliance, a blue tinge and softened the plastic somewhat.

Table 4-1: Compositions (wt\%) of the formulations supplied by PolyPacific

<table>
<thead>
<tr>
<th>FR Formulation</th>
<th>1707-7</th>
<th>1707-8</th>
<th>1707-9</th>
<th>1707-10</th>
<th>1707-11</th>
<th>1707-12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene Powder</td>
<td>94.65</td>
<td>89.45</td>
<td>84.25</td>
<td>79.05</td>
<td>93.15</td>
<td>92.15</td>
</tr>
<tr>
<td>Calcium Stearate</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Irgafos 168</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Irganox 1010</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Sb₂O₃:LDPE (80:20)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.5</td>
<td>2.5</td>
</tr>
<tr>
<td>PE-68</td>
<td>5.2</td>
<td>10.4</td>
<td>15.6</td>
<td>20.8</td>
<td>5.2</td>
<td>5.2</td>
</tr>
</tbody>
</table>
4.1.2 Additional Formulations Prepared at the CSIRO

The range of compositions was later expanded with formulations prepared at the CSIRO laboratories in Highett, Melbourne. Polypropylene powder used for these formulations contained the same loading of calcium stearate, Irgafos 168 and Irganox 1010 as indicated in Table 4-1 (0.05% each). Neat samples of the chemically stabilised polymer and PE-68 were also obtained for analysis.

Nominally 10 g extrusions of each formulation were prepared using a bench-scale co-rotating twin screw extruder with a two minute residence time. Each sample was held in the extruder for four minutes at 150 rpm and 190°C. Table 4-2 lists the formulations in processing order. The components were weighed using an electronic balance to an accuracy of ±0.01 g. Duplicates of two PolyPacific formulations (16 ≡ 1707-11 and 17 ≡ 1707-9) were also created a few days following the initial sample preparation so that the comparability of the results from both sets of formulations could be verified. The extruder output was not processed any further.

![Figure 4-1: (a) A sample of polypropylene exiting the extruder. (b) Colour variation between samples with different PE-68 loadings](image)

The FR was combined with Sb$_2$O$_3$ in the ratio 10.4:1.2 (i.e. that equivalent to 10.4:1.5 PE-68:(Sb$_2$O$_3$:LDPE)) without the complication of polypropylene. Due to the hardness of the Sb$_2$O$_3$:LDPE pellets, a 37.1 mg pellet was heated at 50°C/min to 520°C in the Q600 (Section 4.2.1) to reduce it to a fine powder residue. More than 95% of the LDPE was driven off. Since Sb$_2$O$_3$ transforms from its low temperature cubic form to an orthorhombic structure at about 556°C (Centers, 1988), it was considered unaltered. This residue (3.0 mg) was combined with PE-68 (26.0 mg) and was presumed to become a homogeneous mixture once the FR melted. This sample is labelled “PE-68/Sb$_2$O$_3$ Mixture”.

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Table 4-2: Compositions (wt%) of the formulations prepared at the CSIRO in processing order

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Stabilised Polypropylene Powder</th>
<th>PE-68</th>
<th>Sb2O3:LDPE (80:20)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>92.2</td>
<td>7.8</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>87.0</td>
<td>13.0</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>74.0</td>
<td>26.0</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>88.1</td>
<td>10.4</td>
<td>1.5</td>
</tr>
<tr>
<td>5</td>
<td>87.1</td>
<td>10.4</td>
<td>2.5</td>
</tr>
<tr>
<td>6</td>
<td>91.3</td>
<td>5.2</td>
<td>3.5</td>
</tr>
<tr>
<td>7</td>
<td>94.3</td>
<td>5.2</td>
<td>0.5</td>
</tr>
<tr>
<td>8</td>
<td>77.7</td>
<td>20.8</td>
<td>1.5</td>
</tr>
<tr>
<td>9</td>
<td>76.7</td>
<td>20.8</td>
<td>2.5</td>
</tr>
<tr>
<td>10</td>
<td>82.9</td>
<td>15.6</td>
<td>1.5</td>
</tr>
<tr>
<td>11</td>
<td>81.9</td>
<td>15.6</td>
<td>2.5</td>
</tr>
<tr>
<td>12</td>
<td>Polypropylene run through extruder</td>
<td>68.8</td>
<td>31.2</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>80.9</td>
<td>15.6</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>86.1</td>
<td>10.4</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>75.7</td>
<td>20.8</td>
</tr>
<tr>
<td>16</td>
<td>Polypropylene run through extruder and collected</td>
<td>93.3</td>
<td>5.2</td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>84.4</td>
<td>15.6</td>
</tr>
</tbody>
</table>

4.1.3 Flame Retardant Analogues

Bisphenol A dipropyl ether (BA-DPE; Figure 4-3a) and tetrabromobisphenol A dipropyl ether (TBBA-DPE; Figure 4-3b) were synthesised from stocks of bisphenol A (BA; Sigma-Aldrich; white granulated solid; 99+%) and tetrabromobisphenol A (TBBA; Sigma-Aldrich; white granulated solid; 97%). These compounds were received in milligram quantities manufactured according to the scheme shown in Figure 4-2 (X ≡ H or X ≡ Br). Unfortunately, the selectivity of the organic processes did not allow bromine atoms to be added to the propyl groups without also contaminating the aromatic rings, as required to synthesise bisphenol A bis(2,3-dibromopropyl ether).

Figure 4-2: Synthesis scheme for (tetrabromo)bisphenol A propyl ether
Bisphenol A diglycidyl ether (BADGE; Sigma-Aldrich; clear liquid; ~97%; Figure 4-3c) was also acquired.

Figure 4-3: (a) Bisphenol A dipropyl ether (b) Tetrabromobisphenol A dipropyl ether (c) Bisphenol A diglycidyl ether

4.2 Simultaneous Thermal Analysis

4.2.1 TG/DSC Set 1

Simultaneous TG/DSC experiments were initially conducted on the pelletised PolyPacific formulations (Table 4-1) using the TA Instruments SDT Q600 based at the CSIRO in Highett, Melbourne. This instrument has sample and reference balance beams configured within a horizontal furnace (Figure 4-4). For each test, a small shaving of sample material (5.5 – 7.3 mg) was placed in a 110 μL platinum crucible on the sample beam. An identical platinum crucible on the reference beam was charged with approximately the same weight of powdered alumina. All temperature programs were constructed as:

1. Equilibrate at 40°C
2. Ramp at 20°C/min to 140°C
3. Ramp at 2, 5 or 20°C/min to 600°C
4. Air cool

A digitally controlled 100.0 ± 0.1 mL/min flow of nitrogen maintained the sample and reference materials in an inert atmosphere.
Data sets were collected for all formulations in Table 4-1 for the above specifications with a ramp of 20°C/min at Step 3 of the temperature program. Only formulations 1707-7 to 1707-10 were also run with a ramp of 5°C/min at Step 3, and 1707-8 was run again at 2°C/min. Note that these tests precisely replicated the method used at the CSIRO two months prior to collect data for all formulations in Table 4-1 with a heating rate of 10°C/min at Step 3. These data were made available to this study.

The Q600 had a set sampling interval of five seconds that supplied data signals comprised of a maximum of 2800 points for a Step 3 ramp of 2°C/min, to a minimum of 350 points at 20°C/min.

4.2.2 TG/FTIR

The Q600 was coupled with a Nicolet FTIR spectrometer fitted with a mercury-cadmium-telluride detector for a limited time. After replicating the experimental setup of “TG/DSC Set 1” for Sample 2 in Table 4-2 using a heating rate of 10°C/min at Step 3, nitrogen flow was throttled to 50.0 ± 0.1 mL/min to accommodate the FTIR. The interface between the instruments was maintained at 180°C. Background IR signals were averaged from 512 scans collected before each experiment. Spectra were linked from 40 scans collected at 30 second intervals. Wavenumber resolution was 0.5 cm⁻¹.

Sample 2 from Table 4-2 (4.7 – 9.1 mg), neat polypropylene powder and the collected extrusion (9.2 – 12.8 mg), granulated PE-68 (10.0 – 16.0 mg), an Sb₂O₃:LDPE pellet (25.9 mg) and the sample “PE-68/Sb₂O₃ Mixture” (25.0 mg) were all tested at 10°C/min.
4.2.3 TG/DSC Set 2

The vast majority of thermal analysis experiments were undertaken using the single-stem vertical furnace Setaram Labsys TG-DTA/DSC in the School of Chemical Engineering at The University of Adelaide. The two gas inlets of the Labsys were connected to cylinders of instrument-grade nitrogen and air to allow for easy switching between inert and oxidative atmospheres (mixing NOT supported). Supply pressure was always regulated to 1.5 bar. Gas flow rate was manually adjusted before each experiment with the corresponding inlet needle valve and indicated on a downstream rotameter. This rotameter was particularly susceptible to tacky condensable gas and required frequent cleaning. Nylex tubing that carried the effluent would also perish periodically. Removable components that carried the effluent were rinsed/sonicated with a solvent (e.g. ethanol or white spirits) as the need arose. The lack of digital control and the unavoidable build up of tar significantly impacted on the stability of the gas flow rate, which was very sensitive to operating pressure. However, the flow rate tended not to deviate by more than 5% when the rotameter, Labsys components and Nylex tubing were in good condition.

Two 1600ºC TG-DSC probes were utilised. The first was broken shortly after it was commissioned and had to be replaced. Temperature correction and transducer sensitivity calibrations were performed in accordance with the Labsys manual (Setaram, 2004) with supplied metal standards (indium, tin, lead, zinc, aluminium and silver). Data for the temperature correction and sensitivity calibrations were acquired simultaneously from the DSC signal. Both these aspects of commissioning were expected to depend on the crucible type and the nature and flow rate of the gas (Setaram, 2004), but ultimately all calibration results were found to be independent of gas flow rate. All experiments were conducted with 110 μL alumina crucibles. Presentation and appraisal of the calibration results are provided in Appendix A4.

Most temperature programs were run under nitrogen and had the structure:

1. Isotherm at 25ºC for 5 minutes
2. Ramp at \( \lambda ^{°} \text{C/min} \) to 600ºC
3. Isotherm at 600ºC for 10 minutes (initially excluded)
4. Ramp at 30°C/min to 20ºC

For very slow heating rates (<2ºC/min) and reasonably high onset temperatures, a faster ramp to an intermediate isotherm was added to shorten the overall length of the experiment. Data resolution varied automatically from 1 – 10 seconds to supply signals comprised of a minimum of 900 points.
For all experiments, the required width of the temperature range for the nominated constant ramp rate had to be discovered through trial-and-error. The residue (char) remaining each time a brominated compound was pyrolysed was best removed by raising the temperature quickly to 1000°C under 100 mL/min air. A higher flow rate was visibly more effective at cleaning the sample crucible and appeared to reduce the rate of condensate accumulation in the apparatus.

**Calcium Carbonate**

Calcium carbonate (7.9 – 11.2 mg) was decomposed under 33 mL/min nitrogen after each calibration according to the following temperature program:

1. Isotherm at 20 or 25°C for 20 minutes
2. Ramp at 30°C/min to 1000°C
3. Ramp at 30°C/min to 20°C

The above experiments were designed to confirm that the Labsys generated typical results and also to track any progressive changes in output.

**Water**

Milli-Q water (61.8 – 70.8 mg) was evaporated at 0.5, 1, 2, 3 and 5°C/min under nitrogen at 100 mL/min as a means to validate the kinetic analysis method for a weight loss associated with a large endotherm.

**PE-68**

Characterising the flame retardant, PE-68, was the primary focus. A wide range of PE-68 sample weights were used (2.4 – 44.8 mg) at 0.5, 2, 3, 5, 7, 10, 15, 20 and 40°C/min under both 33 mL/min and 100 mL/min nitrogen, but the majority of experiments were conducted using 10 – 16 mg at 10°C/min. PE-68 (29.1 – 30.5 mg) was also combusted in 33 mL/min air at 2 and 10°C/min. The effect of switching the atmosphere from nitrogen to air at 310°C and 350°C during a 10°C/min ramp for PE-68 samples of 11.0 – 11.3 mg was assessed.

**FR Analogues**

Decomposition of the parent compound of PE-68, TBBA (10.3 – 29.3 mg), was compared at 10°C/min under 100 mL/min nitrogen. Other available chemical analogues, BADGE (10.7 – 12.3 mg) and TBBA-DPE (11.3 mg) were analysed at 10°C/min; BA-DPE (10.2 – 18.1 mg) at 5, 10 and 20°C/min all under 100 mL/min nitrogen.

**Polypropylene**

The extruded polypropylene sample (12.8 – 16.7 mg) was decomposed under 100 mL/min nitrogen at 5, 7, 10, 15 and 20°C/min specifically to provide comprehensive input for the kinetic analysis method.
FR Formulations

Sample 3 (6.3 – 26.0 mg), Sample 12 (6.8 – 23.6 mg) and Sample 17 (7.7 mg) from Table 4-2 were pyrolysed at 5°C/min also under 100 mL/min nitrogen, representing a range of different PE-68 loadings. Sample 12 (7.1 – 8.3 mg) was also decomposed under the same conditions at 10°C/min, as was Sample 16 (7.8 mg) at 20°C/min purely to verify the comparability of the results from the Q600. PolyPacific formulation 1707-8 (5.4 – 21.0 mg) was pyrolysed under nitrogen at 1.5 bar prior to the installation of the rotameter with an un-calibrated 800°C TG-DSC probe as an initial test of the comparability and to explore the effects of sample weight variation.

4.2.4 Experimental Considerations

For the analysers in this study, heat flux was inferred from the temperature differential between sample and reference crucibles with the aid of a sensitivity calibration (Appendix A4). Both analysers support very high temperature applications and therefore suffer from poor sensitivity and a greater susceptibility to problems caused by asymmetrical thermal expansion, such as thermal drift (Cattiaux, 2010).

Experimental hindrances to collecting good quality thermodynamic data are substantive compared to thermogravimetry. The baseline indeterminacy alluded to in Section 3.1 can relate to jumps that occur in direct proportion to the heating rate and thermal mass of the sample, heat capacity dependence on temperature, irreversible chemical changes altering the thermal mass and thermal drift (Bandara, 1986, Reutzel-Edens, 2004, Cattiaux, 2010), all of which were evidenced in the collected data. The effects of heating rate step changes were avoided by setting the temperatures at which they occurred well below that of any expected thermal event. Sensible heat effects cannot be eliminated with blank runs unless an inert material with precisely the same heat capacity is used; even then, the reduction in thermal mass as the sample degrades cannot be corrected in this manner. Mathematical correction is possible if the compounds involved and their thermal properties are known (Bandara, 1986). In this study these effects were left uncorrected.

The majority of experimental runs were paired with blank runs using the same experimental configuration and temperature program to roughly subtract the effects of buoyancy and thermal asymmetry. Subtraction of a corresponding baseline run from both the TG and heat flow signals essentially negated the influence of the alumina reference material, if it was used. Some experiments did not have a baseline subtracted because either the heating rate was deemed slow enough for it to be redundant (0.5°C/min) or the purpose of the particular experiment did not require such accuracy (e.g. confirming the temperature range of weight loss).
Alumina crucibles were used in the Setaram analyser in four different configurations: with or without alumina of a similar weight to the sample in the reference crucible, and with or without small pieces of aluminium foil (~3 mg) pressed firmly over both sample and reference crucibles. Whether the reference crucible was empty or charged with crushed alumina ultimately made no difference to the corrected signals. Foil coverings vastly improved the thermal separation of the crucibles, even though they were not hermetic seals, and were used when sample enthalpy was to be computed from the experiment.

4.3 Cone Calorimetry

The CSIRO fire testing laboratories in Highett houses a cone calorimeter to obtain heat release rates, effective heats of combustion, CO and CO₂ concentrations, weight loss profiles, smoke formation rates and ignition delays in accordance with AS/NZS 3837:1998 (Section 2.4.2). This apparatus differs from the conventional calorimeter specifications, as shown in Figure 4-5. Changing the flow system from induced-draft (vacuum) to forced-draft (pressurised) by repositioning the fan is the main alteration, which enables tests to be carried out at sub-atmospheric oxygen levels without necessitating an infallible seal around the chamber (Leonard et al., 2000).

Figure 4-5: Modified cone calorimetry experimental setup at the CSIRO (cf. Figure 2-1) (Copyright © 2000 John Wiley and Sons. Used with permission from Leonard et al. (2000))
Fire performance of all PolyPacific formulations (Table 4-1) was assessed using this apparatus at an atmospheric oxygen level (baseline of 20.95%). The O₂ analyser (operating at 108.4 Pa) and CO/CO₂ analyser were calibrated daily. Rather than methane, the calibration constant required for Equation 2-1 was derived daily from a 70 – 200 g aliquot of methanol. It was computed as 0.0414 – 0.0416. A standard-sized plaque of poly(methyl methacrylate) charged with carbon black was combusted at 50 kW/m² (756°C) after each calibration run to check the normality of the output signals. No abnormalities were cited at any stage.

An irradiance of 25 kW/m² (575°C) was selected for the sample tests and a piezo spark igniter was used to ignite the volatiles. Conditioned sample plaques (11.5 – 13.3 g) that were manufactured smaller than standard (50 x 50 x 6 mm vs. 100 x 100 x 25 mm) were placed on a kaolin board with sufficient kaowool packing the sample holder to locate the top surface 25 mm below the base of the cone (Figure 4-6). Each sample plaque was wrapped in aluminium foil to leave only the top surface exposed to the heater and a lip of approximately 5 mm. As the sample liquefied, the foil served as a container to prevent the flow of sample and was generally effective.

Each test was preceded by a baseline recording of 75 seconds before the piezo spark igniter was ignited. Time to ignition was estimated by eye and the igniter was retracted from the sample once the combustion appeared to be self-sustaining. Each formulation was tested at least in triplicate. Data signals were resolved to five seconds for the average test duration of six minutes.

Figure 4-6: A 50 x 50 x 6 mm PolyPacific sample plaque undergoing combustion in the cone calorimeter
5 Kinetic Analysis Method

Chapter 3 highlights the indeterminism of the inverse kinetic problem and the dissent of prominent researchers in the field, as well as the lack of a thorough dissection of a trusted kinetic analysis method. These three factors prompted the development of a new method to treat the thermogravimetric (TG) data collected for the flame retardant system. One aim of the algorithm described in this chapter is to output one or a set of independent kinetic triplets using nominally constant heating rate TG experiments as input. The second aim is to critically assess the applicability/uniqueness of the kinetic output with reference to $F$-statistics. Developing a new algorithm is advantageous in that the inherent difficulties associated with kinetic analysis can be properly explored and a comprehensive documentation of all required steps is possible. This addresses a perceived gap in the literature.

A flow diagram of the algorithm written in Visual Basic for Applications in Excel is presented in Figure 5-1 and Figure 5-2, which is stepped through in the subsequent sections of this chapter. A list of parameters must be populated before the code can be run that defines the location of critical data and controls the nature of the kinetic solution. Parameters of the latter subset are identified in purple in Figure 5-1 and Figure 5-2 at the instance of their first use, and throughout this chapter. Many definitions within the code such as convergence criteria and those governing the component conversion signal refinement can be tailored to suit different situations. Any values nominated here correspond to settings used for the validation.

To summarise the procedure: An Excel workbook must first be populated with multiple sheets of TG data and configured to certain specifications (Appendix A5.1). Weight, time and temperature signals for at least three TG experiments are required data input. These data are processed to obtain model-free kinetic parameters in accordance with the Invariant Kinetic Parameters (IKP) method (Section 3.4.6). A preset but customisable list of Arrhenius functions of conversion is integrated into this method. The IKP, $A_{inv}$ and $E_{inv}$, are then associated with each listed function of conversion $j$ in turn and are optimised, if possible, to $A_j$ and $E_j$ with a unique model fitting algorithm. Apparent or user-defined kinetic parameters may be substituted for the IKP at this stage. Evaluation of the final models is achieved with $F$-testing and the best fitting models may be visually inspected for their correlation back to the original data before finalising the solution. If multiple processes have been enabled in the calculation and overlap, the entire algorithm must be run repeatedly until the solution converges.

The Visual Basic code is commented and reproduced in its entirety in Appendix A5.2.
A New Adaptation of The Method of Invariant Kinetic Parameters and its Application to a Flame Retardant System

Figure 5-1: Flow chart for the algorithm “Data Preparation and Invariant Kinetic Parameter Determination”. Each rectangle and diamond is colour coded to indicate how many times its block of code must be run (key supplied)
Figure 5-2: Flow chart for the algorithm “Model Fitting and Kinetic Solution Evaluation”. Each rectangle and diamond is colour coded to indicate how many times its block of code must be run (key supplied in Figure 5-1).
5.1 Data Preparation

The most critical parameter shaping how the TG data is processed is the maximum number of processes used in the kinetic model (HighProcess). Multiple independent processes (HighProcess > 1) should be considered if the rate of weight loss (conversion rate) does not reduce to zero between maxima, or if an isoconversional analysis identifies activation energy as a significant function of conversion (Section 3.4.2). The layout of the algorithm is such that an educated guess must be made prior to being presented with the results of the Friedman isoconversional analysis.

The user is also obligated to input estimates for onset and completion temperatures on every data sheet for each process, preferably by inspecting the signal for rate of weight loss where these temperatures appear the most distinct. Differential scanning calorimetric (DSC) data can also be referenced for this purpose.

5.1.1 Noise Estimation

Noise in the weight signal ($\Delta m_v$) is defined to be within the scope of the maximum excursion from a linear regression of this signal up to the onset temperature that the user nominates. If any discontinuities/anomalies are observed in the weight signal at low temperature, the option to exclude data from the regression calculation below a certain temperature is available. This calculation is only performed on the first iteration. No dependence on weight or temperature is accommodated, but the magnitude of the noise is evaluated independently for each spreadsheet (i.e. heating rate/experiment). Overall weight change is contracted by $2\Delta m_v$.

5.1.2 Initialisation Direct from TG Data

Initialising a realistic solution set for $P$ overlapped process from TG data is not trivial. The conversion function for each component process $p$ must be derived from a selected portion of the weight signal and associated with some fraction $x_p$ of the overall weight loss. Applying the concept of a “separation point” (Mamleev et al., 2000b), which in actuality is a measure of $x_p$ (Section 3.4.7), requires the completion of one stage and the onset of the next to be set to the same temperature. This algorithm has no such restriction. For each process, weight loss is normalised to the total weight lost between the user-specified onset and completion temperatures to define the component conversion signal ($\alpha_{pvi}$); $x_p$ is set to the proportion of the overall weight loss that occurs over this active temperature range. The complete set of fractions is rescaled to sum to unity. Noise is accounted for, but any distortion caused by overlapping processes is neglected at this stage.
In further contrast to the algorithm presented by Mamleev et al. (2000b), the distribution of weight fractions is allowed to vary with the experiment counter \( v \) (i.e. \( x_p \rightarrow x_{pv} \)), accommodating parallel processes that are balanced differently from sample to sample. This flexibility should highlight whether the same kinetic scheme is suitable across multiple experiments and eliminate “averaging” errors, with particular benefit to the kinetic analysis of non-uniform samples.

For iterations following the first, the weight fractions are set to the results of the optimisation described in Section 5.5.4.

5.1.3 Component Conversion Signal Refinement

Inaccuracies in the initial component conversions and fractions caused by poor specification of onset and completion temperatures can be minimised by referencing these solution sets back to the TG data. Component conversions \( (\alpha_{pvi}) \) are recalculated from the overall experimental conversion \( (\alpha_{vi}) \) and the rest of the solution using a normalised arrangement of Equation 3-57 extended to \( P \) processes:

\[
\alpha_{p*vi} = \frac{1}{x_{p*v}} \left( \alpha_{vi} - \sum_{p=1}^{P} x_{pv} \alpha_{pvi} \right)
\]

After a signal is recreated according to Equation 5-1, the data range of at least five rows in size covering the greatest continual increase in conversion is assigned to the process. Changes within the scope of the noise and insignificant pauses or down trends (less than 50 rows where conversion does not increase or less than five rows of down trends) are ignored. Noise in terms of conversion is amplified in inverse proportion to \( x_{pv} \). The range is terminated if the conversion has been static for long enough (more than 10 rows) and another process becomes active to preserve the quality of the component conversion signal. This signal is then rescaled such that it covers the full range from 0 to 1, plus excursions equivalent to the noise. The already refined signals for \( p < p^* \) are substituted into Equation 5-1 so that the final solution set is internally consistent and the sequential nature of the calculation can be exploited.
The option to omit a process is provided if a viable and unique range is not apparent following the transformation of Equation 5-1. Since more than one process can give the illusion of single-step kinetics, the choice to remove a process should be one later confirmed by the isoconversional analysis. In the case of well separated processes, or only one active process, this refinement algorithm entirely eliminates errors induced by poor specification of onset and completion temperatures, as the weight fractions are also recalculated based on the updated active range(s) at this stage of the first iteration. Excessive overlap and the associated signal distortion may prompt the user to bypass this algorithm entirely. However, the signals must be refined in this manner in any subsequent iteration in order to progress the optimisation of the kinetic solution. This manner of improving the specification of the kinetic problem is thought to eliminate the need to seek independent optimised solutions for every permutation, as Mamleev et al. (2000b) imply is necessary.

5.1.4 Incomplete Process Accommodation

The case where the end of the weight signal does not correspond to the complete conversion of a process is addressed in a limited capacity. Experiment(s) where one particular process is incomplete will at this stage erroneously show complete conversion signals for this component \( \tilde{\alpha}_{p*vi} \) and overall \( \tilde{\alpha}_{vi} \), as well as a fraction for the process \( p^* \) computed based on this situation \( \tilde{x}_{p*} \). Provided the weight fraction distribution from at least one experiment can be used as a basis for complete conversion, each affected component conversion signal can be recalculated:

\[
\alpha_{p*vi} = \tilde{\alpha}_{p*vi} \left( 1 - x_{p*} \right) \left( \frac{\tilde{x}_{p*}}{1 - \tilde{x}_{p*}} \right) \tag{5-2}
\]

As such, it must be assumed that \( x_p \) are invariant with respect to the experiment counter (hence dropping the subscript \( vi \)). Overall conversion must also be recalculated for the affected experiments:

\[
\alpha_{vi} = \tilde{\alpha}_{vi} \left( 1 - x_{p*} \left( 1 - \tilde{x}_{p*} \right) \right) \tag{5-3}
\]

These signal transformations are activated automatically if a component conversion signal does not plateau and the above condition is met.
5.1.5 Temperature Signal Adjustment

Sample temperature can differ from the thermocouple temperature or exhibit a significant gradient through the sample (Section 3.1), raising the question of how best to utilise the temperature signal in the kinetic analysis. The temperature signal should correspond to the sample surface temperature if the thermocouple (measured) temperature has been corrected using metal standards in accordance with Appendix A4 (Bockhorn et al., 1999b). Following data pre-processing outlined under the preceding headings, a pseudo-dynamic energy balance may be employed to develop an approximate signal for the sample temperature at the centreline of the cylindrical crucible:

\[
T(t_i) \approx T_m(t_0) + \left( t_i - t_0 \right) - \frac{C_p \rho R^2}{4k_c} \Delta T_m \frac{\Delta \rho}{\Delta t} - \frac{\rho R^2}{4k_c} \sum_{p=1}^{p} \Delta H_{R,p} x_p \frac{\Delta \alpha_p}{\Delta t}
\]

where \( \frac{\Delta X}{\Delta t} = \text{Slope}(X_{i-1} : X_{i+j}, t_{i-1} : t_{i+j}); \quad X = T_m, \alpha_p \)

Note that the subscript \( v \) is dropped for clarity and, in this instance, the entirety of the sample is considered reactive (i.e. initial weight is readjusted to \( m_0 = m_0 - m_x \)).

Equation 5-4 is designed merely to provide an indication of the centreline temperature, as the transient nature of the equation is effectively ignored to make the problem easily tractable (Appendix A3.1). The omission of the lag from surface to centre means that Equation 5-4 is particularly inaccurate while the heating rate is not constant; however, this effect is mitigated by recalculating the linear driving forces at each row.

The parameters required as constant user inputs are:

- Sample density \((\rho)\)
- Sample heat capacity \((C_p)\)
- Sample thermal conductivity \((k_c)\)
- Inside crucible radius \((R)\)
- Enthalpy of reaction(s) \((\Delta H_{R,p})\)
Obviously the first three constants listed represent physical properties that are likely to be functions of temperature and no doubt change as the sample transforms. It is recommended that these parameters are selected to give a “worst case” estimate of the centreline temperature. Enthalpy of reaction(s) can be estimated from an integrated simultaneous DSC signal that has had a calibration applied. While Bockhorn et al. (1999b) correlate the sample weight loss solely to a decrease in density, here density and sample diameter are considered constant and the sample depth is thought to reduce, as that interpretation seems more compatible with the physical reality for a contained molten sample. Equation 5-4 implies that the sample supplies/absorbs all the energy associated with the enthalpy changes regardless of sample size. No axial flow of energy is included nor are the effects of any currents in the melt. The solution according to Equation 5-4 is truly “worst case”.

The facility to compute bulk sample temperature if the measured temperature is taken as that of the furnace atmosphere and refractory is also provided:

\[
T(t) \approx \frac{\Delta T_m}{\Delta t} (t - t_0) + \sum_{p=1}^{n} K_p \frac{\Delta \alpha_p}{\Delta t} \left(1 - e^{-\frac{(t-t_0)}{\tau}}\right) + T(t_0) e^{-\frac{(t-t_0)}{\tau}}
\]

where \( \tau = \frac{\bar{m}_i C_p}{[h + 4\sigma \varepsilon [T_m(t_i)]^\gamma] A} \)
and \( K_p = \frac{\Delta H_{R,p} x_p \bar{m}_i}{[h + 4\sigma \varepsilon [T_m(t_i)]^\gamma] A} \);

either for \( A = \pi R^2 \) (Axial) or \( A = \frac{2\bar{m} R_0}{\rho R^2} \) (Radial);

\( \bar{m}_i = \frac{m_{i-1} + m_i}{2} - m_x \)

Thermal equilibrium is assumed initially and the linear driving forces are defined as for Equation 5-4.

The additional constants appearing in Equation 5-5 are:

- Outside crucible radius \((R_0)\)
- Convective heat transfer coefficient \((h)\)
- Stefan-Boltzmann constant \((\sigma)\)
- Emissivity \((\varepsilon)\)

Again, selecting parameters for a “worst case” scenario is recommended, i.e. those that correspond to the highest reasonable time constant \( \tau \) in Equation 5-5. Heat transfer is calculated strictly in either the radial direction or the axial direction, not both. Convective and radiative modes of heat transfer may be activated, but the thermal resistivity and heat capacity of the crucible must be neglected to retain a simple explicit relationship between sample temperature and time. This can be justified by the fact that
the heat transfer rate would be about 8,000 W/m²K through a 2 mm thick alumina crucible wall (Askeland, 1998), which is over twenty times higher than the highest radiative transfer rate of 38 W/m²K at 600°C (Section 3.1). Confounding thermal effects due to thinner platinum crucibles (used in the TA Instruments Q600) would be even less of a concern.

The weight averaged over the preceding and current row has the residual weight subtracted in order to remain in keeping with the specification of zero weight at 100% conversion. There is no “residual” weight if an incomplete process is identified. If a residue is observed, a Boolean variable in the code can be easily switched so that the residue is not subtracted and is accommodated properly in the calculation (Appendix A5.2). Note that the radial solution is independent of average weight.

If there is effectively no noise, the most accurate versions of Equation 5-4 and Equation 5-5 are obtained by setting \( j \) to zero. Noisy data can be dealt with by increasing \( j \) and thus the number of rows of data over which the linear driving forces of measured temperature and conversion are computed. These linear driving forces are fixed \( j \) rows from the last row (if sample still remains in the crucible) and the remaining elements of the temperature signal are calculated by incrementing \( t_i \). Calculated temperature is set to the measured temperature if/when no sample remains.

Temperature signal selection for the subsequent kinetic analysis is left to the user. Ideally, it should be left unaltered then set to the calculated signal in independent applications of the algorithm. Another approach is to restrict the computational range(s) to the zone where the calculated temperature does not deviate significantly from that dictated by the nominal heating rate.

### 5.2 Friedman Isoconversional Analysis

A Friedman isoconversional analysis is performed on the TG data according to the method outlined in Section 3.4.2. This method is selected over the integral methods also presented in Section 3.4.2 as the TG data should be of high enough quality that there is no reason not to take advantage of its purity and simplicity. Prior to running the algorithm, the user must specify the highest overall conversion (IsoconvMax) and the number of equidistant points between 0 and this value (NoPoints) that will be used to create \( E(\alpha) \). Overall conversion is differentiated with respect to time using a quadratic Savitzky-Golay filter (Savitzky and Golay, 1964) fitted to a user-defined, odd number of points \( N(\text{FilterN}) \):

\[
E(\alpha) = \frac{d}{dt} \ln(1 - \alpha)
\]
The greater the noise, the more points should be used to fit the filter. Each $E_\alpha$ is illustrated with a 95% confidence interval computed from the standard error in the slope of the corresponding linear regression and the relevant $t$-statistic. These intervals allow the significance of trends in activation energy with conversion to be judged from a sound basis.

Application of the Friedman method does not directly impact on the mathematical outcome of the kinetic analysis. However, as the computation is effectively paused after this and the IKP analysis, its purpose is to help the user take stock of whether the solution is consistent at this stage, and in particular, whether the number of processes specified is reasonable. If not, the algorithm can be aborted and restarted with different user specifications. Assuming nil or negligible changes to the temperature signal and avoidance of the “incomplete process” aspect of data pre-processing, a Friedman analysis need only be run on the first iteration as it utilises overall conversion rate that is independent of the predicted kinetic solution.

### 5.3 IKP Adaptation

#### 5.3.1 Limited Computational Ranges

As documented in Section 3.4.6, the IKP method should only be applied to (overall) conversion ranges where $E(\alpha)$ is constant within reasonable limits of uncertainty, i.e. to TG data most likely manifesting from single-step kinetics. A continuous computational range (LowerCompLimit to UpperCompLimit) must be assigned to each process in terms of its component conversion from the outset. If multiple processes are active and a computational range is found to interfere with the conversion range $0.1 – 99.9\%$ (i.e. Sig to $1 – \text{Sig}$) of any other process(es), it will be automatically contracted such that it does not, provided the contracted range consists of a sufficient number of rows (more than 10) to develop a reliable solution.

The final range(s) utilised in the IKP method should be compared with the results of the isoconversional analysis on the first iteration prior to running the model fitting algorithm. Wider/different computational ranges can be set for subsequent iterations as the solution resolves in a similar manner to the algorithm presented by Mamleev et al. (2000b) for complex kinetics (Section 3.4.7). The effects of any interfering
process(es) should be cancelled out when Equation 5-1 is applied if the previously computed kinetic solution is sufficiently accurate. The choice of computational range is then not as critical.

### 5.3.2 Temperature Integral Approximation

The IKP method requires sets of apparent kinetic parameters to describe the artificial compensation effects of Equation 3-50. A linear model fitting method specific to constant heating rate experiments is selected to generate these parameters (Equation 3-35), which calls for an approximation to the temperature integral. Orfao’s very accurate fourth order rational approximation (Equation 3-24) is chosen that must be evaluated iteratively. It is initialised using the Murray and White approximation ($Q\left(\frac{k_j}{RT}\right) = 1$), also discussed in Section 3.4.1. Selecting a highly accurate implicit approximation incurs practically no computational time penalty compared to an explicit approximation; the solution behaves as expected and converges very rapidly. Furthermore, it is a trivial exercise to adapt the algorithm to suit an iterative solution.

Note that the end of the computational range is automatically reset to the row where the maximum temperature is recorded if the range would otherwise extend beyond this to assist in confining the data to the zone of constant heating rate.

### 5.3.3 Functions of Conversion

A wide range of functions of conversion must be used to generate the artificial compensation effects, irrespective of their likely correspondence to the TG data to be analysed (Section 3.4.6). As such, the preset list of 22 functions (HighMech = 22) is not expected to be altered; however, the diffusion mechanisms are deliberately listed last so that they are the easiest to exclude if a super correlation is poor and does not suggest any diffusion mechanisms are active (i.e. the IKP are vastly different from all the diffusion apparent kinetic parameters).

All 22 functions of conversion and rate constant interpretations are presented in Table 5-1 with the detail necessary to promote an informed interpretation of analysis results. While the conceptual meanings of the rate constant ($k$) and order ($n$) included in Table 5-1 can be found in the text of some articles, they are not readily accessible. A list of assumptions critical to the development of the idealised equations for $f(\alpha)$ and $g(\alpha)$ has not been cited in the literature at all but is clearly relevant. The origins of these assumptions are detailed in Appendix A2.
Table 5-1: Physical depiction, TG signal shapes, equations and critical assumptions for each model. Note \( f(\alpha) = \frac{1}{k} \frac{d\alpha}{dt} \) and \( g(\alpha) = \int_{0}^{\alpha} \frac{d\alpha}{f(\alpha)} = kt \) where \( k = A \exp\left(-\frac{E}{RT}\right) \)

**P^3/A P1 P2 P3 P4**  
Nucleation and Unrestricted Nucleus Growth: Power Law (Pn)

1. Only valid at the beginning of the process \((k_t << 1, \text{ where } k_t \text{ refers to the rate constant for the } n^{th} \text{ decomposition step, or the growth rate constant, } k_G, \text{ once } i \geq p)\)

2. Nucleation is irreversible and occurs only at initial potential nucleation sites \((N_0(0))\)

3. All germ nuclei \((N_i, 0 \leq i < p)\) of the same size have the same first order activity

4. Growth rate constant \((k_G)\) is independent of nucleus size and extent of conversion

5. Product density and nucleus shape are constant regardless of nucleus size

\[ f(\alpha) = n\alpha^{1-n} \quad g(\alpha) = \alpha^{\frac{1}{n}} \]

\[ k = \left(\frac{\alpha^{1-n}k_Gk_{p-1}k_{p-2}...k_0N_0(0)}{V(\infty)(p+\lambda)!}\right)^{\frac{1}{n}} \]

\[ n = p + \lambda \]

\[ p: \text{ number of decomposition steps or product molecules required for a growth nucleus} \]

\[ \lambda: \text{ number of dimensions controlling nuclei grow} \]

\[ \sigma: \text{ shape factor (} \frac{4}{3} \pi \text{ for spherical growth)} \]

\[ V(\infty): \text{ product volume when reaction is complete} \]

**A1 A^3/A A2 A3 A4**  
Nucleation and Nucleus Growth: Avrami Erofe'ev (An)

1. Assumptions 1-5 for Pn mechanisms apply

2. Nucleation and nucleus growth are purely random

3. Fraction of Pn rate reduction due to nuclei ingestion and coalescence increases linearly from zero to one as conversion increases from zero to one:

\[ \frac{d\alpha}{dt} = (1-\alpha)\frac{d\alpha_{p_n}}{dt} \]

*\(k\) and \(n\) as for Pn mechanisms
A New Adaptation of The Method of Invariant Kinetic Parameters and Its Application to a Flame Retardant System

P-T Nucleus Growth and Autocatalysis: Prout-Tompkins (P-T)

1. Potential nucleation sites within defect-free material \((N_0)\) have either all nucleated initially \((N(0) = N_0)\) or nucleate much slower than nuclei catalyse the formation of new nucleation sites (branching).

2. Conversion is initialised as a small non-zero value.

3. Active nuclei branch and terminate via first order kinetics:

\[ k_i = k \frac{\alpha}{\alpha_i} \]

where \(k\) is the constant of proportionality relating rate of nuclei branching to number of active branches if termination rate is zero.

\(\alpha_i\): conversion at the time of inflection, \(t_i\), for any isothermal experiment with a rate constant \(k\). Final conversion = \(2 \alpha_i\)

4. Conversion rate is directly proportional to the number of active nuclei branches.

\[ f(\alpha) = \alpha \left(1 - \frac{\alpha}{2\alpha_i}\right) \]

\[ g(\alpha) = \ln \left(\frac{\alpha}{2\alpha_i - \alpha}\right) + kt_i \]

\[ k: \text{constant of proportionality relating rate of nuclei branching to number of active branches if termination rate is zero} \]

\(\alpha_i\): conversion at the time of inflection, \(t_i\), for any isothermal experiment with a rate constant \(k\). Final conversion = \(2 \alpha_i\)

Constant Heating Rate

R1 R2 R3 Contracting Volume: One-, Two- and Three-Dimensional (Rn)

1. Reactant consists of any number of 100% reactive particles of uniform size, reactivity, shape and density.

2. The dimensions that contract are equivalent.

3. Weight is lost from the outer surface of the particles.

4. Inert material is permitted only as a separate substrate.

\[ f(\alpha) = n(1 - \alpha)^{1/2} \]

\[ g(\alpha) = 1 - (1 - \alpha)^{\frac{1}{n}} \]

\(k\): fractional rate of reduction in any one of the \(n\) dimensions.

\(n\): number of equivalent contracting dimensions.
### Kinetic Analysis Method

**F0 F1 F2 F3 Reaction Order: Zero, First, Second and Third (Fn)**

1. The concept of “concentration” is meaningful in the reactant phase
2. \( xX + yY + zZ \rightarrow \text{Products} \)

#### Notable Connections to Other Mechanisms

- **F0 (n = 0)** is equivalent to \( R_1 \) and \( P_1 \) (conceptually \( p = 0 \) and \( \lambda = 1 \))
- **F1 (n = 1)** is equivalent to \( A_1 \) (conceptually \( p = 1 \) and \( \lambda = 0 \))

All \( R_n \) forms can be expressed in terms of \( F_n \) forms according to

\[
F_n = \left[ \frac{n}{n_g} \right]^{1-n} \left( 1 - n \right) \]

#### Constant Heating Rate

\[
k = k' [X_0]^{-x} [Y_0]^{y} [Z_0]^{z}; \quad n = x + y + z
\]

\( k' \): analogous to a homogeneous rate constant with respect to reactant \( X \)

### Random Scission: Minimum Length of Non-Volatile Chain (L)

1. Only polymer backbone bonds are thermally labile and break via first order kinetics
2. Probability of radical transfer and termination are very high compared to propagation (low kinetic chain length)
3. Termination only via disproportionation
4. Radical numbers are steady, both overall and for each chain length
5. No radicals volatilise before further reaction; polymer chains of less than \( L \) backbone atoms in length volatilise instantly
6. Polymer chains initially are identical in length and much longer than \( L \)
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D1(*) D2(*) D3(*) Diffusion and Anti-Diffusion: One-, Two- and Three-Dimensional (Dn, Dn*)

D1, D1*:
\[
f(\alpha) = \frac{1}{\alpha} \quad g(\alpha) = \frac{\gamma}{2} \alpha^2
\]

D2: \[
f(\alpha) = \left[ -\ln \left( 1 - \alpha \right)^{\gamma} \right]^{-1} \quad g(\alpha) = \frac{\gamma}{2} \left[ \frac{(1 + \alpha) \ln(1 + \alpha) - \alpha}{1 - \alpha} \right]
\]

D2*: \[
f(\alpha) = \left[ \ln \left( 1 + \alpha \right)^{\gamma} \right]^{-1} \quad g(\alpha) = \frac{\gamma}{2} \left[ 1 + \frac{\alpha}{1 - \alpha} \left( 1 - \alpha \right)^{\gamma} \right]
\]

D3: \[
f(\alpha) = \left[ 1 - \left( 1 - \alpha \right)^{\gamma} \right]^{-1} \quad g(\alpha) = \frac{\gamma}{2} \left[ 1 + \frac{\alpha}{1 + \alpha} \right] \left( 1 - \alpha \right)^{\gamma}
\]

D3*: \[
f(\alpha) = \left[ 1 - \left( 1 + \alpha \right)^{\gamma} \right]^{-1} \quad g(\alpha) = \frac{\gamma}{2} \left[ 1 + \frac{\alpha}{1 + \alpha} \right] \left( 1 + \alpha \right)^{\gamma}
\]

1. Reactant \( A \) consists of any number of particles of uniform size, shape and density
2. Fick's Law is applicable in \( A \) equivalent dimensions
3. Equal reactant and product molar volumes
4. An evenly distributed product layer \( P \) grows from \( r_2 \) towards the centre of the particle \( r_1 \) (variable) that is the cause of the diffusive resistance
5. Diffusing reactant or product concentration \( C \) is constant at \( r_1 \) and zero at \( r_2 \)

4*. An evenly distributed product layer \( P \) deposits outwards from \( r_1 \) \((r_2 \text{ variable})\), hollowing out the particle, that is the cause of the diffusive resistance
5*. Diffusing reactant concentration \( C \) in the continuous phase is constant at \( r_2 \) and zero at \( r_1 \)

\[ D: \text{diffusivity through product layer} \]
\[ \rho_A: \text{density of dispersed phase reactant} \]

All TG signals were generated using \( A = 10^{10} \text{ min}^{-1} \) and \( E = 100 \text{ kJ/mol} \), except P-T where \( A = 10^7 \text{ min}^{-1} \) and \( E = 10 \text{ kJ/mol} \) for \( k_t = 10 \). Isothermal temperature was set to 450ºC and heating rate to 10ºC/min. \( L(T) = [2.7e^{0.0035T} - 2] \) to match linear alkane normal boiling points. In this illustration \( L \) ranges from 10 to 13. Categorisation: Acceleratory, deceleratory, sigmoidal and linear

†To account for different molar volumes for \( aA \rightarrow pP \), replace \( \alpha \) with \( zM \), where

\[ z = \frac{pM_p}{\rho_p} \quad \rho_v \quad M_x: \text{molecular weight of} \ x \]

‡See Appendix A2.7 for modification to \( k \)

*Alternate conditions for anti-diffusion
The IKP method has not been seen associated with the Prout-Tompkins mechanism in the literature, and certainly not with a random scission scheme (Appendix A2.6) that allows the minimum length of non-volatile chain \( L \) to vary with temperature, or at the least take on any value aside from two. A computationally expensive numerical solution is necessary to solve for \( f(x(\alpha, L), L) \) and \( g(x(\alpha, L)) \) for \( L \neq 2 \) that is not penalised any further by setting \( L = L(T) \). This numerical solution is included in this algorithm, although considering its expense, provision is made to exclude it (by setting Scission = 0) if its correspondence to the data under analysis is highly improbable.

As discussed in Appendix A2.3, the Prout-Tompkins mechanism must include a constant term that should be derived from an isothermal experiment. If such an experiment is available, it is proposed that the constant is assigned to the time to the inflection point in the conversion signal multiplied by an estimated invariant rate constant at that temperature. This implies running the algorithm to the point of finding the IKP, aborting the analysis and restarting it with the estimated constant. Ambiguity associated with \( t_i \) and the invariant pre-exponential factor in particular translates to high uncertainty. Without an isothermal experiment, it is recommended that \( k_{ti} \) is set to a value that returns apparent kinetic parameters that are similar to the IKP and, if possible, significant linear \( F \)-statistics in order to give the Prout-Tompkins mechanism the best chance of corresponding to the experimental data.

5.3.4 Linear \( F \)-Testing

Every apparent kinetic solution is independently \( F \)-tested by applying Equation 3-38. The model that returns the highest \( F \)-statistic for each experiment and process is highlighted in yellow and, given no other basis for comparison, models returning \( F \)-statistics within an order of magnitude of this maximum are also highlighted in light yellow as statistically significant. The formatting of the program output in Excel relating to these intermediate statistics is exemplified in the following chapter (e.g. Table 6-4).

5.3.5 Invariant Kinetic Parameters

Activation energy and the natural logarithm of pre-exponential factor obtained from each super correlation (Equation 3-51) are presented with 95% confidence intervals computed in the same manner as those for \( E_\alpha \). The uncertainty in pre-exponential factor is therefore asymmetric.

It is recognised that the definition of pre-exponential factor varies depending on whether \( f(\alpha) \) or \( g(\alpha) \) is normalised with respect to any of the constants of integration. However, the uncertainty inherent in the pre-exponential factor is likely to overwhelm any small integration constant, particularly if it is unrefined.
5.4 Model Fitting Refinement

The clear existence of a super correlation (Equation 3-51), implying that the kinetic solution does not vary with heating rate, means that the analysis can legitimately proceed to model fitting. This algorithm attempts to fit the raw weight signals as far as is practicable rather than simplify these signals using statistical distributions (Section 3.4.7). Multiple processes are treated in isolation at this stage. Each experiment is also treated independently until the shape assessments (Section 5.4.5) are complete and the kinetic parameters are due to be modified or evaluated.

If refinement is requested, the goal is to associate each function of conversion in Table 5-1 with the pair of kinetic parameters that creates the best match to the maximum or median experimentally-derived conversion rates in terms of magnitude and location on the temperature scale. Minimum discrepancy between model and experimentally-derived conversion at these points is also sought. Complete solutions for every model must be generated according to the algorithm reported in Section 5.4.3 whether refinement is requested or not.

It should be highlighted that while constant heating rate experiments are requisite for the accuracy of the IKP method, the refinement process has no such limitation. Creating a heating rate signal by numerically differentiating temperature with respect to time achieves this flexibility in part.

5.4.1 Shape Classification (Experimental)

Shape of the experimentally-derived component conversion signal is classified following two applications of the Savitzky-Golay filter (Equation 5-6) to yield rate and curvature signals. Holoborodko’s self-proclaimed noise robust filter for a second derivative may be called instead (Holoborodko, 2010):

\[
\alpha''(t_i) \approx 2^{-N} \sum_{n=1}^{N-1} n^2 s(n) \left( \frac{\alpha_{i+n} + \alpha_{i-n} - 2\alpha_i}{(t_{i+n} - t_{i-n})^2} \right), \text{ for } N \geq 5
\]

where

\[
s(n) = \frac{[2N-10]s(n+1) - [N+2n+3]s(n+2)}{N-2n-1}, \quad s\left(\frac{N-1}{2}\right) = 1, \quad s\left(\frac{N+1}{2}\right) = 0
\]

Better noise handling is achieved for the case studies with real data using the Savitzky-Golay filter.
Whether the curvature is positive (concave up), negative (concave down) or mixed (encompasses at least one functional maximum) in the predetermined computational range are the classification criteria. In the case of mixed curvature, the existence of a true maximum conversion rate is only assumed if the curvature changes sign once. If multiple zeros in the curvature signal are apparent, the user is shown a plot of the rate and curvature signals and must indicate whether the maximum conversion rate is to be considered true or an artefact of the noise.

The row where the true maximum rate occurs is recorded if its existence is assumed or confirmed by the user. Otherwise, the row corresponding to the median conversion rate is recorded. To minimise the errors caused by poor correspondence of the conversion range end points to the user-defined limits, the limits are contracted to match the lowest and highest conversions in the range.

5.4.2 Kinetic Parameter Initialisation

The user is allowed to initialise the kinetic parameters to the IKP, the apparent kinetic parameters averaged over all the experiments or values of their own choosing. Considering the invariant pre-exponential factor in particular may be significantly in error, if the IKP are used, refinement is critical. Averaged apparent kinetic parameters are considered the fairest choice for initialisation, particularly if the isoconversional analysis has a high degree of associated uncertainty, as they are tailored to each function of conversion. Refinement of averaged apparent parameters may be considered more optional.

In the case of a two-process analysis, it is recommended that user-defined activation energies are set to the minimum and maximum indicated $E_\alpha$ from the Friedman isoconversional analysis. The compensation effects calculated for the first sheet of experimental data are used to provide reasonable suggestions for pre-exponential factors as they are likely to be otherwise unstipulated.

5.4.3 Kinetic Solution Generation

As rate of change of conversion and conversion are interrelated, their solutions must be sought iteratively. This computationally expensive process is chosen in preference to applying a shortcut such as the “auxiliary function” (Mamleev et al., 2000a) (Equation 3-40), which is by definition inconsistent for all but the correct kinetic triplet. Referencing rigorous kinetic solutions that are internally consistent promotes more confidence in the optimisation results.

The practice of setting an arbitrary small value for conversion for, say, the second data row and calculating a starting rate based on this conversion was tested and cannot be recommended. No matter
how small this value is, the temperature range over which a simulated decomposition occurs is
unnaturally dependent for many mechanism types, particularly those that are initially acceleratory. This
strong dependency raises doubts regarding the validity of other means of initiation seen in the literature,
such as defining an induction period before the mechanism proper that is visually consistent with the
experimental data (Appendix A2.8), or adding in a “q-factor” to the Sestak-Berggren equation (Burnham
and Dinh, 2007):

\[ f(\alpha) = (1 - \alpha)^q [1 - q(1 - \alpha)]^\alpha \] 5-8

Explicit Euler and fourth order Runge-Kutta methods were both trialled and found to be unsuitable due
to this dependency on initial value(s). Pérez-Maqueda et al. (2002) and Budrugeac et al. (2007) state
that they simulate data with a fourth order Runge-Kutta method built in to Mathcad that is presumed to
be implicit. If it is not, it may explain why both studies omit the purely acceleratory power law (Pn) from
the table of available solid-state mechanisms.

The implicit, stable midpoint integration method (Equation 5-9) is used on the basis that it has a higher
order of accuracy at no additional computational expense compared to the backwards Euler method
that was also trialled.

\[ \alpha(t_{i+1}) = \alpha(t_i) + (t_{i+1} - t_i)\alpha'(t_i) \frac{\alpha(t_i) + \alpha(t_{i+1})}{2}, \text{ where } \alpha(t_0) = 0 \] 5-9

For the Prout-Tompkins mechanism, if the integral function of conversion is zeroed at the first row of
data as is the case for all other models in Table 5-1, conversion must be initialised as a function of the
integration constant:

\[ g(\alpha_0) = \ln\left( \frac{\alpha(t_0)}{1 - \alpha(t_0)} \right) + k t_i = 0 \quad \Rightarrow \quad \alpha(t_0) = \frac{\exp(-k t_i)}{1 + \exp(-k t_i)} \] 5-10

Two factors influence the integrity of the solution: The validity of the conversion initialisation and the
data resolution, particularly when fast processes are concerned. Conversion at the second row is
initialised to the user-defined conversion precision (e.g. XPrecision = 10^-6) for all but the Prout-
Tompkins mechanism and is recalculated according to Equation 5-9 until either convergence, the rate
equation becomes incalculable, or the iteration counter reaches a preset limit. If the rate equation
becomes incalculable and conversion has not exceeded one, it is set to zero and an attempt to iterate to a non-zero conversion is made for the next row, and so on. If conversion does not converge before the preset iteration limit, the last calculated value is set for that row and the user is notified of the quality of the convergence. This same procedure is followed for all subsequent rows until conversion reaches or exceeds one, minus the conversion precision. Conversion is always initialised to that of the preceding row once this value is non-zero.

For acceleratory processes, the solution diverges if the result of the preceding iteration is assigned to \( \alpha_{(i+1)} \) and used to estimate a new value for \( \alpha_{(i+\frac{1}{2})} \). Setting \( \alpha_{(i+1)} \) to the average of the last two iterations instead solves this problem. Random scission with \( L = L(T) \) requires the computation of a signal for the fraction of bonds broken according to a first order model, followed by a simple transformation to conversion.

This algorithm effectively deals with difficult to initiate functions of conversion that are zero at zero conversion. Complete simulations agree with those generated using the temperature integral approximation of Orfao (Equation 3-24) that is considered exact. Values for conversion satisfying this integral equation are found by minimising the difference between the analytical integral form of the relevant rate equation and the approximation at each row (from Khawam and Flanagan (2005c), although their Equation 15 is in error):

\[
g(\alpha) \frac{AE}{\beta R} - p\left(\frac{E}{RT}\right) = \min
\]

Solution generation with Equation 5-11 consumes similar computational time compared with the midpoint integration technique selected. Numerical integration is more flexible as it is valid not just for constant heating rate experiments. Even constant heating rate experiments cannot replicate the specified temperature program perfectly.

### 5.4.4 Shape Classification (Prediction)

Predicted conversion rate signals are calculated by substituting the converged solutions directly into the rate equations. Every rate signal can be differentiated analytically to give an exact expression for curvature. The same classification and row selection criteria are used for these kinetic solutions using the conversion limits saved following the classification of the experimentally-derived component conversion signal. No provisions are made for artefactual maxima as these are calculated signals. If a
maximum rate does not exist between the conversion limits, the first instance where the signal passes through the median rate is recorded.

5.4.5 Shape Assessment

It is sensible to include only those models that can match the shape of the experimentally-derived component conversion signal within the computational range. Outside this range, the data may be of insufficient quality for curvature to be indicative of the underlying model. Dollimore et al. (1992) subscribe to this idea and base inclusion on such parameters as the conversion at its functional maximum rate, the asymmetry of the conversion rate peak and whether the onset and completion temperatures are sharp or diffuse. However, these parameters are not always available, particularly in the case of complex kinetics. It is believed possible to automate model inclusion more generally and accurately.

Provided an artefactual maximum is not identified when a true maximum is confirmed in any other data sheet, and either the entire computational range or a true maximum is encompassed, the shape assessment proceeds. This is simply a matter of accepting each kinetic model that has the same type of curvature as the experimentally-derived signal (positive, negative or mixed; presence or not of a confirmed zero). If the maximum is artefactual, then all models will be passed due to the implied poor quality of the signal. Note that the kinetic parameters will influence the model shape to some extent so they need to be reasonably accurate.

Predicted conversion at the recorded point (maximum or median conversion rate) must be within the wide bounds of ±0.2 from the matching point in the experimentally-derived component conversion signal to be deemed similar enough for a model to pass the shape assessment. At least one instance of a pass is required to attempt to refine the kinetic parameters.

5.4.6 Pre-exponential Factor Refinement

If refinement is requested, pre-exponential factors for passed models are recalculated under the presumption that \( A_j \) is entirely responsible for the discrepancies between the conversion rates and temperatures at the selected points:
A New Adaptation of The Method of Invariant Kinetic Parameters and its Application to a Flame Retardant System

\[ a_j = \frac{d\alpha_j}{dt} \approx A \exp\left(\frac{-E_j}{RT_j}\right) f_j(\alpha_*) \]

\[ \frac{d\alpha_j(t_*)}{dt} \approx A_j \exp\left(\frac{-E_j}{RT_j}\right) f_j(\alpha_j(t_*)) \]

\[ A \approx a_j \exp\left(\frac{E_j}{RT_*} \left[ \frac{1}{T_j} - 1 \right] \right) \frac{f_j(\alpha_j(t_*))}{f_j(\alpha_*)} A_j; \quad T_j = \frac{T_*}{T_j} \]

where \( i^* \) is the point recorded for the experimentally-derived conversion signal and \( ij^* \) is the corresponding point for model \( j \)

\( A \) and \( E \) are considered the unknown optimal kinetic parameters. Equation 5-13 will only be accurate as far as the resolution allows if the function of conversion and activation energy are correct.

This simple one-step refinement correlates the kinetic parameters with much more accuracy than the compensation effect, and effectively reduces the uncertainty in pre-exponential factor to a comparable level to that of activation energy. Pre-exponential factors for each model are averaged over all available experiments, as by definition the kinetic parameters cannot vary with heating rate.

Avoiding the use of a point that could be affected by another process (likely towards the limits of the computational range) is desirable and motivates the choice of a median rate in the case of no functional maximum. Essentially, this optimisation algorithm represents an extreme case of weighting variation with conversion. Modification to include more points can be accomplished with ease.

The kinetic parameters must be calculated as pairs. That is, when activation energy is changed and a kinetic solution is subsequently regenerated, pre-exponential factor must be refined with Equation 5-13 and a new kinetic solution generated before evaluation.

### 5.4.7 Activation Energy Refinement

As is true for the pre-exponential factor refinement, this aspect of the procedure is conducted independently for as many models as initially pass the shape assessment. An activation energy, or more precisely, a pair of kinetic parameters, is sought in the vicinity of the initial input that minimises the residual sum of squares between the conversions of the experimentally-derived and predicted signals at \( T_j^* \) over all the available experiments. This simply means that conversion is matched as accurately as possible at the selected point.
In the first instance, the residual sums of squares are compared for three pairs of kinetic parameters centred on the refined input with a constant interval of $E_{\text{Step}} = 2\%$ between the activation energies (i.e. 98\%, 100\% and 102\% of input $E$). Activation energy is then stepped in the direction of the best matched solution such that a constant interval is maintained between the two best activation energies and this new activation energy. If the central pair is the best matching, the step size is halved by setting the new activation energy halfway between the two best activation energies. Kinetic solutions (generated from refined pre-exponential factors in all cases) are evaluated against one another in sets of threes in this manner until the solution converges or fails and must be reset. The approach to the final model is therefore tested from above and below as a matter of course, as recommended in the literature (Section 3.4.4).

### 5.4.8 Model Convergence/Failure

Residual sums of squares with respect to conversion at the selected point are computed before and after pre-exponential factor refinement. If the variance does not reduce after pre-exponential factor refinement for any of the first three activation energy trials, the associated model will default to the input kinetic parameters. Either Equation 5-12 is inappropriate or the input parameters are already at an optimum in this case.

If Equation 5-13 does lead to a reduction in the residual sum of squares for at least the input activation energy, the pre-exponential factor default is reset to this first refined value.

The model is classified as failed and the kinetic parameters are reset to their defaults if either:

- A specified activation energy does not allow the model to pass the shape assessment before or after the application of Equation 5-13; or
- Too many iterations (>50) have been computed (with a stricter limit of 10 if the stepping interval for activation energy has not been at least halved)

The model is classified as converged and the lowest and highest activation energies of the current set of three are used to define a minimum possible uncertainty if either:

- Activation energy has converged to better than five significant figures; or
- Temperature reaches its resolution limit for any experiment (i.e. $T_j = 1$)
Every model that initially passes the shape assessment is presented with a superscript attached to the mechanism code indicating whether the best possible Arrhenius parameters are unrefined (°), only refined with respect to pre-exponential factor (¹) or both refined (²). As many superscripts as there are processes are printed in order for each included model. The output as described doubles as mechanism labels for the table showing the non-linear relative probabilities and linear $F$-statistics (Section 5.5.3).

### 5.5 Final Model Evaluation

The best version of each model that initially passes the shape assessment is available for selection regardless of the result of the refinement procedure. If no models pass on the first iteration, then all 22 unrefined models are considered. Statistics relating to the relative and absolute quality of the fit should be used to confirm that the chosen set of $P$ models is clearly the best permutation to describe the TG data and, if applicable, supply to the next iteration of the entire algorithm. Conversions and conversion rates are shown graphically to assist the user with this evaluation.

#### 5.5.1 Identifying the Most Probable Model(s)

Every viable permutation for the $P$ processes is considered in full detail so that the most complex case of $22^P$ distinct sets of overlapping processes can be fairly assessed. Viable permutations refer to the subset that includes only those process/model combinations marked for evaluation. Residual sums of squares between overall experimental and predicted conversions are computed according to Equation 3-39 using the current distribution of weight fractions. Although these permutations are applicable to the whole of every TG data set, the user is asked to limit the conversion range of the summations to either the previously defined computational range or the entire active range ($X_{Precision}$ to $1 - X_{Precision}$) with respect to each process in turn. Choosing the entire active range is recommended, unless there is a specific reason to exclude data outside the narrower computational limits, as the permutations are discriminated better and more critically with this option. The most probable model for the subject process is assigned based on the permutation that yields the minimum residual sum of squares over the chosen range. Ideally, the results for each process should point to the same permutation. The user is notified if this is not the case.

This level of rigor is unnecessary if multiple processes have been specified but do not overlap. Other process/model combinations that are inconsequential to the model selection for a particular process are
marked as such if the user is informed of an apparent inconsistency in permutation selection. In the case of a single process, the concept of “rigor” in this context is not relevant.

There is scope to transform the elements of the residual sums using the weighting function suggested by Mamleev et al. (Equation 3-46). The factor required for this transformation is derived very simply:

\[
\phi_j = \psi_j \frac{1}{g_j(\alpha)} \frac{dg_j(\alpha)}{d\alpha} \left(\frac{1}{(\alpha_{\psi} + \alpha(t_{vi}))^{1/2}}\right) = \frac{\psi_j}{f_j(\alpha)g_j(\alpha)} \left(\frac{1}{(\alpha_{\psi} + \alpha(t_{vi}))^{1/2}}\right)
\]

Mechanism \(j\) and the component conversion in Equation 5-14 are chosen as those of the model and process currently the subject of the residual sum of squares calculation. If the permutations were not associated with a particular process, then this choice would not be as trivial.

The final version of the algorithm does not apply the transformation of Equation 5-14 where \(\psi_j = 1\) because of the concern that allowing the extremes of conversion to contribute more statistically would lead to erratic results for anything but perfectly simulated weight signals (Section 3.4.4). Even for a perfect simulation, the distortions primarily at low and high conversions caused by incorrect assignment of component conversions and/or weight fraction distributions would be penalised more by this weighting function. Furthermore, the reported ability to relate smaller residuals to more accurate activation energies (Section 3.4.4) is made redundant by the isoconversional and IKP analyses.

In the unlikely event that none of the model predictions overlap with the experimentally-derived component conversion signal for a particular process, rate ratios collected and averaged over all the available experiments \((A_j)\) are used to set the most probable model. The unrefined model with a rate ratio closest to unity on a logarithmic basis is chosen. If not even this can be executed because no models initially pass the shape assessment, the unrefined first order model is set. Of course if this is necessary, the chance of the predicted conversion matching the TG data well is extremely unlikely.

### 5.5.2 Linear F-Testing

\(F\)-statistics are calculated in an identical manner to that for the IKP method using the sets of unrefined and refined (if requested) kinetic parameters for all 22 functions of conversion. As the kinetic parameters are not considered apparent at this stage, the \(F\)-statistics are averaged over all experiments. Only the model with the highest \(F\)-statistic is highlighted in yellow for each set. An indicator of the overall solution
validity is the positive correspondence of the highlighted model(s) in the set of finalised kinetic parameters to the most probable model(s) predicted from the above non-linear method.

To assist with determining which permutations to consider in the finalisation, $F$-statistics for every model with activation energy within the 95% confidence interval of the corresponding invariant activation energy are printed in bold.

### 5.5.3 Probabilities Relative to the Most Probable Model

It is possible to judge how well the most probable model can be differentiated from other models by fitting the ratios of the non-linear variances to the applicable $F$-distribution (Equation 3-48). Assuming the most probable model only deviates randomly from the true solution (i.e. the model is correct), its $F$-statistic is legitimately one and the tail area of the $F$-distribution from this point is exactly half of the total area under the probability density function. Therefore, rather than subscribe to the arbitrary normalisation criticised in Section 3.4.4, all probabilities arising from integrating the tail of the $F$-distribution up to an $F$-statistic by definition greater than or equal to one are simply doubled. Then the fact that only half of the probability density function is admissible is properly accounted for and the most probable model will automatically be assigned a probability of $P(F > 1) = 100\%$ (highlighted in yellow). The $F$-statistic defining 95% of the tail area from $F_{j^*} = 1$ is used to demarcate the statistically significant models (e.g. Figure 5-3), which are highlighted in light yellow in the table generated by the algorithm. Many examples of this output, including the use of yellow highlights and bold mentioned in Section 5.5.2, and the labelling described in Section 5.4.8, are presented in the following two chapters.

![Figure 5-3: The probability density function and doubled cumulative distribution for an F-distribution with four degrees of freedom (i.e. five experiments). Any model with F-statistic between the dotted yellow lines ($1 < F_j < 9.6$) is within the 95% confidence interval of the most probable model $j^*$](image-url)
Variances are affected by the choice of permutation in the case of multiple overlapping processes. To eliminate any unknown bias, the same model associations as those for the best fitting permutation are retained for the other processes when evaluating each viable model for the subject process. If none of the viable models overlap with the subject process, then all the probabilities will be identical and reinforce the message that differentiation is impossible.

5.5.4 Finalisation

An essential part of the predicted kinetic solution finalisation is the re-optimisation of the distribution of weight fractions using, by default, the most probable model for each process. As before, each experiment is treated independently. Rather than compute new distributions directly from Equation 3-58 (modified so that it does not average across all experiments), each $x_{pv}$ is optimised using the bisection method beginning with the three points 0, 0.5 and 1. The residual sum of squares between overall experimental and predicted conversion over the active range of process $p$ is the quantity minimised, translating to a reapplication of Equation 5-1. Weight fractions that are not the subject of the optimisation retain the values they held previously. If any $x_{pv}$ are altered, then the entire procedure must be repeated until the distribution is internally consistent. If this is not achieved within 100 iterations then the previous distribution must stand. Note that a solution set found using this bisection method is not rescaled. Failure of the weight fractions to sum to unity or converge at all is an indication of the inadequacy of the permutation.

Inconsistent or poorly differentiated statistics cannot be overlooked if they arise. It is recommended that the user consults the whole statistical picture and requests the visualisation of full kinetic solutions for any permutations of significance when prompted. Correlations between the conversion rate signals for any experiment can be inspected graphically before deciding whether to supersede the most probable model predictions. Any superseding model has its linear $F$-statistic highlighted in green (e.g. Table 7-3). The user may then choose to send the final selected permutation and associated weight fraction distribution to the next iteration in an attempt to resolve a unique, highly probable solution. Depending on the nature of the statistical picture, the user may instead rerun the entire algorithm with different user inputs (number of processes, computational ranges, etc.). It is possible to add or substitute a specific Sestak-Berggren equation (Section 3.3.1) into the list of 22 functions of conversion derived from, for example, a Combined Kinetic Analysis (Section 3.4.5).
5.6 Concluding Remarks

Developing kinetic analysis software from scratch promotes circumspection in a field that has been criticised as lacking in that regard. The complete and detailed description supplied here should help novice researchers appreciate what is required of a kinetic analysis method, even one designed for no more complication than overlapped independent Arrhenius processes.

It is possible for an ostensibly single-step weight loss to in fact be the manifestation of two or more overlapped processes, such as the simulation for the ICTAC project (Brown et al., 2000) that is reproduced in the following chapter. This type of complexity can be identified from an isoconversional analysis. Reconciling the implications of the Friedman analysis with the statistics presented at every stage of the analysis is perhaps the most pertinent recommendation to be made. The omission of an isoconversional analysis in the article that inspired this algorithm (Mamleev et al., 2000b) is considered an oversight.

Only weight signals arising from the summation of independent modes of weight loss, each described by their own Arrhenius kinetic triplet, may be properly characterised with this method. The following chapter shows how this algorithm performs when analysing synthesised variants of this type of data. When interpreting the results from real data inputs, it is important to be able to justify the weight loss through other means and be willing to accept failure when faced with an inconclusive statistical output. This is also exemplified in the following chapter.
6 Kinetic Analysis Method Validation

This nuanced kinetic analysis algorithm evolved into its final form through careful application to synthesised and real thermogravimetric (TG) data. Trial-and-error was used to develop the best performance possible in all the scenarios tested and described in this chapter. Synthetic TG data were used as the primary bases for validation. Noisy data signals were simulated and used in the development phase so that the algorithm was robust enough to treat real data with reasonable but finite signal-to-noise ratios. In this chapter, analysis results for the evaporation of water are shown as well as those for calcium carbonate decomposition, where the latter analysis was performed on TG data appropriated from literature. This enabled direct comparisons to be made to previous attempts to model the same data.

6.1 Synthetic Data

Any valid kinetic analysis method must be capable of reliably returning the kinetic models used to simulate TG data. This is the “only way” (Vyazovkin, 2000) to truly validate a method, as real TG data will always be associated with errors and uncertainties that are impossible to quantify exactly. Care must be taken to simulate the TG data correctly, or else a method may be perceived as validated when in actuality the simulation does not correspond to the chosen kinetic model(s). Numerical integration according to the midpoint method described in Section 5.4.3 was employed to simulate the following kinetic solutions.

6.1.1 Non-Overlapped Models

Two models were selected to simulate a simple case where decomposition stages do not overlap (Figure 6-1). The kinetic triplets are:

\[ A_1 = 1.3367 \times 10^{12} \text{ min}^{-1}; \quad E_1 = 139.662 \text{ kJ/mol}; \quad \text{Mechanism A}\frac{3}{2} \]
\[ A_2 = 8.374 \times 10^7 \text{ min}^{-1}; \quad E_2 = 139.085 \text{ kJ/mol}; \quad \text{Mechanism P4} \]

The first model (Model 1) was assigned a 70% weight fraction. TG data were created in Excel for heating rates of 2, 5, 7, 10, 15 and 20°C/min with a resolution of six seconds at 2°C/min. This resolution was scaled in inverse proportion to heating rate to maintain a consistent number of data rows in every sheet (reminiscent of how the Labsys collected data (Section 4.2.3)). An isotherm at 40°C was set for the first 40 rows in each case before imposing the heating rate up to a maximum temperature of 600°C (~2900 rows).
It was essential to verify that the algorithm could accurately pre-process the TG data for this simple case, i.e. return the conversion signals and weight fractions of the simulation without error regardless of the quality of the user input. Very poor initial temperature specifications, at some heating rates not coinciding with a weight loss range at all, were used to test this ability. The simulation was also ended prematurely (overall conversion at 84% at 600°C) for the heating rate of 20°C/min to verify the “incomplete process” aspect of data pre-processing (Section 5.1.4). Both these challenges were successfully overcome by the algorithm; the conversion signals and weight fractions derived from the TG data resolved to match the simulation precisely for every data sheet.

Kinetic solution summaries for the first and only required iteration of the algorithm based on this “perfect” pre-processed data are presented in Table 6-1. The Savitzky-Golay filter length was set conservatively as 11 rows. The two options available for kinetic parameter initialisation were tested, namely averaged apparent and invariant kinetic parameters (IKP). As expected, the averaged apparent kinetic parameters associated with the correct mechanisms were already highly accurate and could not be refined any further. Simulated and predicted conversion rates overlay perfectly for the solutions finalised with averaged apparent kinetic parameters and refined IKP.
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Table 6-1: Predicted most probable kinetic triplets and weight fraction distributions for the non-overlapped models case study initialised with different kinetic parameters

<table>
<thead>
<tr>
<th></th>
<th>MODEL 1</th>
<th>MODEL 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulation</td>
<td>Simulation</td>
<td>Simulation</td>
</tr>
<tr>
<td>$E$ (kJ/mol)</td>
<td>139.662</td>
<td>139.085</td>
</tr>
<tr>
<td></td>
<td>$139.665 \pm 0.001$</td>
<td>$139.088 \pm 0.004$</td>
</tr>
<tr>
<td></td>
<td>$138.9 \pm 0.3$</td>
<td>$132 \pm 10$</td>
</tr>
<tr>
<td></td>
<td>$139.60 \pm 0.02$</td>
<td>$139.17 \pm 0.02$</td>
</tr>
<tr>
<td>$A$ (min$^{-1}$)</td>
<td>$1.3367 \times 10^{12}$</td>
<td>$8.374 \times 10^{7}$</td>
</tr>
<tr>
<td></td>
<td>$(1.3374 \pm 0.0003) \times 10^{12}$</td>
<td>$(8.378 \pm 0.006) \times 10^{7}$</td>
</tr>
<tr>
<td></td>
<td>$(6.5 \pm 0.4) \times 10^{11}$</td>
<td>$&lt; 30 \times 10^{7}$</td>
</tr>
<tr>
<td></td>
<td>$1.32 \times 10^{12}$</td>
<td>$8.49 \times 10^{7}$</td>
</tr>
<tr>
<td>Mechanism</td>
<td>$A^{3/2}$</td>
<td>P4</td>
</tr>
<tr>
<td></td>
<td>$A^{3/2}$</td>
<td>P4</td>
</tr>
<tr>
<td></td>
<td>$A^{1}, F1$</td>
<td>P4</td>
</tr>
<tr>
<td></td>
<td>$A^{3/2}$</td>
<td>P4</td>
</tr>
<tr>
<td>Weight (%)</td>
<td>70.0</td>
<td>30.0</td>
</tr>
<tr>
<td></td>
<td>70.0</td>
<td>30.0</td>
</tr>
<tr>
<td></td>
<td>85.4 – 85.8</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>70.0</td>
<td>29.7 – 29.9</td>
</tr>
</tbody>
</table>

$^*$Average values. Uncertainty is equated to the observed variation in the apparent parameters across all heating rates

$^*$Uncertainty matches the 95% confidence intervals in the slope and intercept from the super correlation

$^#$Optimistic estimation for activation energy uncertainty defined by the temperature resolution limit

Figure 6-2: Conversion rate at 2°C/min illustrating the error arising from the IKP solution set. Regenerated conversion rates using the apparent kinetic parameters and refined IKP (Table 6-1) coincide with the simulation exactly

Figure 6-3: Friedman analysis for the non-overlapped models case study over heating rates of 2, 5, 7, 10, 15 and 20°C/min showing 95% confidence intervals. Activation energies for the three highest conversions exclude data for 20°C/min
Conversely, the unrefined invariant pre-exponential factor for the purely acceleratory P4 mechanism (Model 2) was calculated with an overwhelming uncertainty, and distinct errors in both the IKP for Model 1 led to incorrect mechanism selection (Table 6-1). Unrefined IKP coupled with an A1, F1 mechanism for Model 1 and the correct P4 mechanism for Model 2 are clearly inadequate at describing the simulation (Figure 6-2). This inadequacy caused an erroneous weight fraction distribution to be calculated; Model 2 was so far displaced along the temperature scale using the IKP that it was inactivated (i.e. $x_2 = 0$). Conversion rate rather than conversion signals are shown in Figure 6-2 as the discrepancies are then easier to see.

Activation energies for Model 1 and Model 2 were set to very similar values to judge whether a Friedman analysis could differentiate these after factoring in 95% confidence intervals. A large degree of uncertainty in activation energy well before changes due to Model 1 conclude at 70% overall conversion is apparent from the Friedman analysis (Figure 6-3). At 85.5% overall conversion, the 95% confidence interval is small enough to imply that the activation energy of $138.9 \pm 0.4$ kJ/mol is distinctly lower than the constant activation energy indicated up to at least 40% overall conversion ($E_{19\%} = 139.65 \pm 0.02$ kJ/mol). Of course, the presence of two independent weight loss stages can be readily discerned from the weight signals in this case (Figure 6-1); the Friedman analysis is therefore more useful in terms of the values for activation energies it suggests, which are accurate.

Table 6-2: Non-linear relative probabilities (for refined averaged apparent kinetic parameters only) and averaged linear F-statistics for refined and unrefined averaged apparent kinetic parameters for the non-overlapped models case study

<table>
<thead>
<tr>
<th>Non-Linear Relative Prob (Ref)</th>
<th>F-Statistic (Ref)</th>
<th>F-Statistic (App)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P4°</td>
<td>876.8</td>
<td>8.9E+10</td>
</tr>
<tr>
<td>P3°</td>
<td>6.2E+18</td>
<td>6844.9</td>
</tr>
<tr>
<td>P2°</td>
<td>4.5E-19</td>
<td>1789.1</td>
</tr>
<tr>
<td>P23°</td>
<td>6.2E-20</td>
<td>853.5</td>
</tr>
<tr>
<td>A4°</td>
<td>8.3E-24</td>
<td>1705.0</td>
</tr>
<tr>
<td>A3°</td>
<td>7.6E-23</td>
<td>4108.6</td>
</tr>
<tr>
<td>A2°</td>
<td>3.2E+20</td>
<td>8196.7</td>
</tr>
<tr>
<td>A32°</td>
<td>5.2E+22</td>
<td>1002.9</td>
</tr>
<tr>
<td>A1, F1°</td>
<td>90.319</td>
<td>90319.8</td>
</tr>
<tr>
<td>R1, P1, F0°</td>
<td>1.2E-19</td>
<td>10887.0</td>
</tr>
<tr>
<td>R2°</td>
<td>3.4E+20</td>
<td>20586.8</td>
</tr>
<tr>
<td>R3°</td>
<td>2.8E+20</td>
<td>30121.9</td>
</tr>
<tr>
<td>F2°</td>
<td>1.4E+21</td>
<td>4553.4</td>
</tr>
<tr>
<td>F3°</td>
<td>1.4E+19</td>
<td>5126.0</td>
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<tr>
<td>L(T)°</td>
<td>7.4E-18</td>
<td>1705.0</td>
</tr>
<tr>
<td>D1(°)</td>
<td>7.1E-20</td>
<td>5455.0</td>
</tr>
<tr>
<td>D2°</td>
<td>7.4E+20</td>
<td>1705.0</td>
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<td>D3°</td>
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</tr>
<tr>
<td>D3**</td>
<td>6.9E+20</td>
<td>4929.8</td>
</tr>
</tbody>
</table>

= Most Probable Mechanism
= Within 95% Confidence Interval
*Unrefined E, Unrefined A; †Unrefined E, Refined A; ‡Refined E, Refined A
Unequivocal statistical significance was assigned to the correct mechanisms following linear $F$-testing when either the averaged apparent kinetic parameters (Table 6-2) or refined IKP (Table 6-3) were used for evaluation. For the former case, only the P4 mechanism for Model 2 was associated with activation energy within the 95% confidence interval of the corresponding invariant activation energy. As the IKP for Model 1 were associated with relatively small uncertainties but significant errors, no mechanisms have their linear $F$-statistics formatted bold in Table 6-2 even though the A$_{3/2}$ model is accurate with a very large $F$-statistic (2.2 x 10$^{12}$). As shown in Table 6-2 and Table 6-3, all other probabilities relative to the most probable model were calculated to be effectively zero based on either averaged apparent kinetic parameters or refined IKP. If the inputs were unknown, it could have been said with confidence that either set of most probable kinetic triplets closely matches that used to simulate the data.

Table 6-3: Non-linear relative probabilities and averaged linear $F$-statistics for refined (left) and unrefined (right) IKP for the non-overlapped models case study

<table>
<thead>
<tr>
<th>Non-Linear Relative Prob (Ref)</th>
<th>F-Statistic (Ref)</th>
<th>Non-Linear Relative Prob (IKP)</th>
<th>F-Statistic (IKP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P4'</td>
<td>1</td>
<td>62.7</td>
<td>1</td>
</tr>
<tr>
<td>P3'</td>
<td>3.3E-12</td>
<td>119.9</td>
<td>0.94</td>
</tr>
<tr>
<td>P2'</td>
<td>4.5E-14</td>
<td>411.7</td>
<td>0.84</td>
</tr>
<tr>
<td>P2'/3*</td>
<td>1.3E-14</td>
<td>364.7</td>
<td>0.47</td>
</tr>
<tr>
<td>A4*</td>
<td>3.7E-16</td>
<td>80.6</td>
<td>0.17</td>
</tr>
<tr>
<td>A3*</td>
<td>6.3E-16</td>
<td>149.1</td>
<td>0.24</td>
</tr>
<tr>
<td>A2*</td>
<td>2.9E-14</td>
<td>397.0</td>
<td>0.46</td>
</tr>
<tr>
<td>A3/2*</td>
<td>1.4E+00</td>
<td>16.8</td>
<td>0.72</td>
</tr>
<tr>
<td>A1, F1*</td>
<td>7.6E-15</td>
<td>612.8</td>
<td>11.7</td>
</tr>
<tr>
<td>R1, P1, F0*</td>
<td>7.1E-18</td>
<td>10.2</td>
<td>2.4</td>
</tr>
<tr>
<td>R2*</td>
<td>2.1E-12</td>
<td>2871.0</td>
<td>0.61</td>
</tr>
<tr>
<td>R3*</td>
<td>9.1E-13</td>
<td>3242.1</td>
<td>0.23</td>
</tr>
<tr>
<td>F2*</td>
<td>4.1E-16</td>
<td>271.7</td>
<td>0.25</td>
</tr>
<tr>
<td>F3</td>
<td>204.9</td>
<td>15.1</td>
<td></td>
</tr>
<tr>
<td>L2*</td>
<td>1.0E-09</td>
<td>14725.1</td>
<td>0.11</td>
</tr>
<tr>
<td>L(T)'</td>
<td>1.1E-10</td>
<td>7159.0</td>
<td>0.03</td>
</tr>
<tr>
<td>D1(1)°</td>
<td>3.8E-15</td>
<td>109.1</td>
<td>0.22</td>
</tr>
<tr>
<td>D2(1)°</td>
<td>2.9E-16</td>
<td>123.7</td>
<td>0.02</td>
</tr>
<tr>
<td>D2*</td>
<td>2.0E-15</td>
<td>72.4</td>
<td>0.14</td>
</tr>
<tr>
<td>D3*</td>
<td>2.3E-16</td>
<td>118.3</td>
<td>0.01</td>
</tr>
<tr>
<td>D3*'</td>
<td>1.7E-15</td>
<td>59.0</td>
<td>0.12</td>
</tr>
</tbody>
</table>

= Most Probable Mechanism
E = Within 95% Confidence Interval
Unrefined E, Unrefined A; Unrefined E, Refined A; Refined E, Refined A

By contrast, the linear $F$-statistics relating to unrefined IKP indicate a mere bias towards the R1, P1, F0 mechanism for Model 1, i.e. not even the correct mechanism, and are all insignificant for Model 2 (Table 6-3). The most probable mechanism associated with the unrefined IKP for Model 1 was computed erroneously as A1, F1 (R1, P1, F0 was excluded based on its shape). P4 was selected as the most probable for Model 2, but without statistical significance. In fact, almost every other model that was deemed to pass the shape assessment falls within the 95% confidence interval of the most probable for both Model 1 and Model 2. Notice of inconsistent permutation selection was given, which reinforces this
ambiguity. The algorithm reported that the A1, F1 mechanism for Model 1 was best paired with a D3* mechanism for Model 2, whereas the P4 mechanism for Model 2 was best paired with an F2 mechanism for Model 1. These poor statistics emphasise that the unrefined IKP are too much in error to be of any use for reliable mechanism discrimination.

**Effect of Noise**

Random noise in these same input models was simulated by pre-processing the “perfect” weight signals with the same function as that used by Mamleev et al. (2000a), i.e. $m_{\text{noisy}} = m[1 + 0.05(\chi - 0.5)]$, where $\chi$ is a random number between 0 and 1 (Figure 6-4).

![Figure 6-4: Overall conversion fraction and rate for the non-overlapped models simulated at 15°C/min compromised with noise](image)

The algorithm was then run with the same user input as before. This introduction of ~5% uncertainty degraded the $F$-statistics for the apparent models to worthlessness (Table 6-4 cf. Table 6-5). The super correlations from which the IKP were derived are accurate, but associated with greater uncertainties in their slopes and intercepts compared to their noise-free counterparts, whereas the 95% confidence intervals estimated for the compensation parameters appear unaffected (Figure 6-5). Activation energy for Model 1 was computed as $E_1 = 139 \pm 6$ kJ/mol using a computational range of 10 – 90%
component conversion and signal refinement. Uncertainties in the regression were found to reduce if the lower temperature data with more scatter were excluded by adjusting the computational range to 60 – 90%; in that case, \( E_1 = 140.5 \pm 2.3 \text{ kJ/mol} \). Model 2 was associated with fewer data points and thus was more affected by the noise \( (E_2 = 140 \pm 30 \text{ kJ/mol}) \). Furthermore, a continuous conversion range for Model 2 could not be identified for a heating rate of 20ºC/min in the noisy data, which contributed towards the greater uncertainty in \( E_2 \).

The magnitude of the 95% confidence intervals for the compensation parameters appears quite large (Figure 6-5), but in fact they have a very similar relative size compared to the error bars presented by Liu and Guo (2001) that are noted to confirm a compensation effect as “correct”. As these error bars were generated from simulated data, they are likely to indicate the minimum uncertainties possible in these parameters.

![Figure 6-5: Super correlations used to derive IKP for Model 1 and Model 2 without noise (a) and with noise (b). Approximate 95% confidence intervals are shown for the compensation parameters](image)
### Table 6-4: Maximum linear F-statistics and the 22 apparent kinetic models for the non-overlapped models case study. Statistics are listed for each heating rate in the order 2, 5, 10, 15 and 20°C/min with the accompanying active and computational ranges in terms of temperature, and weight factors

<table>
<thead>
<tr>
<th>P4</th>
<th>P3</th>
<th>P2</th>
<th>P1</th>
<th>A4</th>
<th>A3</th>
<th>A2</th>
<th>A1</th>
<th>F1</th>
<th>P-T</th>
<th>R1, F0</th>
<th>R2</th>
<th>F3</th>
<th>L(T)</th>
<th>D1(ºC)</th>
<th>D2(ºC)</th>
<th>D3(ºC)</th>
</tr>
</thead>
</table>

### Computational range

- **272-349ºC**
- **551-596ºC**
- **250-321ºC**
- **536-579ºC**
- **482-520ºC**

### Best F-Statistic

<table>
<thead>
<tr>
<th>F-Stat</th>
<th>Within an Order of Magnitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00E+11</td>
<td><strong>6.80E+12</strong></td>
</tr>
<tr>
<td>3.83E+11</td>
<td><strong>2.36E+13</strong></td>
</tr>
<tr>
<td>1.96E+11</td>
<td><strong>5.01E+12</strong></td>
</tr>
<tr>
<td>3.94E+11</td>
<td><strong>4.00E+11</strong></td>
</tr>
<tr>
<td>1.38E+12</td>
<td><strong>2.39E+12</strong></td>
</tr>
<tr>
<td>6.44E+11</td>
<td><strong>3.09E+11</strong></td>
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<tr>
<td>3.58E+11</td>
<td><strong>1.33E+11</strong></td>
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<tr>
<td>8.57E+11</td>
<td><strong>5.96E+11</strong></td>
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<tr>
<td>1.39E+10</td>
<td><strong>2.61E+10</strong></td>
</tr>
<tr>
<td>6.71E+10</td>
<td><strong>5.36E+10</strong></td>
</tr>
</tbody>
</table>

### A New Adaptation of The Method of Invariant Kinetic Parameters and its Application to a Flame Retardant System

- A3/F-Stat = 183-395ºC
- A3/F-Stat = 183-395ºC
- A3/F-Stat = 183-395ºC
- A3/F-Stat = 183-395ºC
- A3/F-Stat = 183-395ºC
- A3/F-Stat = 183-395ºC
- A3/F-Stat = 183-395ºC
- A3/F-Stat = 183-395ºC
- A3/F-Stat = 183-395ºC
- A3/F-Stat = 183-395ºC

---

**Active range**: Computational range
<table>
<thead>
<tr>
<th>P3</th>
<th>P4</th>
<th>P2 P3</th>
<th>A3</th>
<th>A2</th>
<th>A1</th>
<th>F1</th>
<th>R1</th>
<th>P2</th>
<th>F2</th>
<th>R2</th>
<th>F3</th>
<th>L2</th>
<th>LT</th>
<th>D1/T1</th>
<th>D2/T2</th>
<th>D3/T3</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.329</td>
<td>0.459</td>
<td>0.329</td>
<td>0.459</td>
<td>0.329</td>
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<td>0.459</td>
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<td></td>
</tr>
<tr>
<td>A1</td>
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<td>0.459</td>
<td>0.329</td>
<td>0.459</td>
<td>0.329</td>
<td>0.459</td>
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<td>0.329</td>
<td>0.459</td>
<td>0.329</td>
<td>0.459</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 6-5: Maximum linear F-statistics and the 22 apparent kinetic models for the non-overlapped models case study compromised with noise.** Statistics are listed for each heating rate in the order 2, 5, 7, 10, 15 and 20°C/min with the accompanying active and computational ranges expressed in terms of temperature, and weight fractions. Note that the L(T) model was deliberately excluded to reduce the computational time, and at 20°C/min the second model could not be identified.

**Kinetic Analysis Method Validation**

---

**Active range:** Computational range
It is difficult to compare the performance of the simple unrefined (standard) IKP method to the optimisation algorithm of Mamleev et al. (2000a), although the IKP method appears to stand up very well. Mamleev et al. (2000a) report a 9% error in activation energy and do not mention its uncertainty. IKP as a method for activation energy determination is certainly more appropriate than a differential Friedman analysis in this instance.

Refinement of the IKP or the averaged apparent kinetic parameters using this algorithm was impossible due to the magnitude of the noise. The apparent kinetic parameters were clearly compromised more by random error than the IKP (Table 6-4 cf. Table 6-5 and Figure 6-5). When associated with the correct mechanism, the apparent activation energies were calculated consistently higher than expected and ranged from 150 – 180 kJ/mol for Model 1 and 190 – 240 kJ/mol for Model 2 (Table 6-5). Unrefined IKP were therefore used to judge the non-linear relative probabilities. As anticipated, these results were too unreliable and suggested much the same inconsistent picture as in the case of no noise. A P4 mechanism was selected for Model 2 solely on the basis of midrange rate ratios, as no models overlapped with the simulated data. Poor statistics readily alert the user to the fact that the algorithm failed to arrive at an unambiguous solution automatically, however, and since the IKP are still accurate, at least some of the 22 mechanisms could be excluded simply on the basis of excessively low or high apparent activation energies. It would have been possible to refine the IKP manually with reference to the conversion rate signals if the inputs were unknown.

6.1.2 Partially Overlapped Models

The performance of this algorithm in the case of partially overlapped models is best demonstrated by comparing its output to that of Mamleev et al. (2000b) for the same kinetic triplets they use to simulate TG data:

\[ A_1 = 6 \times 10^7 \text{ min}^{-1}; E_1 = 83.736 \text{ kJ/mol}; \text{ Mechanism F2} \]
\[ A_2 = 6 \times 10^1 \text{ min}^{-1}; E_2 = 41.868 \text{ kJ/mol}; \text{ Mechanism A1, F1} \]

The first model (Model 1) was assigned a 30% weight fraction (i.e. a normalised “separation point” (Section 3.4.7) at 70%) and heating rates of 3, 6 and 9ºC/min were set as per Mamleev et al. (2000b). Time and temperature signals were setup similarly to the non-overlapped models, except the resolution was set to five seconds at 3ºC/min. An 800ºC final temperature amounted to just over 3000 rows of data for each heating rate.
Rather than estimate onset and completion temperatures for the two models, the “separation point” concept was trialled. This meant initiating the calculation from the erroneous assumption of no overlap. Visual inspection of the simulated conversion rates led to the selection of separation points close to but consistently lower than the actual weight fraction associated with Model 2, corresponding to overall conversions of 38.6% (300°C) at 3°C/min, 37.0% (327°C) at 6°C/min (Figure 6-6) and 36.3% (344°C) at 9°C/min. Weight fraction distributions were deliberately skewed according to this interpretation to test the ability of the algorithm to correct these percentages back to 30%. Mamleev et al. (2000b) do not document their initial “crude” guess for separation point, so it is difficult to compare the performance of the two algorithms in this regard.

It was found that the distortion caused by overlap was problematic and the component conversion signal refinement had to be bypassed for the first iteration. Component conversion computational ranges were initially set to 10 – 20% and 80 – 90% for Model 1 and Model 2 respectively, also to replicate the method of Mamleev et al. (2000b). Savitzky-Golay filter length was again set at 11 rows.

The first iteration identified the maximum linear $F$-statistic with the correct mechanism for Model 2 for all three heating rates, albeit without a clear distinction from other An mechanisms, but did not for Model 1.
Instead, the L2 mechanism has the highest $F$-statistic for Model 1 (Table 6-7). However, its apparent activation energy is well below the invariant activation energy (39 – 40 kJ/mol cf. $88 \pm 9$ kJ/mol) and the correct F2 mechanism ($E = 77 – 79$ kJ/mol) has an $F$-statistic within an order of magnitude of the maximum. Improper component conversion specifications were the obvious cause of this inability to immediately gain determinacy, as no such delay was observed for the non-overlapped models.

Model fitting on this first iteration resulted in similar non-linear statistics with either refined IKP or refined averaged apparent kinetic parameters (Table 6-6). Better determinism was obtained from the averaged apparent kinetic parameters as only two models each for Model 1 and Model 2 were identified as significantly probable in this case. The correct F2 mechanism for Model 1 is shown as 6% probable relative to the selected F3 mechanism, whereas the A1, F1 mechanism is correctly highlighted as the most probable for Model 2, with mechanism L2 7% probable. Statistical ambiguity is worse for Model 1 likely due to the fact that its entire active range (curtailed at 36 – 39% overall conversion) is disrupted by Model 2, but not vice versa (Figure 6-6). Inspecting the conversion rate signals for any heating rate revealed that any permutation aside from these four should be discarded. The weight fraction distribution was shifted in the correct direction by the bisection optimisation method upon selecting the correct permutation. The linear $F$-statistics for the finalised models were not definitive on this first iteration. Reducing the filter length, since the quality of the data was high, offered no improvement.

Table 6-6: Non-linear relative probabilities for solutions finalised with refined IKP (left) and refined averaged apparent parameters (right) after the first iteration of the partially overlapped models case study

<table>
<thead>
<tr>
<th>Non-Linear Relative Prob (IKP)</th>
<th>Non-Linear Relative Prob (App)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>P2</td>
</tr>
<tr>
<td>P4'</td>
<td>0.010</td>
</tr>
<tr>
<td>P3'</td>
<td>0.010</td>
</tr>
<tr>
<td>P2'</td>
<td>0.011</td>
</tr>
<tr>
<td>P2/3'</td>
<td>0.020</td>
</tr>
<tr>
<td>A4''</td>
<td>0.012</td>
</tr>
<tr>
<td>A3''</td>
<td>0.012</td>
</tr>
<tr>
<td>A2''</td>
<td>0.014</td>
</tr>
<tr>
<td>A3/2''</td>
<td>0.017</td>
</tr>
<tr>
<td>A1, F1''</td>
<td>0.032</td>
</tr>
<tr>
<td>P-T''</td>
<td>0.011</td>
</tr>
<tr>
<td>R1, P1, F0''</td>
<td>0.013</td>
</tr>
<tr>
<td>R2''</td>
<td>0.019</td>
</tr>
<tr>
<td>R3''</td>
<td>0.022</td>
</tr>
<tr>
<td>F2''</td>
<td>0.232</td>
</tr>
<tr>
<td>F3'</td>
<td>0.020</td>
</tr>
<tr>
<td>L2''</td>
<td>0.011</td>
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<tr>
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<td>0.173</td>
</tr>
<tr>
<td>D3''</td>
<td>0.041</td>
</tr>
</tbody>
</table>

= Most Probable Mechanism = Within 95% Confidence Interval
*Unrefined E, Unrefined A; *Unrefined E, Refined A; *Refined E, Refined A E Within 95% Confidence Interval of Einv
Table 6-7: Maximum linear F-statistics and the 22 apparent kinetic models from the first iteration of the partially overlapped models case study. Statistics are listed for each heating rate in the order 3, 6 and 9°C/min with the accompanying active and computational ranges expressed in terms of temperature, and weight fractions

<table>
<thead>
<tr>
<th>Heating Rate</th>
<th>F1 Statistic</th>
<th>F2 Statistic</th>
<th>F-Stat</th>
<th>A1, F1</th>
<th>F-Stat</th>
<th>A1, F1</th>
<th>F-Stat</th>
<th>A1, F1</th>
<th>F-Stat</th>
<th>A1, F1</th>
<th>F-Stat</th>
<th>A1, F1</th>
<th>F-Stat</th>
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<th>F-Stat</th>
<th>A1, F1</th>
<th>F-Stat</th>
<th>A1, F1</th>
</tr>
</thead>
<tbody>
<tr>
<td>3°C/min</td>
<td>12.633</td>
<td>18.706</td>
<td>32.073</td>
<td>102.284</td>
<td>13.981</td>
<td>20.236</td>
<td>34.039</td>
<td>47.339</td>
<td>74.928</td>
<td>94.374</td>
<td>112.001</td>
<td>89.597</td>
<td>110.641</td>
<td>89.971</td>
<td>72.354</td>
<td>112.001</td>
<td>89.597</td>
<td>110.641</td>
</tr>
<tr>
<td>9°C/min</td>
<td>5.224</td>
<td>9.971</td>
<td>23.673</td>
<td>52.256</td>
<td>5.548</td>
<td>9.497</td>
<td>23.736</td>
<td>37.255</td>
<td>66.784</td>
<td>86.857</td>
<td>106.903</td>
<td>89.971</td>
<td>109.971</td>
<td>90.971</td>
<td>72.354</td>
<td>110.641</td>
<td>89.597</td>
<td>110.641</td>
</tr>
</tbody>
</table>

Table 6-8: Maximum linear F-statistics and the 22 apparent kinetic models from the second iteration of the partially overlapped models case study. Statistics are listed for each heating rate in the order 3, 6 and 9°C/min with the accompanying active and computational ranges expressed in terms of temperature, and weight fractions

<table>
<thead>
<tr>
<th>Heating Rate</th>
<th>F1 Statistic</th>
<th>F2 Statistic</th>
<th>F-Stat</th>
<th>A1, F1</th>
<th>F-Stat</th>
<th>A1, F1</th>
<th>F-Stat</th>
<th>A1, F1</th>
<th>F-Stat</th>
<th>A1, F1</th>
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<th>F-Stat</th>
<th>A1, F1</th>
<th>F-Stat</th>
<th>A1, F1</th>
</tr>
</thead>
<tbody>
<tr>
<td>3°C/min</td>
<td>12.633</td>
<td>18.706</td>
<td>32.073</td>
<td>102.284</td>
<td>13.981</td>
<td>20.236</td>
<td>34.039</td>
<td>47.339</td>
<td>74.928</td>
<td>94.374</td>
<td>112.001</td>
<td>89.597</td>
<td>110.641</td>
<td>89.971</td>
<td>72.354</td>
<td>112.001</td>
<td>89.597</td>
<td>110.641</td>
</tr>
<tr>
<td>9°C/min</td>
<td>5.224</td>
<td>9.971</td>
<td>23.673</td>
<td>52.256</td>
<td>5.548</td>
<td>9.497</td>
<td>23.736</td>
<td>37.255</td>
<td>66.784</td>
<td>86.857</td>
<td>106.903</td>
<td>89.971</td>
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<td>90.971</td>
<td>72.354</td>
<td>110.641</td>
<td>89.597</td>
<td>110.641</td>
</tr>
</tbody>
</table>

The Method of Invariant Kinetic Parameters and its Application to a Flame Retardant System
A Friedman analysis (Figure 6-7) confirms the effect of Model 2 on the integrity of Model 1. Referring to the decision tree (Figure 3-4), the convex decreasing first phase of $E(\alpha)$ should indicate a change in the limiting model, not overlapping independent models. This contraction validates the perception that it is unwise to place much weight on the curvature of $E(\alpha)$. Moreover, $E_{\alpha}$ at the extremes of conversion are a very close match to the true activation energies ($77 \pm 6$ kJ/mol and $42 \pm 2$ kJ/mol). This analysis increased confidence in the correct permutation because the F2 and A1, F1 mechanisms were uniquely assigned these same apparent activation energies ($77 \pm 1$ kJ/mol and $45 \pm 1$ kJ/mol respectively).

Due to the poor initial specification of the weight fraction distributions, only a very gradual expansion of the computational ranges with successive iterations ensured a smooth approach to the correct solution. The second iteration was computed after expanding the initial ranges to 5 – 25% and 75 – 95% for Model 1 and Model 2 respectively. A degree of self-determinism due to the recalculation of the component conversion signals from the previously selected permutation means that the statistics for the second iteration are less contradictory compared to the first iteration, as shown by the linear $F$-statistics computed for the apparent models (Table 6-7 and Table 6-8). Neither averaged apparent activation energy for the selected permutation was refined for this second iteration, but the weight fraction distributions were stepped in the right direction.
### Table 6-9: Predicted most probable kinetic triplets and weight fraction distributions for the partially overlapped models case study initialised with a weight fraction for Model 1 between 36 – 39%. Computation ranges in terms of conversion are shown as well as the status of the finalised kinetic parameters for selected iterations

<table>
<thead>
<tr>
<th></th>
<th>M O D E L 1</th>
<th>M O D E L 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Simulation</td>
<td>1st Iteration*</td>
</tr>
<tr>
<td>Computational range</td>
<td>10 – 20%</td>
<td>1 – 30%</td>
</tr>
<tr>
<td>$E$ (kJ/mol)</td>
<td>83.736</td>
<td>84 ± 1</td>
</tr>
<tr>
<td>$A$ (min⁻¹)</td>
<td>$6 \times 10^7$</td>
<td>$7.3 \times 10^7$</td>
</tr>
<tr>
<td>Mechanism</td>
<td>F2</td>
<td>F2</td>
</tr>
<tr>
<td>Weight (%)</td>
<td>30.0</td>
<td>32.6 – 33.0</td>
</tr>
</tbody>
</table>

*Refined apparent kinetic parameters (optimistic error in activation energy)
*Refined apparent pre-exponential factor only (error in activation energy estimated from variation in apparent activation energies across all heating rates)
^Unrefined apparent kinetic parameters (error estimated from variation in apparent parameters across all heating rates)

### Table 6-10: Predicted most probable kinetic triplets and weight fraction distributions for the partially overlapped models case study initialised with a weight fraction for Model 1 of 33%. Computation ranges in terms of conversion are shown as well as the status of the finalised kinetic parameters for the first three iterations

<table>
<thead>
<tr>
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<th>M O D E L 2</th>
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<td>Simulation</td>
<td>1st Iteration^</td>
</tr>
<tr>
<td>Computational range</td>
<td>10 – 20%</td>
<td>10 – 20%</td>
</tr>
<tr>
<td>$E$ (kJ/mol)</td>
<td>83.736</td>
<td>79.2 ± 0.1</td>
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<tr>
<td>$A$ (min⁻¹)</td>
<td>$6 \times 10^7$</td>
<td>$2.2 \times 10^7$</td>
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<tr>
<td>Mechanism</td>
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<td>F2</td>
</tr>
<tr>
<td>Weight (%)</td>
<td>30.0</td>
<td>29.0 – 29.7</td>
</tr>
</tbody>
</table>

^Refined invariant kinetic parameters (optimistic error in activation energy)
*Refined apparent pre-exponential factor only (error in activation energy estimated from variation in apparent activation energies across all heating rates)
#Unrefined apparent kinetic parameters (error estimated from variation in apparent parameters across all heating rates)
Computational ranges were expanded again for the third iteration to 1 – 30% and 70 – 99% for Model 1 and Model 2 respectively, and were held constant for the fourth iteration to consolidate the solution. The next five iterations had the inner computational limits moved by 5% each time such that by the ninth iteration the computational ranges were 1 – 65% and 35 – 99% for Model 1 and Model 2 respectively. Nine iterations in total were sufficient to produce a kinetic solution that showed the correct models had statistical superiority in all contexts (apparent and averaged linear $F$-statistics and non-linear relative probabilities), as well as activation energies within the 95% confidence intervals of the invariant activation energies. Notably, the quality of the prediction was close to its asymptotic limit by the sixth iteration, and at this stage the departure from the simulated conversion rate was almost imperceptible (Figure 6-8). Table 6-9 shows abbreviated numerical results with uncertainties where calculable.

Confident identification of the correct permutation was possible on the first iteration. Only the correct mechanisms satisfied the criteria of significant linear $F$-statistics and non-linear relative probabilities, and agreement with the invariant/Friedman activation energies. If the inputs were unknown, all four permutations suggested by the non-linear relative probabilities could have been thoroughly tested for their legitimacy. This approach is quicker and superior to manually testing every permutation independently, which would be required if using the algorithm of Mamleev et al. (2000b). Furthermore, the inputted weight fractions for Model 1 of 36 – 39% represent the worst reasonable guesses a user
could make. When a better guess of 33% was used to initialise the computation, the solution converged to a statistically unambiguous solution in only three iterations (where the final iteration employed a computational range of 10 – 90% for both models; Table 6-10). No other permutations aside from the correct one were favoured at any stage from this better initial specification.

6.1.3 Totally Overlapped Models

Totally overlapped models represent a significant challenge as no distinctive aspects of the component conversion signals are resolved. The ICTAC project alluded to in Section 5.6 works with kinetic triplets that manifest ostensibly single-step sigmoidal overall conversion signals (Figure 6-9) that were used to test the algorithm:

\[ A_1 = 10^{10} \text{ min}^{-1}; E_1 = 80 \text{ kJ/mol}; \text{Mechanism A1, F1} \]
\[ A_2 = 10^{15} \text{ min}^{-1}; E_2 = 120 \text{ kJ/mol}; \text{Mechanism A1, F1} \]

These models were evenly weighted at 50% weight fraction. Heating rates of 0.5, 1 and 2°C/min were selected to match those used for the ICTAC project (Brown et al., 2000). The time signal was resolved to five seconds at 0.5°C/min and was scaled in inverse proportion to heating rate as before, yielding ~2900 rows of data starting at 45°C and ending at 158°C.

![Figure 6-9: Overall conversion fraction and overall and correctly weighted component rates for the totally overlapped models simulated at 0.5°C/min](image)
The deconvolution of these two models was given the best possible chance of success by assigning both to the entire conversion range and computing the sets of IKP based on the extreme computational ranges of 0 – 10% and 90 – 100%. With these specifications, both models were automatically weighted correctly at 50%. Linear model fitting generated erroneous apparent kinetic parameters, but in similar fashion to the noisy data case, the invariant activation energies are reasonable at $E_1 = 60 \pm 20 \text{kJ/mol}$ and $E_2 = 115 \pm 10 \text{kJ/mol}$. The Friedman analysis also implies the existence of two distinctly different activation energies of the correct magnitude (Figure 6-10). In this instance, the decision tree (Figure 3-4) is in accord as an increasing sigmoidal trend in $E(\alpha)$ is known to unambiguously represent overlapping independent models (Section 3.4.7).

![Figure 6-10: Friedman analysis for the totally overlapped models case study over heating rates of 0.5, 1 and 2°C/min showing 95% confidence intervals](image)

Mechanism A1, F1 did not even pass the shape assessment using the nominal unrefined invariant activation energy of 60 kJ/mol. In order to refine either set of IKP, the predicted models had to be related back to the incorrectly specified component conversion signals. Invariant activation energy for Model 2 was refined to a lower value when associated with the A1, F1 mechanism, not a higher one that was required to progress towards the correct solution. The algorithm as described appeared unable to automatically arrive at a statistically unambiguous solution for this scenario.
6.2 Real Data

A kinetic analysis method that has been successfully tested with simulated TG data must perform well with real data inputs before it can be said to have practical relevance. Comparisons are made to known physical realities and trusted kinetic analyses to judge the soundness of this algorithm. As both the following examples were interpreted with single-step kinetics, component conversion signal refinement was enabled on the first and only iteration. Clearly complex real kinetic data are not suited for validation because the unknown nature of this complexity leaves too much scope for interpretation.

As discussed in Section 3.1, imperfect temperature measurements are a feature of real data. A physical scenario that leads to a worst case Biot number less than 0.1 implies temperature uniformity throughout the sample, at least. Therefore, a sufficiently small Biot number of the appropriate form may justify the omission of the sample centreline temperature calculation (Section 5.1.5), but only if the sample does not undergo a large enthalpy change. If it does, this temperature calculation is mandated. Physical properties of the sample and furnace are required for both simple and rigorous calculations.

Platinum and alumina crucibles were considered conductive enough not to limit the flow of heat (Section 5.1.5). The convective heat transfer to the surface would have only been poorly estimated; in any case, the radiation term was likely to dominate. Equation 5-1 was therefore selected with the convective heat transfer coefficient set to zero:

\[ \text{Bi}(T) = \frac{\frac{x \varepsilon T_x^3}{k_c}} \]

Furnace “wall” temperature \( T_\infty \) was simplified as the thermocouple (measured) temperature and emissivity \( \varepsilon \) was set to unity. The inside radius of an alumina crucible (2.5 mm) was the logical choice for the characteristic length \( x \).

6.2.1 Evaporation of Water

When subjected to constant heating rate experiments ranging from 0.5 – 5°C/min in the Labsys (TG/DSC Set 2: Water), water evaporated at a rate that continually increased until no liquid remained. Figure 6-11 shows an example of this behaviour, and the correlation of the predicted kinetic solution discussed later in this section. The Savitzky-Golay filter length was retained as 11 rows for this case study.
A New Adaptation of The Method of Invariant Kinetic Parameters and its Application to a Flame Retardant System

Figure 6-11: Normalised weight loss rate for a 68.9 mg sample of water heated at 5°C/min under 100 mL/min N₂, and the predicted kinetic solution using $E = 50$ kJ/mol, $A = 3 \times 10^5$ min⁻¹ and an R₁, P₁, F₀ mechanism

Heating rate was limited at 5°C/min to minimise the heat transfer effects. The worst case Biot number computed from Equation 5-1 using the hottest temperature measured during evaporation of 140°C and a thermal conductivity of 0.6 W/mK (Ramires et al., 1995) was only 0.017. While the excessive latent heat of water necessitated a full energy balance in itself, the fact that the set point temperature was always significantly overshot once all the water evaporated (Figure 6-12) further emphasised this need. Centreline temperature calculated according to Equation 5-4 appears fairly realistic in relation to the magnitude of this overshoot. Based on the temperature relationships at 5°C/min shown in Figure 6-12, the upper limit for the computational range was set as 24%. The lower limit of 5% was dictated by the 3°C/min experiment that had the longest induction period before the thermocouple temperature started ramping at the required heating rate. However, a discontinuity in the weight signal at 0.5°C/min at 15% conversion attributed to a jump in system pressure meant that either this data sheet had to be excluded or the lower limit had to be raised to 15.5%. Both treatments were explored and delivered similar outcomes.

Regardless of whether the measured or calculated centreline temperature signals were input, a consistent, justifiable and verified single-step solution was found, albeit with more associated uncertainty compared to the analysis of the simulated acceleratory model. Furthermore, the refinement algorithm converged to effectively the same solutions regardless of whether the averaged apparent
kinetic parameters or the IKP were used for kinetic parameter initialisation. The fact that both pre-exponential factor and activation energy were refined in many cases (Table 6-11) suggests inaccurate initial parameters, but acceptable correlations back to the experimental data. Importantly, after refinement from averaged apparent kinetic parameters, the most probable mechanism was identified as R1, P1, F0, which corresponds to “One-dimension moving of interface boundary or evaporation of flat surface” (Vlaev et al., 2008). Only this mechanism can be justified for water evaporating from a crucible.

![Figure 6-12: Temperature measured by the thermocouple for evaporation of 68.9 mg of water at 5ºC/min under 100 mL/min N2. Centreline temperature calculated from Equation 5-4 assuming the measured temperature is that of the water at the inside surface of the crucible at each time step (j = 0). Illustrates the greatest discrepancy between these temperature signals at 24% conversion](image)

This R1, P1, F0 mechanism was invariably associated with refined activation energies (~50 kJ/mol) that lie within the 95% confidence intervals calculated for both the IKP (63 ± 24 kJ/mol; Figure 6-13) and Friedman analyses (Figure 6-14). An activation energy of around 50 kJ/mol agrees with standard Arrhenius fits for the evaporation of water presented by Cappa et al. (2005) (55 ± 5 kJ/mol) and Speedy et al. (1996) (47 ± 1 kJ/mol), despite the fact that both these research groups use significantly more elaborate smaller-scale experiments compared to thermogravimetric analysis.
The only mechanisms of a purely acceleratory nature, or close to it, under constant heating rate conditions found with comparable activation energies were the $P^2/3$ and other contracting volume mechanisms. These better fitting models on a non-linear basis were consistently associated with activation energies closer to the perceived “correct” activation energy. Averaged linear $F$-statistics for the apparent models were improved in some respects after kinetic parameter refinement, but are not conclusive (Table 6-11). It should be noted that conclusive results are harder to obtain the smaller the computational range, partly because not as many models can be excluded based on shape. In addition, weight loss that simply accelerates does not exhibit a functional maximum, which can be a useful feature for mechanism discrimination.

Table 6-11: Non-linear relative probabilities (for refined kinetic parameters only) and averaged linear $F$-statistics for both refined and unrefined apparent kinetic parameters (left) and IKP (right) for evaporation of water at 0.5, 1, 2, 3 and 5°C/min under N$_2$ using narrow computational limits of 15.5 – 24% and the measured temperature signal.

<table>
<thead>
<tr>
<th>Non-Linear Relative Prob</th>
<th>F-Statistic (App)</th>
<th>(Ref)</th>
<th>Invariant Kinetic Parameters</th>
<th>F-Statistic (Ref)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Averaged Apparent Kinetic Parameters</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P_1^*$</td>
<td>$F_1^*$</td>
<td>$F_1$</td>
<td>$P_4^*$</td>
<td>$0.002$</td>
</tr>
<tr>
<td>$P_3^*$</td>
<td>$0.004$</td>
<td>$0.5$</td>
<td>$0.5$</td>
<td>$P_3^*$</td>
</tr>
<tr>
<td>$P_2^*$</td>
<td>$0.010$</td>
<td>$1.8$</td>
<td>$1.8$</td>
<td>$P_2^*$</td>
</tr>
<tr>
<td>$P_{2/3}^*$</td>
<td>$0.192$</td>
<td>$29.3$</td>
<td>$29.3$</td>
<td>$P_{2/3}^*$</td>
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<tr>
<td>$A_{4}^*$</td>
<td>$0.003$</td>
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<tr>
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<td>$0.6$</td>
<td>$0.6$</td>
<td>$A_{3}^*$</td>
</tr>
<tr>
<td>$A_{2}^*$</td>
<td>$0.022$</td>
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<td>$2.9$</td>
<td>$A_{2}^*$</td>
</tr>
<tr>
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<td>$0.171$</td>
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<td>$503.9$</td>
<td>$589.0$</td>
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</tr>
<tr>
<td>$P_{-1}^*$</td>
<td>$0.035$</td>
<td>$353.5$</td>
<td>$353.5$</td>
<td>$P_{-1}^*$</td>
</tr>
<tr>
<td>$R_{1}, P_{1}, F_{0}^*$</td>
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<td>$246.5$</td>
<td>$R_{1}, P_{1}, F_{0}^*$</td>
</tr>
<tr>
<td>$R_{2/1}$</td>
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<td>$R_{3}^*$</td>
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<td>$D_{1}(<em>)^</em>$</td>
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<td>$16.4$</td>
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<td>$16.7$</td>
<td>$16.7$</td>
<td>$D_{3}^{**}$</td>
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</tbody>
</table>

* Most Probable Mechanism = Within 95% Confidence Interval

When the crude energy balance was neglected and the computational limits were set to 5 – 95%, the computed non-linear probabilities and the linear $F$-statistics clearly show that a $P^2/3$ mechanism ($E \sim 70$ kJ/mol) and an $R_1, P_1, F_0$ mechanism ($E \sim 50$ kJ/mol) are the only viable choices (Table 6-12 and Table 6-11). Only these mechanisms have significant non-linear probabilities as well as activation energies within the 95% confidence intervals of the invariant activation energy.
Table 6-12: Maximum linear $F$-statistics and the 22 apparent kinetic models for evaporation of 61.8 – 70.8 mg water under 100 mL/min N$_2$ for a 5 – 95% computational range. Statistics are listed for each heating rate in the order 1, 2, 3 and 5ºC/min with the accompanying active and computational ranges expressed in terms of temperature, and weight fractions

<table>
<thead>
<tr>
<th>Eitt</th>
<th>P4</th>
<th>P3</th>
<th>P2</th>
<th>P2/3</th>
<th>A4</th>
<th>A3</th>
<th>A2</th>
<th>A3/2</th>
<th>A1, F1</th>
<th>P-T</th>
<th>R1, P1, F0</th>
<th>R2</th>
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<th>D2</th>
<th>D2*</th>
<th>D3</th>
<th>D3*</th>
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</table>

$=$ Best $F$-Statistic  $=$ $F$-Stat Within an Order of Magnitude

Figure 6-13: Super correlation from which the IKP were derived for evaporation of 61.8 – 70.8 mg water. Heating rates of 0.5, 1, 2, 3 and 5ºC/min under 100 mL/min N$_2$ and a computational range of 15.5 – 24% were used. The lower limit for the computational range had to be raised; data below this conversion at 0.5ºC/min were compromised.

Figure 6-14: Friedman analysis for evaporation of 61.8 – 70.8 mg water over heating rates of 0.5, 1, 2, 3 and 5ºC/min under 100 mL/min N$_2$ showing 95% confidence intervals. Conversions below 15% at 0.5ºC/min were inconsistent with the rest of the data and were excluded.
Table 6-13: Non-linear relative probabilities (for refined kinetic parameters only) and averaged linear F-statistics for both refined and unrefined apparent kinetic parameters (left) and IKP (right) for evaporation of water at 1, 2, 3 and 5°C/min under N₂ using wide computational limits of 5 – 95% and the measured temperature signal

<table>
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<tr>
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<th>Invariant Kinetic Parameters</th>
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<td>Non-Linear Relative Prob</td>
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<td>Fj1</td>
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<tr>
<td></td>
<td>D1(*)¹</td>
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<tr>
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The superiority of the R1, P1, F0 mechanism was only confirmed when the model fitting refinement was initialised with averaged apparent kinetic parameters, repeating the observation made for the narrower computational range (Table 6-11). For this wide computational range, only pre-exponential factor required correction (Table 6-13). Four or five heating rates for the Friedman analysis are sufficient to demonstrate that the activation energy for a P²₃ mechanism is too high (Figure 6-14).

A simple reversible process, such as evaporation, can show increasing activation energy with conversion (Section 3.4.7). While the nominal values shown in Figure 6-14 do follow an increasing trend, it cannot be judged as significant because of the large confidence intervals.

Figure 6-11 exemplifies a typical kinetic solution regenerated with the refined IKP for the narrow computational range (15.5 – 24%) and the R1, P1, F0 mechanism. Volatility at room temperature would have introduced random errors by invalidating the assumption of zero initial conversion. Translation along the temperature axis to account for this would have altered the apparent best fitting kinetic parameters, but not the most probable mechanism. However, the fact that the kinetic parameters used to generate such good predictions are average values suggests that these errors were minimal.
6.2.2 Calcium Carbonate

The new kinetic analysis method was applied to selected TG data published for calcium carbonate decomposition in inert atmospheres of nitrogen (Brown et al., 2000) and argon (Sanders and Gallagher, 2005). Calcium carbonate loses weight over the range 550 – 900°C at heating rates ranging from 1 – 25°C/min (Brown et al., 2000) and 2 – 31.8°C/min (Sanders and Gallagher, 2005) according to an ostensibly single-step process. As the data were extracted from small graphs, the resolution was poor. At worst, 26 rows characterised the weight loss, necessitating a short Savitzky-Golay filter of five rows.

Results generated from this algorithm are less conclusive compared to the preceding study for water, but match expectation well. Friedman analyses of these data indicate constant activation energy in the range 190 ± 20 kJ/mol (Figure 6-15). These analyses are corroborated by the invariant activation energies, computed from limits of 5 – 95%, of 189 ± 8 kJ/mol and 187 ± 13 kJ/mol from the data of Brown et al. (2000) and Sanders and Gallagher (2005) respectively. These activation energies agree with those derived by seven different contributors to the ICTAC project (Brown et al., 2000), and the 194 kJ/mol (no error) quoted by Sanders and Gallagher (2005). No relationship between activation energy and conversion is apparent (Figure 6-15), despite the implication that a simple reversible reaction is likely to manifest increasing activation energy with conversion (Section 3.4.7). Continuing the analysis with the assumption of a single-step process was therefore not invalidated.

Figure 6-15: Friedman analyses of the data for calcium carbonate pyrolysis extracted from Brown et al. (2000) and Sanders and Gallagher (2005) (over various heating rates) showing 95% confidence intervals
Both the cited articles are inconclusive regarding the mechanism that should be associated with the agreed upon kinetic parameters. The researchers contributing to the ICTAC project primarily focus on acquiring one or two pairs of activation energy and pre-exponential factor to describe the decomposition of calcium carbonate. Accordingly, many of the applied methods are model-free, but those that are not do not consistently use the same mechanism (Brown et al., 2000). Sanders and Gallagher (2005) state that the Thermokinetics software they use to analyse their data selects a Prout-Tompkins mechanism, which must be either the Sestak-Berggren equation (Equation 3-10) or another variant (e.g. Equation 5-8) as they indicate that there are two parameters to optimise in its function of conversion. They reject this mechanism because it has these extra parameters and instead select the three-dimensional contracting volume mechanism (R3), as it has an order in the range of their fitted value (2.5 to 3.7).

Figure 6-16 illustrates the typical correlation of the Prout-Tompkins \((kt_i = 3.0)\) and cylindrical and spherical contracting volume models optimised with this algorithm to the experimental conversion rate for a size fraction <44 µm (Sanders and Gallagher, 2005). For this size fraction, Sanders and Gallagher (2005) determine an optimal contracting volume order of 3.7 with \(E = 192\ kJ/mol\) and \(A = 7.73 \times 10^8\ \text{min}^{-1}\). This order has no obvious physical significance. The statistics shown in Table 6-14 broadly agree with Sanders and Gallagher (2005), as they are inconclusive but favour the refined spherical contracting volume model. However, a higher order than three would cause the activation energy to optimise to a higher value than that of the R3 model (221 kJ/mol), which itself is already significantly above the invariant or model-free activation energy. Therefore it cannot be said that this algorithm is comprehensively validated by comparison to this previous study, or that the decomposition of calcium carbonate can be explained by any of the available 22 variants of single-step models.

Interestingly, the conversion rate derived from the kinetic triplet of Sanders and Gallagher (2005) recreated with this algorithm did not actually correspond to the true conversion rate (Figure 6-16). The error in temperature based on the positions of peak conversion rate is about 50ºC at 2ºC/min. This implies that there is a significant computational flaw in at least one of these methods of kinetic solution generation. A lot of attention was paid to this important aspect in this study. Furthermore, conversion rates generated with this algorithm from the kinetic triplets used for validation in Section 6.1.2 do match published graphs of conversion rates for the same kinetic triplets (Mamleev et al., 2000b), and the midpoint numerical integration was verified to match the exceptionally accurate integral approximation of Orfao (2007). Perhaps a difference in how the solution was initialised or integrated by Sanders and Gallagher (2005) resulted in the optimisation of the contracting volume model to an order greater than three.
Table 6-14: Non-linear relative probabilities (for refined kinetic parameters only) and averaged linear F-statistics for both refined and unrefined apparent kinetic parameters (left) and IKP (right) for the data extracted from Sanders and Gallagher (2005) for calcium carbonate pyrolysis

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<td>D3°</td>
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</table>

Figure 6-16: Conversion rate computed with filter length N = 5 from data extracted from Sanders and Gallagher (2005) for calcium carbonate at 2°C/min under argon. The rate regenerated from the optimised kinetic triplet reported by Sanders and Gallagher (2005) (\(E = 192\) kJ/mol, \(A = 7.73 \times 10^8\) min\(^{-1}\); R3.7 mechanism) is shown, and the predictions obtained using this algorithm. Kinetic parameters were initialised as their averaged apparent values.
6.3 Concluding Remarks

Both synthetic and real applications of this algorithm highlight the benefit of providing comprehensive statistics to quantify the uncertainties that always exist. These statistics ward against one of the easiest traps for a novice researcher to fall in to: Quoting the results of a kinetic analysis to an unrealistic precision with no room for doubt. Furthermore, if the statistics permit the confident assignment of a certain mechanism, Table 5-1 and Appendix A2 encourage more insightful connections to be made to the substance under analysis.

Sacrificing the potential to resolve very high precision solutions leads to gains in stability, which is ultimately more important when processing real data. This algorithm is designed to be aborted in the case of multiple overlapping processes once all ambiguity has been eliminated, if possible, rather than run until activation energy, say, is computed to more than four significant figures. If this is attempted, resolution limitations will either lead to convergence to erroneous values, or oscillatory behaviour of insignificant quantities. More than one point can be used for the optimisation or the Savitzky-Golay filter length can be shortened if greater determinism is sought.

Mamleev et al. (2000b) report that 10 – 15 iterations for each permutation are required to finalise their precise solution for partially overlapped models, whereas this algorithm only needs to be run at best two or three times to arrive at a solution that is indistinguishable from the input model. The user must be tasked with making a very good guess for the initial weight fraction distribution to limit the number of permutations to trial, and to reduce the number of iterations required to arrive at an unambiguous solution. Furthermore, the more probable a model, the closer its activation energy to the invariant value, which suggests there is no advantage to using a scale of reduced time (Mamleev et al., 2000a).

It should be obvious from this chapter that the practice of assessing the relative probabilities of all 22 mechanisms by affiliating them with the IKP without first refining at least the invariant pre-exponential factor is seriously flawed. A totally inaccurate impression of the relative fits of the mechanisms is likely. Rather, it is recommended to use the averaged apparent kinetic parameters and refine them with model fitting, if possible, before evaluating residual sums of squares. The IKP are useful in the same way as the activation energy from the Friedman analysis, and for verifying the existence of a super correlation for a set of experiments.

A thoroughly consistent, unambiguous statistical picture will always be portrayed for well-separated processes provided the kinetic solutions are developed from the averaged apparent kinetic parameters.
or the refined IKP. Only when a superb correlation to an $n$-order model is obvious will it be possible for its refined activation energy to be outside the 95% confidence interval of the invariant activation energy.

Unfortunately, the algorithm as it stands cannot reliably treat totally overlapped processes, although a Friedman analysis may identify them, and the utility of the temperature signal recalculation is limited. Any method tailored to produce global kinetic solutions that are simple functions of conversion, such as this algorithm, is likely to be suitable for application to TG data relating to small molecules or uncomplicated physical processes, not large polymers with a size distribution and complex mode of degradation. Even calcium carbonate decomposition cannot be unambiguously characterised, most likely because of the confounding effect of reaction reversibility. These limitations have critical relevance to the application of this new method to the flame retardant system under study.
Chapter 6 suggests that despite attempting to reflect best practice based on a careful dissection of the literature (Chapter 3), the kinetic analysis method developed was not expected to handle the full complexity of the thermal decomposition of the flame retardant (FR) system under study. Because of this, the polypropylene substrate and the FR, tetrabromobisphenol A bis(2,3-dibromopropyl ether) (TBBA-BDPE), were subjected to thermogravimetric (TG) experiments as separate samples. Section 7.1.1 and Section 7.2.1 discuss the results of their respective kinetic analyses. Particular attention was paid to the decomposition of neat TBBA-BDPE as it is a comparatively small molecule, i.e. more likely to deliver conclusive results, and had not previously been characterised in this way. To further simplify the systems, pyrolysis, not oxidation, was investigated primarily.

Deductions made from features apparent in the differential scanning calorimetric (DSC) and Fourier transform infrared spectroscopic (FTIR) data collected simultaneously to the TG data are presented. Benson’s Group Additivity Method was applied semi-quantitatively to a characteristic endothermic feature in the heat flow signal for TBBA-BDPE decomposition, which led to the hypothesis of a major decomposition pathway. Its validity is discussed with reference to the behaviour of TBBA-BDPE analogues and literature studies relating to the decomposition of tetrabromobisphenol A (TBBA) in particular. The role of antimony trioxide ($\text{Sb}_2\text{O}_3$) when combined with TBBA-BDPE and in the FR system was also explored with small-scale pyrolysis; again, the results of which are correlated to the literature.

Fire performance data collected with the modified cone calorimeter apparatus (Section 4.3) are presented and qualitatively assessed with reference to the preceding deductions.

### 7.1 Polypropylene Degradation

Simultaneous TG/DSC experiments according to the method **TG/DSC Set 2: Polypropylene** supplied data consistent with that found in the literature for polypropylene pyrolysis. As exemplified in Figure 7-1, after a distinct endotherm associated with melting above 150°C, polypropylene lost weight in the temperature range 350 – 510°C according to an ostensibly single-step process that coincided with an endotherm of 400 – 500 J/g. The temperature at which the peak rate of weight loss occurred increased from 450 to 475 °C as the heating rate was increased from 5 – 20°C/min (Figure 7-2). No residue was observed.
Noise in the weight signals was estimated to vary from 0.4% (20°C/min) to 0.72% (7°C/min). These signals have good integrity compared to the noisy data simulated for the validation (Section 6.1.1).

Figure 7-1: Heat flow and weight signals for a 16.7 mg polypropylene sample at 5°C/min under 100 mL/min N₂

Figure 7-2: Normalised weight loss rate at heating rates 5 – 20°C/min for 12.8 – 16.7 mg polypropylene samples under 100 mL/min N₂
7.1.1 Kinetic Analysis

All five sets of TG data for polypropylene pyrolysis shown in Figure 7-2 were input into the new kinetic analysis method. This analysis effectively serves as a validation, similar to that undertaken for calcium carbonate (Section 6.2.2), but using data acquired from the Labsys. Figure 7-1 and Figure 7-2 show that the weight loss of polypropylene during pyrolysis also appears best represented by a single Arrhenius process. Given the dissent evident in the literature (Section 2.6.1), it is likely to be more complex. However, unlike calcium carbonate decomposition, it is conceivable that the random scission scheme reduced to a composite function of conversion (Appendix A2.6) could describe the complexity. Testing this model formed an integral part of the kinetic analysis.

First, an assessment was made regarding the temperature uniformity of the polypropylene samples pyrolysed in the Labsys. Polypropylene has a low thermal conductivity (0.16 W/mK (Bockhorn et al., 1999b)) and completely decomposes at high temperatures (~500ºC at 20ºC/min). When substituted into Equation 6-1, these values imply a maximum Biot number of 0.4; greater than the normally cited critical value of 0.1 (Section 3.1). The approximate energy balance calculation available in the method (Equation 5-4) was therefore called.

Integration of the second peak in the heat flow signal (Figure 7-1) indicated that polypropylene absorbed 400 – 500 J/g during pyrolysis, or about a fifth of the latent heat of water. The higher heating rates chosen (5 – 20ºC/min) and the sigmoidal degradation shape made this enthalpy requirement from the sample overwhelm the centreline temperature calculation above about 12% conversion for 20ºC/min (Figure 7-3). When this pyrolysis enthalpy was neglected, the calculated centreline temperature lagged the measured temperature by a maximum of 7ºC at 20ºC/min. This rough energy balance could not provide the assurance of uniform sample temperature. However, it is reasonable to expect the surroundings to have supplied at least some of the energy to pyrolyse the sample, which would have been molten and thus a better conductor than the thermal conductivity of polypropylene would imply.

Despite all the different dependencies of activation energy on conversion cited for polypropylene (Section 3.4.7), the Friedman analysis based on the measured temperature indicates a constant activation energy of 160 – 240 kJ/mol (Figure 7-4). When the calculated centreline temperature (excluding pyrolysis enthalpy) was substituted for the measured temperature, the activation energy maintained this independence from conversion but increased to 190 – 300 kJ/mol (Figure 7-4).
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Figure 7-3: Discrepancy between the temperature measured during the pyrolysis of a 12.8 mg polypropylene sample at 20ºC/min under 100 mL/min N₂ and the centreline temperature calculated using a reaction enthalpy of 400 J/g ($C_p = 1.9$ J/molK and $\rho = 1150$ kg/m$^3$; $j = 5$)

Figure 7-4: Friedman analyses for polypropylene pyrolysis over heating rates of 5, 7, 10, 15 and 20ºC/min showing 95% confidence intervals utilising both measured and calculated centreline temperatures. The large error bars computed for non-zero reaction enthalpies (in brackets) are omitted for clarity.
When the pyrolysis enthalpy was introduced into the centreline temperature calculation up to a maximum of 500 J/g, a dramatic but statistically insignificant increasing trend in $E(\alpha)$ manifested (Figure 7-4). This demonstrates how critical a systematic error in the temperature signal can be to artefactual $E(\alpha)$ variation, and undermines the faith in the increasing trend in activation energy computed by the Advanced Isoconversional Method for polypropylene pyrolysis (Section 3.4.7). This result could merely be an exemplification of the adage “garbage in; garbage out”. The true relationship between activation energy and conversion was impossible to verify. Savitzky-Golay filter length for the differentiation was found to be inconsequential to the results.

The implication of constant activation energy validated the progression to the Invariant Kinetic Parameters (IKP) method and refinement assuming a single process. As there was only one process to consider, the conversion refinement routine was activated. Solutions were sought using the measured and calculated centreline (excluding pyrolysis enthalpy) temperatures and both narrow and wide computational ranges (32 – 78% and 5 – 95%). For any combination of these inputs, the invariant activation energy corresponded to the appropriate Friedman analysis and was associated with comparable uncertainty (i.e. 142 – 244 kJ/mol (measured temperature) and 155 – 308 kJ/mol (centreline temperature)). These high uncertainties in the IKP meant that averaged apparent kinetic parameters were chosen to initialise the model fitting phase of computation, abiding by the recommendation in Section 6.3. Only one iteration was necessary as the decomposition was interpreted as a single step.

Important characteristics of the derived kinetic solutions are shared by all four combinations of temperature signal and computational range: All the more probable kinetic solutions (Table 7-1) offer comparatively poor correlations back to the experimental data (Figure 7-5 and Figure 7-6), although their activation energies match the anticipated range (210 – 285 kJ/mol, as reported in Section 2.6.1) within uncertainty limits. This outcome implies that if any of the five mechanisms $R_n$, $A^3/2$ or $A1$, $F1$ are used for rigorous model fitting, an activation energy that agrees with the Friedman analysis would be computed (Figure 7-4). Being able to visualise both the regenerated conversion rate signals and the statistical ambiguity was pivotal to drawing the conclusion that none of these more probable models were actually applicable.

The fact that various sub-unity orders have been reported for a global $n$-order mechanism describing polypropylene decomposition (Section 2.6.1) agrees with the inconclusive nature of the statistics and the favouring of the $R2$ and $R3$ mechanisms, which are mathematically equivalent to reaction orders of 0.5 and 0.67 respectively. Reports of activation energies between 210 – 285 kJ/mol (Chan and Balke,
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1997b) can be reconciled with the somewhat lower range indicated by this Friedman analysis if these are the results of model fitting a first order reaction (A1, F1), which is likely. This particular mechanism was always associated with the highest activation energy of all the more probable mechanisms (Figure 7-5 and Figure 7-6). It is hard to fathom how an A1, F1 mechanism is assigned 100% absolute probability in one instance (Morice et al., 1997), notwithstanding the difference in atmosphere compared to this study, unless the other similar shaped mechanisms are excluded or associated with very poor kinetic parameters. The perception is that the activation energy range and mechanism uncertainty computed using the new kinetic analysis method matches expectation.

Table 7-1: Non-linear relative probabilities (for refined averaged apparent kinetic parameters only) and averaged linear F-statistics for refined and unrefined averaged apparent kinetic parameters using measured temperature and wide computational limits of 5 – 95% (left) and calculated centreline temperature ($\Delta H_e = 0$) and narrow computational limits of 32 – 78% (right) for polypropylene pyrolysis

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<tr>
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<th>F-Statistic</th>
<th>Non-Linear Relative Prob (Ref)</th>
<th>F-Statistic</th>
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<td>Centreline Temp; 32 - 78% Comp Range</td>
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Non-Linear Relative Prob = Most Probable Mechanism
F-Statistic = Within 95% Confidence Interval

The random scission functions of conversion L2 and L(T) depicted in Figure 7-5 and Figure 7-6 have been derived from significant mathematical complexity (Appendix A2.6) for this very physical scenario. Schemes for random scission of polypropylene (Figure 2-8) and the general case used to develop L2 and L(T) (Figure A2-1) have differences that are acknowledged and shown to be reconcilable (Section 2.6.1), but this is moot as neither model could uniquely describe the weight loss associated with polypropylene pyrolysis. Figure 7-6 illustrates that the initial rate of weight loss from polypropylene was...
higher than that predicted by the refined A1, F1 model, let alone the refined L(T) model that further suppresses the rate at low conversions. Therefore while Sánchez-Jiménez et al. (2010) assign an L2 model to the decomposition of polybutylene terephthalate with confidence, the assignment of an L2 or L(T) model to polypropylene decomposition cannot be justified.

Prout and Tompkins' mechanism development is stated to be analogous to homogeneous chain scission (Brown, 1997). Figure 7-6 includes the P-T model for an integration constant of $k_t^i = 2.0$. This constant generated apparent activation energies (171 – 226 kJ/mol) within the range suggested by the Friedman analysis and that give rise to comparatively significant linear $F$-statistics, according with the recommendations in Section 5.3.3.

The improvement in the correlations of the refined models is clear, even when just pre-exponential factor was refined (Figure 7-5 and Figure 7-6). More models were refined when using the narrow computational range that excluded the maximum, i.e. when refinement was based on a non-descript midrange conversion. The best correlations were computed based on the centreline temperature (excluding pyrolysis enthalpy) and are therefore exemplified in Figure 7-6. Activation energy always tended towards the mechanism invariant value for the models that successfully converged to an optimum (marked by a superscript “2” in Table 7-1).

The facility to input user-defined kinetic parameters was exploited to evaluate the suggestion that polypropylene pyrolysis can be modelled with two overlapped first order processes (Section 2.6.1), keeping in mind that the Friedman analysis certainly does not support this. Pre-exponential factors were calculated using the activation energies proposed by Chan and Balke (1997b) (98.3 kJ/mol and 327.9 kJ/mol) and the compensation effects generated from preliminary IKP analyses. These analyses required a “separation point” to be identified and the use of limited computational ranges as proven successful for the similar simulated data (Section 6.1.2). Figure 7-7 shows the best result obtainable for this scenario, where the separation points (or conversion fractions for the second process) were set to values between 54 – 65\% and the computational limits were set to 5 – 80\% and 20 – 95\%. The concept of adding the effects of two processes appears viable, although this combination of mechanism and kinetic parameters is not suitable. Visually better solutions are generated, at least at the higher heating rates, when an R2 mechanism is associated with the lower activation energy instead of an A1, F1 mechanism.
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Figure 7-5: Conversion rate and selected unrefined averaged apparent models for a 15.5 mg polypropylene sample at 15°C/min under 100 mL/min N₂ using measured temperature and wide computational limits of 5 – 95%. Savitzky-Golay filter length was set to \( N = 11 \).

Figure 7-6: Conversion rate and selected models for a 15.5 mg polypropylene sample at 15°C/min under 100 mL/min N₂ using calculated centreline temperature (\( \Delta H_r = 0 \)) and narrow computational limits of 32 – 78%. Savitzky-Golay filter length was set to \( N = 11 \).
By not pre-determining the two sets of activation energies and mechanisms, and with the same separation points and computational limits, it was possible to obtain the solution shown in Figure 7-8 after a single iteration of the algorithm. Both the averaged apparent kinetic parameters were refined for the lower temperature A1, F1 model, whereas the kinetic parameters were left unrefined for the higher temperature L2 model. While the similar activation energies (236 kJ/mol and 260 kJ/mol (unknown uncertainties)) do not conflict with the Friedman analysis in this case, the fact that the weight fractions do not sum to unity (0.15 + 0.79 = 0.94) is indicative of the need to subtly compensate for a conversion rate that is too high for this heating rate. The visually better correlation to the experimental conversion rate shown in Figure 7-8 compared to any single-step process merely illustrates the fact that there were more parameters to optimise in this case (Section 3.4.7).

Essentially, too much uncertainty associated with every solution trialled invalidated the application of this type of global method to the fundamental study of polypropylene pyrolysis. The corollary of this negative result is that both variants of the random scission scheme must be discounted at least in terms of their suitability to describe polypropylene degradation in a thermogravimetric analyser.
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Figure 7-8: Conversion rate implied by an A1, F1 model with $E_1 = 236 \text{ kJ/mol}$ and $A_1 = 2.5 \times 10^{17} \text{ min}^{-1}$ (15 wt%) and an L2 model with $E_2 = 260 \text{ kJ/mol}$ and $A_2 = 2.6 \times 10^{18} \text{ min}^{-1}$ (79 wt%) and the experimental conversion rate for a 15.5 mg polypropylene sample at 15°C/min under 100 mL/min N₂

7.2 **TBBA-BDPE Degradation**

This section highlights what can be gleaned about TBBA-BDPE degradation from simultaneous thermal analyses that were not complicated with the polymer or Sb₂O₃ synergist. All quantitative analyses apply to data collected in a nitrogen atmosphere.

Experimental observations are correlated with literature expectations discussed in Section 2.5.2 that mainly concern the parent compound, TBBA. Molecular analogues of TBBA-BDPE were also analysed so that it is possible to better speculate on the role of different elements of the TBBA-BDPE molecule.

7.2.1 **Kinetic Analysis**

TG data for the pyrolysis of 14 – 18 mg TBBA-BDPE at 2, 3, 5, 7, 15 and 20°C/min under 100 mL/min nitrogen were selected from a pool of experiments ([TG/DSC Set 2: PE-68](#)) for input into the kinetic analysis method. In all cases, the degradation followed a pattern that could only be described by a complex kinetic scheme (Figure 7-9). Roughly 75% of the reactive weight was converted to volatiles over the rapid first stage of weight loss, while the remainder was lost gradually. Kinetic analysis with at least three processes was necessary to match the changes in curvature.
In stark contrast to the kinetic analysis of polypropylene pyrolysis, the process corresponding to the rapid weight loss was able to be confidently assigned to a specific mechanism: A3. After four iterations of the algorithm, only this and the P3 mechanism were significantly probable and associated with activation energies within the 95% confidence interval of the invariant activation energy (98 – 149 kJ/mol) (Table 7-2). The same theory underpins the P3 and A3 mechanisms at low conversion (Table 5-1); the favouritism of the P3 mechanism simply reaffirms the choice of the A3 mechanism in this case. These models match the experimental signal well at low conversions, but the sigmoidal A3 mechanism could not describe the deceleration of the latter part of the first stage of weight loss when paired with any of the 22 mechanisms for the second stage. Figure 7-9 represents the best correlation of the prediction to the experimental conversion rate, although the five other fits are only marginally less convincing; the statistics would not be as definitive otherwise. Weight fraction assigned to the first process was ultimately computed to vary between 62 – 80% (73 – 75% for the three best correlations). This variation illustrates the significant flexibility in the algorithm that accommodates physical differences in the samples and may have improved the outcome. The computational range for this first process was expanded from an initial input of 5 – 70% to 0 – 100% for the last iteration.

Ironically, the inability of the A3 mechanism to represent the weight loss character at high component conversion actually increased the confidence in its selection. It is understood from the power law derivation that exponential decay terms are truncated for convenience (Appendix A2.1), meaning that the predicted conversion rate will not decelerate as quickly as it should as conversion increases. A longer tail to the A3 mechanism would lead to a better fit (Figure 7-9). Furthermore, when the maximum rate was used to refine the kinetic parameters (facilitating the exclusion of the purely acceleratory P3 mechanism), the statistical certainty degraded dramatically. This response brings into question the validity of the simplistic empirical transformation of the P3 mechanism that creates the sigmoidal character of the A3 mechanism (Table 5-1). It is conceivable that this initial stage of weight loss proceeded according to a nucleation and nucleus growth scheme of order three, but not the simplified mathematical model that is supposed to represent it. As mentioned in Appendix A2.2, the conversion rate at midrange conversions can only conform precisely to an An mechanism if the inhibition of nucleus growth is purely random. Evidence that a product bubbled through the transforming sample was visible set into the residual char when a large amount of TBBA-BDPE (45 mg) was pyrolysed up to 600ºC.

The logic outlined for IKP method variants (Section 3.4.6) was applied in an attempt to find an alternate super correlation with respect to sample weight (2.4 – 28.3 mg all at 10ºC/min) for the first process. It was confirmed that no such compensation effect exists in this case: The linear correlation coefficient for
Table 7-2: Non-linear relative probabilities (for refined averaged apparent kinetic parameters only) and averaged linear $F$-statistics for TBBA-BDPE pyrolysis at six heating rates (2, 3, 5, 7, 15 and 20°C/min) after the fourth iteration

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<th>F-Statistic (Ref)</th>
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- $= Most$ Probable Mechanism
- $= Within 95% Confidence Interval

- Unrefined E, Unrefined A; *Unrefined E, Refined A; **Refined E, Refined A

Figure 7-9: Conversion rate and conversion (inset) of reactive weight for a 14.2 mg TBBA-BDPE sample at 5°C/min under 100 mL/min N$_2$. The A3 model with $E = 129$ kJ/mol and $A = 1.5 \times 10^{11}$ min$^{-1}$ selected as the best fit for the rapid stage of weight loss after four iterations using data at six heating rates (2, 3, 5, 7, 15 and 20°C/min) is shown. This first process (73 wt%) is not shown explicitly and the latter two process are not scaled by their respective weight fractions (21 wt% and 4 wt%) for clarity
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this potential super correlation when developed from the standard incorrect mechanism compensation effects is only 0.2. Therefore, the uncertainties in the IKP derived from the super correlation of Figure 6-5a \( (E_{1,\text{inv}} = 98 - 150 \text{ kJ/mol}; A_{1,\text{inv}} = 10^{10} - 10^{13} \text{ min}^{-1}) \) are likely to absorb the random errors arising from experiments conducted with different sample weights. It was not deemed necessary to reformulate the compensation effects for incremental conversion (Section 3.4.6), as the single-step character of the first stage was verifiable with a Friedman analysis (Figure 7-12).

No gains in determinism for this first process were made by halving the sample weight variation to 16.2 – 18.0 mg by only analysing four experiments, as anticipated. When the two highest heating rates were excluded, however, reasonably convincing statistics were computed that indicate a preference for the A2/P2 mechanism for this first process (Table 7-3). The excellent correlation to experimental data is irrefutable (Figure 7-11). Better consistency was observed averaging the kinetic parameters across four rather than six experiments; while expected, this undermines the selection of the A3 mechanism.

Friedman analyses over the slower four and all six heating rates show constant activation energy up to 65% overall conversion (Figure 7-12). Analysis with six heating rates reduced the 95% confidence intervals to relatively narrow limits (115 – 150 kJ/mol) that agree with the uncertainty in the corresponding invariant activation energy, and implicate the A3 mechanism \( (E = 129 \text{ kJ/mol}) \). Beyond 65% conversion, the activation energy calculation was extremely erratic and cannot be used to speculate on the nature of the degradation. Super correlations are also relatively poor for the second and third processes, making it difficult to settle on a specific permutation that matches the decomposition for all heating rates. It is noted, however, that the second and third order reaction mechanisms (F2/F3) are best able to regenerate the curvature changes.

Figure 7-10: Super correlations used to derive IKP for the first stage of weight loss for TBBA-BDPE pyrolysis from six heating rates (a) and four heating rates (b) on the fourth iteration. Approximate 95% confidence intervals are shown for the compensation parameters

Friedman analyses over the slower four and all six heating rates show constant activation energy up to 65% overall conversion (Figure 7-12). Analysis with six heating rates reduced the 95% confidence intervals to relatively narrow limits (115 – 150 kJ/mol) that agree with the uncertainty in the corresponding invariant activation energy, and implicate the A3 mechanism \( (E = 129 \text{ kJ/mol}) \). Beyond 65% conversion, the activation energy calculation was extremely erratic and cannot be used to speculate on the nature of the degradation. Super correlations are also relatively poor for the second and third processes, making it difficult to settle on a specific permutation that matches the decomposition for all heating rates. It is noted, however, that the second and third order reaction mechanisms (F2/F3) are best able to regenerate the curvature changes.
Table 7-3: Non-linear relative probabilities (for refined averaged apparent kinetic parameters only) and averaged linear F-statistics for TBBA-BDPE pyrolysis at four heating rates (2, 3, 5 and 7°C/min) after the fourth iteration.

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Most Probable Mechanism: = Within 95% Confidence Interval
°Unrefined E, Unrefined A; ¹Unrefined E, Refined A; ²Refined E, Refined A

Figure 7-11: Conversion rate and conversion (inset) of reactive weight for a 16.0 mg TBBA-BDPE sample at 7°C/min under 100 mL/min N2. The A2 model with $E = 194$ kJ/mol and $A = 1.7 \times 10^{17}$ min$^{-1}$ selected as the best fit for the rapid stage of weight loss after four iterations using data at four heating rates (2, 3, 5 and 7°C/min) is shown. This first process (75 wt%) is not shown explicitly and the latter two process are not scaled by their weight fractions (both 13 wt%) for clarity.

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In accordance with Section 3.4.6, a linearised version of the Sestak-Berggren equation (Equation 3-52) was fitted to each experiment to assist with finalising the An mechanism selection. However, two problems arose: The indeterminacy of this inverse kinetic problem generated large uncertainties in the mechanism parameters, and the overlap of the second process distorted the numerical representation of $f(\alpha)$ such that the selection of $\alpha_i$ was compromised. Section 3.3.1 shows that the Avrami-Erofe’ev order is solely dependent on this conversion value (Equation 3-14). While $\alpha_i$ is insensitive to activation energy, obviously the integrity of the component conversion signal is critically important. Highly variable results were obtained using component conversion, but when overall conversion was substituted, the Avrami-Erofe’ev order was calculated consistently using the maxima shown in Figure 7-13 in the range 2.0 – 2.5. Considering the fact that the “true” component conversion $\alpha_i$ for first stage would naturally be higher than that for the overall conversion, the Avrami-Erofe’ev order for the first stage is likely to be greater than 2.5.

The new kinetic analysis method was moderately successful when tasked with model fitting three independent overlapped decomposition processes to real data for TBBA-BDPE pyrolysis. A correct and thorough appraisal of the analysis results clearly demands a good understanding of the mechanism origins. Nucleation and nucleus growth kinetics relate reasonably well to the first rapid stage of weight...
loss, and the over-simplified An mechanism applicable for low conversions is most likely third order. A lower order not less than two was also shown to be feasible. The fact that in theory the Avrami-Erofe’ev order is equivalent to the sum of the number of decomposition steps/product molecules required for a growth nucleus and the number of dimensions controlling nuclei growth was kept in mind when evolving the description for TBBA-BDPE degradation with other analyses.

Figure 7-13: Numerical functions of overall conversion (with respect to reactive weight) derived from the differentiated overall conversion signals and the kinetic parameters $E = 129$ kJ/mol and $A = 1.5 \times 10^{11}$ min$^{-1}$. The range of overall conversion encompassing the maxima is highlighted.

7.2.2 Thermodynamic Analysis

Only semi-quantitative and comparative thermodynamic analyses were conducted on the DSC data in recognition of the experimental issues raised in Section 4.2.4. The changing relative position of the sample and reference crucibles with temperature in the Labsys manifested as an upwards drift in the heat flow baseline (thermal asymmetry), and reduction in thermal load in the sample crucible caused a sympathetic upwards drift or discontinuity. Linear baselines were applied for the integration of thermal events.

Pyrolysis of TBBA-BDPE

The pyrolysis results for TBBA-BDPE collected according to the method TG/DSC Set 2: PE-68 are typified by Figure 7-14. Endothermic melting occurred at about 108ºC as anticipated (Section 2.6) at a
heating rate of 10°C/min. The first stage of rapid weight loss between 275 – 325°C was coincident with a significant heat release of about 30 kJ/mol, whether foil coverings were used or not. Weight in Figure 7-14 is expressed as a percentage of the initial weight, not the reactive weight as shown in the previous section. At all heating rates, 55 – 60% of the initial weight of TBBA-BDPE was lost over this first stage.

![Figure 7-14: Heat flow and weight signals for a 12.2 mg TBBA-BDPE sample at 10°C/min under 100 mL/min N₂ (baseline corrected; closed crucibles). The small exotherm at ~400°C is an artefact caused by the aluminium foil](image)

The exotherm coinciding with this first stage of weight loss was present regardless of whether the decomposition was carried out in a nitrogen or air atmosphere, although it was overshadowed by highly exothermic oxidation in the latter case (Figure 7-15). Oxygen in the atmosphere also brought about a change in the shape of the weight signal after the rapid weight loss. Conversion of the remaining 40 – 45% of the sample was slower initially, but then accelerated until no residue remained, given sufficient time. The shape of the weight signal >325°C is superficially very similar to the shapes of the deceleratory diffusion controlled processes, D2 and D3, for a constant heating rate (Table 5-1).

Figure 7-14 shows that the heat flow away from the sample peaked at 550°C when the weight loss rate also slowed down markedly. This feature was verified by showing that the decreasing trend in heat flow continued until the conclusion of the temperature program when TBBA-BDPE was pyrolysed up to 1000°C (Figure 7-16). While the thermal effects could not be quantified, it is reasonable to conclude that the third and final degradation process was much more endothermic than the second. Lengthy
isotherms at high temperature were not accompanied by any further weight loss; the amount of stable residual material was solely dependent on temperature. Competition between volatilisation and an endothermic char-forming process that continued after the sample weight stabilised at about 20% was likely. The expected endotherm is plainly visible in the heat flow signal that corresponds to the experiment where the char from the decomposition of 44.8 mg of TBBA-BDPE foamed up and sealed the sample crucible (Figure 7-17). Furthermore, the characteristic exothermic peak exhibits two maxima for sufficiently large sample weights, as apparent in Figure 7-17 in particular.

The onset temperature of the first stage of decomposition (275°C) roughly coincides with the temperature at which aliphatic bromine is expected to eliminate as HBr (> 290°C) (Section ). However, heating rates slower than 10°C/min undermined this link as the onset temperatures were even lower; at the slowest heating rate of 0.5°C/min the onset temperature was 255°C. There is no indication that evaporation occurred in the shape of the weight signal (i.e. no acceleratory character akin to water evaporation (Section 6.2.1)). Association of the rapid weight loss with the cleaving of the isopropylidene bridge that is labile around this temperature is discredited by the fact that no exotherm is identified with the pyrolysis of the parent compound, TBBA, that shares this chemical structure.
A New Adaptation of The Method of Invariant Kinetic Parameters and its Application to a Flame Retardant System

Figure 7-16: Heat flow and weight signals for an 11.0 mg TBBA-BDPE sample at 10ºC/min under 100 mL/min N₂ (not baseline corrected; open crucibles)

Figure 7-17: Heat flow signals for open crucibles and an effectively closed sample crucible for TBBA-BDPE samples 44.5 mg/100 mL/min N₂ and 44.8 mg/33 mL/min N₂ respectively at 10ºC/min (baseline corrected)
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Pyrolysis of TBBA

Simultaneous thermal analysis data for TBBA pyrolysis published by Barontini et al. (2004b) were successfully replicated with the experimental method TG/DSC Set 2: FR Analogues. It was essential to close the crucibles with foil to reveal the expected endothermic peak, as it was conspicuously absent with open crucibles (Figure 7-18). The sudden reduction in thermal load that manifests as a jump in the baseline opposing the endotherm contributes to the understatement of this peak. It was not possible to quantify the enthalpy associated with this endothermic event. Aside from precise enthalpies, all features of the data collected for this study could be directly related to the articles cited in Section 2.5.2.

Figure 7-18: Heat flow signals for TBBA samples with (10.9 mg) and without (11.2 mg) foil coverings on both sample and reference crucibles at 10°C/min under 100 mL/min N₂ (baseline corrected). The weight signal for closed crucibles is shown

Evaporation of TBBA, accounting for a loss of 12% of its initial weight (Marsanich et al., 2004, Barontini et al., 2004b), would have been concealed in the weight signal as it competes with degradation and char-forming processes. If 12% of the sample evaporated, roughly 58% of the rapid weight loss must have been due to molecular breakdown (Figure 7-18). This proportion coincides exactly with the weight fraction of bromine in TBBA. The weight loss onset temperatures of TBBA and TBBA-BDPE imply that TBBA was slightly less labile than TBBA-BDPE, which was not expected (Section 2.6.2). This suggests that there was an unanticipated destabilising effect on the aliphatic carbon-bromine bonds in TBBA-BDPE, or more likely, another reaction took place in TBBA-BDPE that has a lower onset temperature.
No exothermic degradation was in evidence nor anticipated for TBBA. The exotherm observed for TBBA-BDPE pyrolysis must have been peculiar to the only elements of the molecule that differentiate it from TBBA; the brominated ether substituents. Furthermore, the heat flow signals for TBBA-BDPE and TBBA are practically identical aside from this exothermic feature. Their degradation above 350°C likely involved similar reactions that resulted in a slightly higher residual weight in the case of TBBA-BDPE. Since the first stages of both TBBA-BDPE and TBBA weight loss are insensitive to atmosphere, any proposed mechanisms must not involve oxygen or any products of a reaction with oxygen.

7.2.3 Mode of Degradation

Benson’s Group Additivity Method

Quantifiable endothermic and exothermic peaks in a heat flow signal can be related to molecular rearrangements using Benson’s Group Additivity Method. This “simple, efficient and reliable” method (Bhattacharya and Shivalkar, 2006) constructs standard heats of formation for organic molecules by adding together the known enthalpies of their constituent chemical groups extracted from an extensive database. The difference between the heats of formation of product(s) and reactant(s) is equivalent to the enthalpy of the proposed reaction.

The NIST Chemistry WebBook accepts drawings of chemical structures and reports their standard heats of formation along with all the applicable group contributions. Corrections to account for ring strain, symmetry and other effects are included (Stein and Brown, 2011) that result in a claimed increment accuracy of 0.5 kJ/mol (Stein and Brown, 2008). This facility was used to compute all the heats of formation for organic molecules trialled in this study.

Reaction Scheme

Beginning with TBBA-BDPE and the understanding that molecular oxygen is unavailable, various inter- and intramolecular reaction pathways were explored that involve the ether groups. Each reaction enthalpy calculated in this way was compared to the integrated exotherm of 30 kJ/mol associated with the first stage of weight loss for TBBA-BDPE. One chemical reaction correlates well:

\[
\begin{align*}
\text{TBBA-BDPE} + 2 \text{HBr} &\rightarrow \text{TBBA} + 1,2,3\text{-tribromopropane} + 2 \text{Br}_2 \\
\Delta H_R^0 \text{gas} &\approx -30 \text{ kJ/mol}
\end{align*}
\]

Reaction 1: Hypothetical thermal degradation pathway for TBBA-BDPE in an inert atmosphere
Reaction 1 is theoretically sound and would release the 30 kJ/mol that was observed experimentally, if it runs to completion. The two chemically equivalent carbon reaction sites in TBBA-BDPE (marked with asterisks) are slightly electropositive given the proximity of the electron withdrawing oxygen and bromine substituents. This leaves these carbon nuclei vulnerable to attack from electron rich species such as bromine, which is depicted bonded to hydrogen as stable HBr in Reaction 1. At each reaction site, bromine forms a bond with the reactive carbon atom as the electron from the C-O bond is pushed onto the oxygen atom; an example of a concerted nucleophilic substitution mechanism. Electropositive hydrogen, originally from the HBr, is attracted to the oxygen and bonds to satisfy the valence of both elements. Hydrogen bromide required for Reaction 1 could be sourced from the aliphatic or aromatic portions of other TBBA-BDPE molecules. Furthermore, the tribromopropane product would thermally decompose itself to release more hydrogen bromide to sustain the reaction.

A certain weight change is implied by Reaction 1, which was compared to the weight signal for TBBA-BDPE pyrolysis. As stated previously, 55 – 60% of the initial weight was lost during the exothermic event. This corresponds to exactly the proportion of weight loss that would occur if Reaction 1 runs to completion and all tribromopropane volatilises (59.5%), which would be expected at temperatures above 270°C (Chemsynthesis). The inability of TBBA-BDPE to tautomerise and supply aromatic bromine at temperatures below 360°C would be negated as soon as the reaction initiates and the ether groups are lost. Reaction initiation could be attributed to the cleavage of the aliphatic bromine, although the low onset temperature would have to be justified. Perhaps the concerted reaction in itself is capable of destabilising the carbon-bromine bonds such that weight loss begins at a temperature lower than that normally required to break these bonds.

While this hypothesis neatly connects the TG/DSC data for TBBA-BDPE pyrolysis, it contradicts observations relating to TBBA pyrolysis, which is critical given that TBBA is a product in Reaction 1. If TBBA-BDPE decomposes principally according to Reaction 1, then its weight and heat flow signals should appear identical to those of TBBA save for the initial exothermic weight loss. Figure 7-14 and Figure 7-18 show that while the heat flow signals offer no real opposition to this expectation, the weight signals do. TBBA lost a similar proportion of weight during its first decomposition stage after taking into account the anticipated evaporation. Considering Reaction 1, TBBA-BDPE should lose proportionally more weight than TBBA at this stage because the brominated ether groups would volatise and add to the weight loss from the TBBA product of Reaction 1. Figure 7-14 and Figure 7-18 clearly show the opposite occurred, where the weight loss exhibited by TBBA-BDPE was less than this mechanism predicts by approximately 20%, if the weight loss of TBBA is used as a basis.
When the temperature was raised from 325°C to 600°C, the partially degraded TBBA-BDPE slowly lost additional weight equivalent to, on average, two bromine atoms from each TBBA-BDPE molecule. This loss can be readily justified by condensation reactions that liberate aromatic bromine. The char residue, amounting to 20% of the initial sample weight by 1000°C, could have conceivably been made up of debrominated aromatics. Barontini et al. (2004b) calculate that half the initial TBBA sample weight transforms to condensable polybrominated aromatic products made up of over 50 wt% bromine. This experimental fact does not challenge the legitimacy of Reaction 1, but it does quash the idea that there is no competitive weight loss from the breaking of the isopropylidene bridge. The same study concludes that only 1% of the total bromine remains in the char residue, which supports the idea that the TBBA-BDPE char was comprised of debrominated aromatics.

The A2/A3 mechanism character of the first stage of weight loss for TBBA-BDPE pyrolysis (Section 7.2.1) most likely manifested from the breaking of the ether linkage and the isopropylidene bridge. Two-step degradation is implied by Reaction 1, although it can reduce to a single step if electropositive carbon successfully destabilises the carbon-bromine bonds and eliminates the need for free HBr. Isopropylidene bridge scission also constitutes single step. If the gaseous nuclei from either degradation process move directly towards the surface of the molten sample, i.e. in one dimension, it is reasonable to propose a nucleation and nucleus growth order between two and three. Incidentally, if free HBr is not required in Reaction 1, then the enthalpy of reaction is more like -100 kJ/mol and could conceivably balance the endothermic isopropylidene bridge scission. Perhaps the two maxima observed in the exothermic event (Figure 7-17) relate to such a complication.

**TBBA-BDPE Analogues**

Three analogues of TBBA-BDPE derived from TBBA were also pyrolysed in a nitrogen atmosphere according to the method **TG/DSC Set 2: FR Analogues**. Results from samples sized between 10.7 – 14.7 mg are shown in Figure 7-19 with those presented previously for TBBA-BDPE and TBBA.

The analogue that only differs by its lack of aliphatic bromine, tetrabromobisphenol A dipropyl ether (TBBA-DPE; Figure 4-3b), exhibits very different weight and heat flow signals compared to TBBA-BDPE (Figure 7-19). Its decomposition pathway did not involve the same exothermic process that occurred in TBBA-BDPE. Weight loss for TBBA-DPE was delayed by close to 100°C at 10°C/min, and the shape of the weight signal suggests that a linear or acceleratory process resulted in the volatilisation of 90% of the initial weight. The nature of this process is endothermic; thus evaporation is implicated. Evaporation, if it did occur, clearly did not proceed alone as TBBA-DPE lost weight above 400°C following the same
changes in curvature as all the other tested compounds, implicating the same condensation reactions. Aromatic bromine likely severed the ether linkages to enable these reactions. Given the clear lack of an exothermic feature and the comparatively high onset temperature for TBBA-DPE pyrolysis, aliphatic bromine must be required to initiate the decomposition of TBBA-BDPE.

Figure 7-19: Heat flow (solid lines) and weight (dashed lines) signals for 10.7 – 14.7 mg samples of structural analogues of TBBA-BDPE at 10ºC/min under 100 mL/min N₂. The evaporation of BA-DPE is not shown for clarity (baseline corrected; closed crucibles)

Since 100% of the bisphenol A dipropyl ether (BA-DPE; Figure 4-3a) evaporated, Bisphenol A diglycidyl ether (BADGE; Figure 4-3c) was chosen to investigate how a total lack of bromine might affect the ether reactivity. An exothermic event coincides with BADGE decomposition (Figure 7-19), but the heat released was vastly greater than that attributable to an analogous reaction to Reaction 1, taking into account the molecular weight discrepancy. In fact, in the absence of bromine, an equivalent attack by oxygen on the electropositive carbon would absorb a small amount of heat (42 kJ/mol), rather than release energy. The instability of the epoxy group in BADGE adds interpretive complications; these groups are likely to rearrange to form aldehydes and ketones. Empirical heat release was estimated to range from 205 – 220 kJ/mol, and was always between that computed for aldehyde rearrangement (251.2 kJ/mol) and ketone rearrangement (190.2 kJ/mol) using Benson’s Group Additivity Method (Stein and Brown, 2011). BADGE was the most thermally stable of all the compounds tested. It may be that
the total absence of bromine radicals delayed its decomposition. Interestingly, BADGE appeared to char in the same manner as the other compounds (Figure 7-19), despite the fact that it does not have aromatic substituents adjacent to the ether oxygen.

Dettmer et al. (1999) cite dibromopropene, not tribromopropane, as a pyrolysis product of TBBS-BDPE (Section 2.6.2). In order to form dibromopropene, HBr must be eliminated from the aliphatic portions of this molecule either before or after the ether linkage is broken, which is an endothermic process. The identification of brominated alkanes and propenes by Balabanovich et al. (2005) during brominated epoxy resin pyrolysis (Section 2.6.2) also suggests that some elimination may occur in the propyl groups of TBBA-BDPE, where the liberated HBr would then attack the ether bonds.

**FTIR Spectroscopy**

Figure 7-20 shows the infrared spectra of the hot (180°C) effluent from the Q600 collected during the pyrolysis of a 16.0 mg sample of TBBA-BDPE at 10°C/min (TG/FTIR). The shape of the absorbance at wavenumbers corresponding to the distinctive P- and R- branches for HBr sympathises very well with the overall weight loss rate (Figure 7-21). Barontini et al. (2004b) found the time to the absorbance maximum for HBr and the time to the peak rate of weight loss to coincide for TBBA pyrolysis. If these times are equated in this case for TBBA-BDPE, the behaviour of the two molecules appears qualitatively very similar. However, absorbance and weight loss rate match even better for TBBA-BDPE as the relative magnitude of the main peak in HBr absorbance is enhanced (Figure 7-21 cf. Figure 3 in Barontini et al. (2004b)). Conceivably this is because the aliphatic bromine present in TBBA-BDPE was liberated at this stage, and evaporation would not have occurred at the onset of weight loss. Perhaps the sharp decrease in weight loss rate from its peak compared to the more gradual reduction in HBr absorbance (Figure 7-21) is a result of the brominated compounds that had already contributed to the weight loss evolving HBr before detection in the FTIR.

As the snapshot at the peak absorbance highlights (Figure 7-20, grey line), a second set of P- and R-branches was briefly detected at a slightly higher frequency (centred on 2880 cm⁻¹ cf. 2560 cm⁻¹ for HBr). This set matches the pattern expected for HCl (NIST Mass Spec Data Center, 2011) and suggests a small impurity in the TBBA-BDPE sample from the manufacturing process. Interestingly, this feature appeared at about 320°C, just after HBr began to evolve, not >370°C as anticipated for aliphatic chlorine under normal circumstances (Section 2.5.2). Carbon monoxide (centred on 2140 cm⁻¹) appeared fleetingly in very low concentration at this same point in the pyrolysis.
Figure 7-20: A series of FTIR spectra for a 16.0 mg TBBA-BDPE sample at 10ºC/min under 50 mL/min N₂ highlighting P- and R-branches for the diatoms HBr, HCl and CO. A slice at 33 mins (peak HBr absorbance) is shown in grey and depicts the distinct P- and R-branches for HCl and the small R-branch for CO.

Figure 7-21: Weight loss rate (black line) recorded for the same 16.0 mg TBBA-BDPE sample (Figure 7-20) with the arbitrarily scaled time-absorbance slice for the HBr P- and R-branches overlayed (purple line). A small baseline error exists in the weight signal at ~140ºC that corresponds to the switch in heating rate from 20ºC/min to 10ºC/min.
A fourth feature centring around 3000 cm\(^{-1}\) is visible in Figure 7-20 just prior to the point when the weight loss signal and HBr absorbance pass through the second local maximum at 460\(^{\circ}\)C. This absorbance increased in intensity up until the end of the temperature program and paralleled the absorbance due to CO. The spectrum of methyl bromide (Chu et al., 2011) matches this feature well, excepting the fact that this suspected overtone (i.e. representation of electron jumps of two vibrational energy levels) is more intense than the fundamental due to the high temperature of the analysed effluent. Reaction pathways that explain this increasing CO and CH\(_3\)Br emission during char formation were not forthcoming, but at least the CO appearance cannot be considered anomalous as it is also detected during TBBA and electronic board pyrolysis (Barontini and Cozzani, 2006).

With reference to the kinetic analysis (Section 7.2.1), it may be that the high temperature charring process that generates CO and CH\(_3\)Br conforms to a second or third order reaction mechanism (F\(_2\)/F\(_3\)). The initial, open char structure formed by the elimination of HBr may have gradually collapsed according to reaction pathways that become progressively more viable the more thermal energy is available. It was observed that the higher the temperature of pyrolysis, the lower the structural integrity of the char residue. This scenario does imply the chemical control of an F\(_2\)/F\(_3\) mechanism.

### 7.3 TBBA-BDPE and Sb\(_2\)O\(_3\)

Sb\(_2\)O\(_3\) was expected to accelerate the emission of HBr once it began to evolve from TBBA-BDPE (Section 2.2.2 and Section 2.5.2). The 29.0 mg sample “PE-68/Sb\(_2\)O\(_3\) mixture” was pyrolysed at 10\(^{\circ}\)C/min and the hot effluent analysed in real time (TG/FTIR) to demonstrate this effect (Figure 7-22 and Figure 7-23). The relatively slow initial increase in HBr absorbance observed for TBBA-BDPE (Figure 7-21) transformed to an almost instantaneous jump from baseline to maximum absorbance when Sb\(_2\)O\(_3\) was present (Figure 7-23), even at this low Sb/Br atom ratio of 0.093.

When the position of the HBr absorbance on the temperature/time scale was translated by the delay between the Q600 and the FTIR assigned in Figure 7-21 (9.3 mins; including time to equilibrate at 40\(^{\circ}\)C), the peak in weight loss rate coincided with the peak in HBr absorbance (Figure 7-23). This is consistent with the fact that the weight signals plotted in Figure 7-23 also overlay. Therefore, while Sb\(_2\)O\(_3\) may have accelerated the release of HBr, HBr was not evolved until a higher temperature. A likely explanation is that the HBr that would have otherwise been detected prior to the absorbance peak was sequestered as SbBr\(_3\) (Section 2.5.2). Bromine was very much in excess in this sample mixture, even on the basis of just aliphatic bromine, and therefore the sublimation of SbBr\(_3\) was anticipated (Section 2.6.2).
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Figure 7-22: A series of FTIR spectra for the 29.0 mg “PE-68/Sb$_2$O$_3$ Mixture” sample (Sb/Br atom ratio of 0.093) at 10°C/min under 50 mL/min N$_2$. Emission of CO is shown to precede HBr.

Figure 7-23: Weight loss rate (black line) recorded for the same 29.0 mg “PE-68/Sb$_2$O$_3$ Mixture” sample (Figure 7-22) with the arbitrarily scaled time-absorbance slice for the HBr P- and R-branches overlayed (purple line). The time scale was adjusted assuming the same delay between the Q600 and FTIR sampling as assigned to TBBA-BDPE (Figure 7-21). The weight signal for the 16.0 mg TBBA-BDPE sample (Figure 7-20) is shown for comparison.
Weight loss rate was non-zero from about 50°C before HBr was detected, which is consistent with the idea that SbBr₃ evolved from the Q600 over this temperature range. Other compounds, such as CO, were detected before HBr and would have contributed to this early weight loss (Figure 7-22). However, the percentage of weight lost from the TBBA-BDPE/Sb₂O₃ mixture over this first complex decomposition stage was practically the same as that for TBBA-BDPE (Figure 7-23). The shape of the weight signal for this first stage also appears unaffected by Sb₂O₃ and the same exotherm coincides (Figure 7-24).

The fact that CO was only detected before HBr for the TBBA-BDPE/Sb₂O₃ mixture suggests that Sb₂O₃ was more involved in the degradation of TBBA-BDPE than previously thought. While the sequestration of bromine by antimony was still likely, it appears that no more bromine as SbBr₃ was formed than would have appeared as HBr in the absence of Sb₂O₃. This bears out the statement in Section 2.5.2 that Sb₂O₃ will only interact with HBr once it has evolved from the FR. Oxygen freed from Sb₂O₃ could have precipitated reactions that led to the observed emission of CO. These hypotheses do not contradict the fact that the reaction(s) giving rise to the characteristic exotherm at the peak rate of weight loss must not be affected by SbO₃.

While the second peak in HBr absorbance occurred at least 30°C lower than the 460°C observed for TBBA-BDPE (Figure 7-23 cf. Figure 7-21), HBr was detected until the temperature program completed.

Figure 7-24: Heat flow and weight signals for the 29.0 mg “PE-68/Sb₂O₃ Mixture” sample (Sb/Br atom ratio of 0.093) at 10°C/min under 50 mL/min N₂.
This implies that HBr did not pass below the detection limit for this 29.0 mg sample as it most likely did for the 16.0 mg sample of TBBA-BDPE. With the HBr absorbance scaled to match the weight loss rate in the latter stages of pyrolysis as it was for TBBA-BDPE, it is apparent that the maximum absorbance was not as significant as it was for TBBA-BDPE. This is attributed to the loss of up to the theoretical maximum of 28% of the total bromine as SbBr₃, which is equivalent to a quarter of the initial sample weight.

### 7.4 Flame-Retarded Polypropylene

#### 7.4.1 Thermal Degradation

All samples of flame-retarded polypropylene subjected to constant heating rate experiments in an inert atmosphere (TG/DSC Set 1) exhibited two clear stages of weight loss. These are distinguishable in both the weight and differentiated weight (conversion rate) signals shown for the PolyPacific formulation with 10.4% TBBA-BDPE (1707-8) (Figure 7-25). A broad endotherm in the heat flow signal associated with melting agrees with the melting point observed for polypropylene (Figure 7-1). Aside from the anticipated large endotherm associated with second stage of weight loss, no other thermal features are apparent. Since it was confirmed that TBBA-BDPE decomposes at temperatures greater than 240 – 270°C (e.g. Figure 7-14) and the temperature ranges for the second stage coincide with those for polypropylene pyrolysis (Figure 7-2), the simplistic assignments of the first stage to TBBA-BDPE loss and the second stage to polypropylene degradation were made.

It was necessary to judge whether it is possible to reproduce the pyrolysis behaviour of the flame-retarded polypropylene by merely weighting and summing the measured signals for the two individual components. If so, it would imply that TBBA-BDPE does not interact with molten polypropylene and its FR activity must be confined to the gas phase. Weight and heat flow signals for polypropylene loaded with 31.2% TBBA-BDPE (Sample 12) pyrolysed at 10°C/min (TG/DSC Set 2: FR Formulations) were selected for this comparison. Sample sizes, as indicated in Figure 7-26, were kept to a minimum so that any irrelevant physical effects did not confound the measurements. The quality of the heat flow signal does not appear sufficient to resolve the exotherm associated with TBBA-BDPE degradation, if it is there to see (Figure 7-26). What is apparent is the transformation of the simple endotherm related to polypropylene degradation to a dual-peaked endotherm. While a clear distinction between the stage of rapid weight loss from TBBA-BDPE and the onset of polypropylene degradation is implied by the weighted summations at 10°C/min, a much less pronounced distinction is shown for Sample 12.
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Figure 7-25: Heat flow, conversion rate and weight signals for 4.3 – 7.1 mg samples of the PolyPacific formulation with 10.4% TBBA-BDPE (1707-8) at heating rates 2 – 20°C/min under 100 mL/min N₂.

Figure 7-26: Heat flow and weight signals for samples of polypropylene loaded with 31.2% TBBA-BDPE (Sample 12) at 10°C/min under 100 mL/min N₂. Signals collected under the same conditions for a 4.5 mg sample of polypropylene and the summation of this and the correct weighting of 4.0 mg TBBA-BDPE to simulate a 31.2% loading are shown. All heat flow signals were re-zeroed after melting (baseline corrected; open crucibles).
To reinforce the latter observation, the kinetic solution that corresponds well to real TG data for TBBA-BDPE pyrolysis (Figure 7-9) was recreated using the temperature program for an experiment conducted on a 7.1 mg sample of the PolyPacific formulation with 10.4% TBBA-BDPE (1707-8) at 5ºC/min (TG/DSC Set 1). Figure 7-27 shows the conversion rate from this experiment with this kinetic solution overlayed, weighted at 10.4%. While the onset temperatures agree, the temperature range for the first stage of weight loss for flame-retarded polypropylene is much broader than that shown for TBBA-BDPE. Therefore, TBBA-BDPE and polypropylene interacted in the condensed phase in at least two different ways: Polypropylene hindered the weight loss, but not necessarily the degradation of TBBA-BDPE, and TBBA-BDPE was able to alter the kinetics of polypropylene degradation up to a certain temperature.

Figure 7-27: Conversion rate for a 7.1 mg sample of the PolyPacific formulation with 10.4% TBBA-BDPE (1707-8) at 5ºC/min under 100 mL/min N₂ (baseline corrected; open crucibles) with the kinetic prediction for pure TBBA-BDPE pyrolysis scaled by 10.4% overlayed

Different sample sizes of the PolyPacific formulation with 10.4% TBBA-BDPE (1707-8) were pyrolysed at 20ºC/min (TG/DSC Set 2: FR Formulations) to explore any impact this variation had on the character of the weight loss signal. The degree of segregation of the two main stages of weight loss was indeed dependent on sample weight (Figure 7-28). This dependence manifests in the weight signals only over the first stage; after about 400ºC these signals effectively coincide. Therefore, while sample weight did not impact on TBBA-DDPE degradation kinetics (Section 7.2.1), it was relevant when TBBA-BDPE was dispersed through a polypropylene substrate. Given HBr would have evolved from the
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degrading TBBA-BDPE and contributed significantly to weight loss, the signal variation in Figure 7-28 is conceptualised by the impediment to HBr egress posed by the sample. It is equivalent to interpret the nucleation and nucleus growth mechanism implied for pure TBBA-BDPE degradation as transmuted to a diffusion controlled mechanism, although the concept of a product layer used in the theoretical development for the Dn mechanisms (Table 5-1) is not relevant. An applicable three-dimensional diffusion model would reflect the observed three-dimensional shape of TBBA-BDPE agglomerations in a polypropylene substrate (Section 2.6). The fact that the weight signal over the second stage does not exhibit a dependence on initial sample weight implies an underlying chemically controlled or phase boundary mechanism (i.e. one concerned with the volatilisation of sufficiently small polymer chains). It is accepted that thermal lag may have affected the kinetics at this relatively high heating rate of 20ºC/min.

A Friedman analysis of the TG data shown in Figure 7-25 for the PolyPacific formulation with 10.4% TBBA-BDPE (1707-8) confirms that it would be futile to apply a simple global kinetic analysis method to this data (Figure 7-29). Uncertainty in $E(\alpha)$ between 10 – 60% overall conversion is enormous, but the apparently precise activation energy at 5% conversion (115 – 123 kJ/mol) coincides with that calculated in Section 7.2.1 for TBBA-BDPE pyrolysis. Furthermore, the activation energy at 70% conversion, 272 – 274 kJ/mol, compares well with the activation energy for polypropylene degradation (Section 7.1.1).

![Figure 7-28: Weight signals for samples of the PolyPacific formulation with 10.4% TBBA-BDPE (1707-8) ranging from 5.4 mg to 21.0 mg at 20ºC/min under 100 mL/min N₂ (baseline corrected; open crucibles)](image-url)

A Friedman analysis of the TG data shown in Figure 7-25 for the PolyPacific formulation with 10.4% TBBA-BDPE (1707-8) confirms that it would be futile to apply a simple global kinetic analysis method to this data (Figure 7-29). Uncertainty in $E(\alpha)$ between 10 – 60% overall conversion is enormous, but the apparently precise activation energy at 5% conversion (115 – 123 kJ/mol) coincides with that calculated in Section 7.2.1 for TBBA-BDPE pyrolysis. Furthermore, the activation energy at 70% conversion, 272 – 274 kJ/mol, compares well with the activation energy for polypropylene degradation (Section 7.1.1).
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Figure 7-29: Friedman analysis for the pyrolysis of the PolyPacific formulation with 10.4% TBBA-BDPE (1707-8) over heating rates of 2, 5 and 20°C/min showing 95% confidence intervals for two different ordinate scales

Figure 7-30 shows the systematic change to the degradation behaviour as the TBBA-BDPE concentration was increased from 5.2% to 20.8% (TG/DSC Set 1). For TBBA-BDPE concentrations of 10.4% and above, the second stage of weight loss split into two clear steps. The influence of TBBA-BDPE on polypropylene appeared limited to the initial acceleration of chain scission, which soon relaxed to its normal rate presumably once all the TBBA-BDPE degradation products were lost or rendered into an inert char. Because of this early, more rapid breakdown of polypropylene to volatile products, the peak rate of weight loss was reduced. This effect was more pronounced at higher TBBA-BDPE concentrations. Aromatic bromine eliminated in the condensation reactions within the degraded TBBA-BDPE is likely to be responsible for this initial acceleration. The efficacy of this acceleration appears to decrease with increasing TBBA-BDPE concentration, which could be due to the increasingly larger agglomerations of TBBA-BDPE (Section 2.6) contacting less intimately with the substrate. Negligible weight always remained above 500°C; i.e. char formation was not encouraged in polypropylene to any measurable degree. Discolouration of the sample crucible by a black deposit is attributed to the charring of TBBA-BDPE.

The Sb/Br atom ratios for the PolyPacific formulations with 5.2% TBBA-BDPE and an additional 1.5% (1707-11) or 2.5% (1707-12) Sb2O3/LDPE are 0.19 and 0.31 respectively. These ratios are above and below the documented optimum of 0.27 (Section 2.6.2). The formulation 1707-11 has double the Sb/Br
atom ratio of the mixture without polymer used for FTIR analysis (Section 7.3). At a heating rate of 20°C/min under 100 mL/min nitrogen (TG/DSC Set 1), the sedate increase in weight loss rate with temperature for the first stage involving TBBA-BDPE when no Sb$_2$O$_3$ was present (1707-7) was transformed to an early peak for both 1707-11 and 1707-12 formulations (Figure 7-31). This peak is attributed to the loss of SbBr$_3$. The diffusion-like character of the first stage of weight loss for the 1707-7 formulation returned to a more convex, nucleation and nucleus growth form when antimony was present. If the SbBr$_3$ molecules were lost to a heavy blanket over the melt, their relatively large size and weight compared to HBr could explain why they had drastically more penetrative power through the polypropylene substrate.

![Figure 7-30: Heat flow, conversion rate and weight signals for 7.0 – 7.1 mg samples of the PolyPacific formulations with 5.2%, 10.4%, 15.6% and 20.8% TBBA-BDPE (1707-7, 8, 9 and 10 respectively) at 5°C/min under 100 mL/min N$_2$](image)

Two maxima manifested in the conversion rate over the first stage of weight loss for the formulation with Sb/Br atom ratio 0.31 (1707-12) (Figure 7-31). With antimony more plentiful, perhaps only a fraction escaped early as SbBr$_3$ while the remainder extracted the aromatic bromine as the complex HBr.SbBr$_3$ (Section 2.6.2). Given that Sb/Br atom ratios between 0.20 and 0.27 do not differ much in terms of performance (Section 2.6.2), the imperative action of Sb$_2$O$_3$ seems to be to increase the rapidity and reduce the temperature of bromine deliverance to the gas phase; the total amount of HBr released being less important. Figure 7-31 clearly shows that Sb$_2$O$_3$ at either concentration was able to create
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the 50°C discrepancy between the first peak in weight loss rate and the onset of polypropylene degradation necessary to optimise the efficacy of gas-phase chemical scavenging (Section 2.2.2).

Figure 7-31: Heat flow, conversion rate and weight signals for 6.9 – 7.3 mg samples of the PolyPacific formulation with 5.2% TBBA-BDPE (1707-7) and an additional 1.5% (1707-11) or 2.5% (1707-12) Sb_2O_3/LDPE at 20°C/min under 100 mL/min N_2

Sb_2O_3 appeared to restore the second stage of weight loss to an ostensibly single-step process. The brief acceleration in weight loss from the onset of the second stage observed for the formulation 1707-7 is absent for the formulations 1707-11 and 1707-12 (Figure 7-31), presumably because there was little or no bromine retained in the latter two samples to eliminate in condensation reactions. Char formation is therefore not promoted by Sb_2O_3 for this FR system. Furthermore, it was possible to estimate the proportion of weight lost over the first stage for the two formulations with Sb_2O_3 because there was a better distinction between the decomposition stages. Effectively the same proportions as the total additive content were computed (6 wt% (1707-11) and 7 wt% (1707-12)).
7.4.2 Cone Calorimetry

Cone calorimetry gives a sense of how the observations made for small-scale pyrolysis translate to a larger-scale fire scenario (Section 2.4.2). Each sample plaque was subjected to an irradiance of 25 kW/m² in the experimental setup (Section 4.3), i.e. half the heat flux that would be generated from a well-established fire. Ignition times varied as much as 20 seconds across each set of three trials (Table 7-4), but when data for every trial for a particular formulation were translated to the same ignition time, the overarching trends coincided. Each trend shown for the six types of processed data presented in this section corresponds to an individual indicative experiment. Only qualitative comparisons are made that do not require more rigour.

The differences between ignition times for the formulations with different TBBA-BDPE loadings were considered insignificant in light of the variability observed for each formulation. Ignition for the formulations containing Sb₂O₃ (1707-11 and 1707-12), however, was obviously delayed (Table 7-4). The “glow inhibitor” label given to Sb₂O₃ was validated; i.e. these formulations would be expected to better resist flaming combustion when an ignition source is present.

Table 7-4: Estimated time to ignition after firing a piezo spark igniter above the sample for each PolyPacific formulation when subjected to an irradiance of 25 kW/m²

<table>
<thead>
<tr>
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<th>Trial 1</th>
<th>Trial 2</th>
<th>Trial 3</th>
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<tbody>
<tr>
<td>1707-7</td>
<td>134</td>
<td>114</td>
<td>120</td>
</tr>
<tr>
<td>1707-8</td>
<td>137</td>
<td>139</td>
<td>152</td>
</tr>
<tr>
<td>1707-9</td>
<td>149</td>
<td>132</td>
<td>136</td>
</tr>
<tr>
<td>1707-10</td>
<td>131</td>
<td>123</td>
<td>131</td>
</tr>
<tr>
<td>1707-11</td>
<td>156</td>
<td>154</td>
<td>155</td>
</tr>
<tr>
<td>1707-12</td>
<td>196</td>
<td>166</td>
<td>167</td>
</tr>
</tbody>
</table>

A reduced peak weight loss rate at higher TBBA-BDPE loadings was predicted by thermogravimetry and observed in this oxidative environment (Figure 7-32). A commensurate change in the heat release rate (Figure 7-33) implies that the ferocity of combustion reduces as the TBBA-BDPE loading increases (Section 2.4). By contrast, the breadth of this main feature in the weight loss rate was certainly not diminished when Sb₂O₃ was present, and the suppression of the rate initially did little to reduce the ultimate peak weight loss rate. Sb₂O₃ did not promote char formation under these conditions; it merely delayed the progression to an intense fire. Very little HBr, due to its premature release, would have
been available above the 1707-11 and 1707-12 sample plaques during the lengthy period of heat release from about 230 – 360 seconds compared to the plaques with an equivalent TBBA-BDPE loading but no Sb$_2$O$_3$ (1707-7). Again, this was anticipated from thermogravimetric experiments.

Figure 7-32: Weight loss rate measured by the cone calorimeter operating at 25 kW/m$^2$ for all the PolyPacific sample plaques

Figure 7-33: Heat release rate inferred from the modified version of Equation 2-1 for all the PolyPacific sample plaques from measurements taken with the cone calorimeter operating at 25 kW/m$^2$
Gas-phase activity is confirmed by the fact that better performance in terms of heat release rate corresponded to a greater rate of smoke formation, particularly at 15.6% and 20.8% TBBA-BDPE loadings (1707-9 and 1707-10) (Figure 7-34). These two formulations exhibited a particularly rapid increase in the rate of smoke formation from the point of ignition. This suggests that a certain minimum TBBA-BDPE loading between 10.4% and 15.6% was required to transition to a mechanism that led to more efficient delivery of HBr to the gas phase, and may have related to the size of the TBBA-BDPE agglomerations in the polypropylene substrate.

Rate of smoke formation from the formulations with Sb$_2$O$_3$ was suppressed for the entirety of their combustion (Figure 7-34). The more immediate and complete extraction of bromine from TBBA-BDPE by Sb$_2$O$_3$ prior to ignition would have left the main phase of combustion with only a small amount of HBr in the volatiles to generate smoke in addition to that ordinarily observed for polypropylene. Antimony was identified in the volatiles prior to ignition by the brilliant white glow at the igniter when either the formulation 1707-11 or 1707-12 was tested. Perhaps the mist of SbO$_3$ expected in the exhaust also adsorbed polymer fragments that would have otherwise been counted as smoke. In any case, a reduced volume of smoke and a delayed ignition are positive attributes to assign to these formulations.

Figure 7-34: Rate of smoke formation inferred from laser attenuation for all the PolyPacific sample plaques measured by the cone calorimeter operating at 25 kW/m$^2$

Trends of effective heat of combustion (Figure 7-35) match well with those of carbon dioxide emission (Figure 7-36). These figures best support the hypothesis that the overall FR effect of TBBA-BDPE/
Sb$_2$O$_3$ synergism for both the formulations 1707-11 and 1707-12 is comparable to the FR effect of the two highest TBBA-BDPE loadings considered here. Given the additive content of these formulations, this hypothesis is in accord with statements regarding Br/Sb$_2$O$_3$ gas-phase synergism cited in Section 2.2.2.

Figure 7-35: Effective heat of combustion calculated according to Equation 2-2 for all the PolyPacific plaques from measurements taken by the cone calorimeter operating at 25 kW/m$^2$.

Figure 7-36: Carbon dioxide emission inferred from the CO/CO$_2$ analyser for all the PolyPacific sample plaques from measurements taken by the cone calorimeter operating at 25 kW/m$^2$. 
In Section 7.4.1, the suggestion was made that the Sb/Br atom ratio for the formulation 1707-12 was high enough at 0.31 for aromatic bromine to be drawn out into the gas phase, thereby forming a secondary peak in the weight loss rate (Figure 7-31). This was touted to enhance the FR efficacy compared to formulations with lower Sb/Br atom ratios (e.g. 1707-11). Cone calorimetry was inconclusive on this matter, although the peak heat release rates (Figure 7-33) and the CO emission profiles (Figure 7-37) favour this description. Perhaps the heavy acid HBr.SbBr₃ comprised of aromatic bromine persisted for longer above the 1707-12 sample plaques and slightly reduced their combustion ferocity compared to the 1707-11 plaques, and caused more incomplete combustion. The distinctively different CO emission profiles observed in the presence of any Sb₂O₃ imply a higher CO concentration, and therefore agree with the comparatively high infrared absorbance attributed to CO during the pyrolysis of the TBBA-BDPE/Sb₂O₃ mixture (Figure 7-22). High levels of CO in the smoke would negate the impact of its reduced formation rate on fire safety, as the toxicity of the smoke would be much higher. Carbon monoxide emission increased while carbon dioxide emission decreased for increasing TBBA-BDPE loading, indicating that TBBA-BDPE encouraged incomplete combustion.

Figure 7-37: Carbon monoxide emission inferred from the CO/CO₂ analyser for all the PolyPacific sample plaques from measurements taken by the cone calorimeter operating at 25 kW/m²


7.5 Concluding Remarks

Multiple techniques were used to evolve the interpretation of polypropylene, TBBA-BDPE and Sb$_2$O$_3$ degradation into a consistent scheme for this complete FR system. Firstly, results from the new kinetic analysis method when applied to polypropylene pyrolysis are matched to literature expectation. The ostensibly single-step degradation of polypropylene is concluded to be too complex to model using a global approach, even if a conversion function derived specifically for random scission is invoked. Thus, changes brought about by the additives of this FR system are only referenced to direct observations and appropriately qualified kinetic analysis results.

When pyrolysed at a constant heating rate, TBBA-BDPE exhibited a characteristic release of energy as it rapidly lost most of its initial weight before condensing to a thermally labile char. The initial decomposition stage of TBBA-BDPE is rationalised with a simple reaction and correlated to the TG and DSC data for TBBA with some reservations. Kinetic analysis results for TBBA-BDPE pyrolysis are reasonably conclusive and are married conceptually to DSC and FTIR data. The mechanism description of nucleation and nucleus growth in one dimension with an overall order of three is suggested to resolve from the concurrent breaking of the ether linkage, isopropylidene bridge and aliphatic C-Br bonds and the finite rate of loss of the volatile fragments. Formation of an open char structure by the elimination of HBr in the condensation reactions that likely followed appeared to be a purely chemically controlled process. This char broke down further as the temperature increased, also under chemical control, and released more bromine as CH$_3$Br until a residue proposed to be almost free of bromine remained.

The type of bromine available is inferred as pivotal to the ultimate performance of TBBA-BDPE. Without destabilised aliphatic C-Br bonds, the principal degradation reactions cannot initiate until a higher temperature. This would no doubt lead to less effective flame retardancy, particularly considering TBBA-BDPE has a synergistic relationship with Sb$_2$O$_3$ because it enhances the rate of bromine release from the onset temperature. The conjecture by Kaspersma et al. (2002) that the role of aliphatic bromine in TBBA-BDPE is to remain in the melt phase and accelerate chain scission within the polymer is discredited. It is likely that the optimum Sb/Br atom ratio is less than one third because either the bromine combined with antimony in compounds in addition to SbBr$_3$ and/or a portion of the aromatic bromine remained after the initial bromine release to eliminate during the charring of degraded TBBA-BDPE. The argument that Sb$_2$O$_3$ is affiliated with aliphatic bromine is strengthened by the fact that the consistent optimum Sb/Cl atom ratio of one third mentioned in Section 2.5.2 must relate to aliphatic chlorine, as aromatic chlorine is not used in FRs. Furthermore, when Sb$_2$O$_3$ was combined with just
TBBA-BDPE, it did not hasten the release of bromine. An important corollary is that the FR itself offered no significant resistance to the movement of HBr into the gas phase.

Combination of TBBA-BDPE with polypropylene caused a deceleration to the decomposition kinetics of the FR, attributed to the need for HBr to diffuse through a bulky substrate. Sb$_2$O$_3$ was shown to facilitate the return to a rapid initial weight loss that improved the performance of the system in a fire scenario, specifically by delaying ignition. A higher gas-phase concentration of bromine in some form 50°C prior to the decomposition of polypropylene appeared to have a similar positive influence than if four times the amount of bromine was available at a suboptimal point in the combustion cycle. The Sb/Br atom ratio was also observed to control the efficacy of the extraction of bromine to the gas phase and was better set at 0.31 than 0.19. However, while Sb$_2$O$_3$ reduced smoke formation, it increased its toxicity by means of a pathway that formed CO seemingly irrespective of the presence of molecular oxygen. In the cone calorimeter tests, eventually the additives were consumed and the polypropylene combusted freely, unless a loading of TBBA-BDPE in excess of 10.4% was used so that HBr continued to evolve until a late enough stage to suppress the peak heat release rate. None of the additive content appeared to remain after the initial weight loss prior to ignition when Sb$_2$O$_3$ was present.

As expected from the literature survey, TBBA-BDPE accelerated the chain scission of the polymer. This effect is obviously counterproductive in terms of gas-phase inhibition as it reduces the temperature discrepancy between TBBA-BDPE and polypropylene decomposition. The primary purpose of TBBA-BDPE is confirmed to be in the supply of bromine to the gas phase, and the impact of the Sb$_2$O$_3$ synergist was most apparent as an ignition delay.
8 Conclusions and Recommendations

This study rectifies a number of perceived deficiencies not only in the current understanding of the polypropylene/tetrabromobisphenol A (bis-2,3-dibromopropyl ether)/antimony trioxide flame retardant (FR) system, but in the implementation of various kinetic analysis methods. These deficiencies can be formulated into the following largely unanswered questions:

- How should kinetic analysis be approached so that only apt kinetic solutions are accepted?
- What are the assumptions and physical bases for the multitude of solid-state mechanisms?
- How do the three components of this FR system interact?
- What are the specific roles of aliphatic and aromatic bromine?
- Should more emphasis be placed on any condensed-phase action of brominated FRs?

Gaps and inconsistencies in the literature have been addressed to the extent discussed both in this chapter, and in greater detail in the concluding remarks for other chapters. Recommendations for future exploration within the two overarching fields of this study are made here.

8.1 New Kinetic Analysis Method

Significant background is supplied in this thesis not only to place the new kinetic analysis method into some much-needed context, but to demonstrate the necessity of completely understanding any selected approach. Critical concepts that are often glossed over or misinterpreted, such as the compensation effect and the treatment of complex kinetics, are explained and their implementation described in the new method. The literature review of Chapter 3 implies that excellent determinism can be an impossible goal; this study delves into the reasons for this and demonstrates the profound benefit of statistical analysis. Plainly visible statistics should keep an injudicious researcher grounded, but can also increase the confidence in a particular kinetic solution beyond doubt when there may otherwise be a reluctance to assign a global solution.

Great care must be taken to pre-process weight signals from thermogravimetric (TG) experiments into the best possible estimates for overall and component conversions and weight fraction distributions. Without a consistent approach to this computational aspect, errors caused by the subjective initial specification of onset and completion temperatures for each process involved in the weight loss would heavily influence the ultimate kinetic solution. Common sense and trial-and-error were used to evolve a flexible refinement algorithm that, at the very least, transforms these errors to small systematic
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variations. No mention of this type of data pre-processing is cited in the literature; even the detailed account in Mamleev et al. (2000b) is not clear on how the component conversion signals and weight fraction distribution are initialised.

The method of Invariant Kinetic Parameters (IKP) can be used to deduce a reasonable estimate for process activation energy from its set of component conversion signals. It is imperative (and easy) to employ a highly accurate approximation for the temperature integral, e.g. the approximation of Orfao (2007), for this purpose. With the normally cited approximation labelled Coats and Redfern (also Murray and White), the computed apparent kinetic parameters would be in error and therefore unnecessarily bias the IKP. While the IKP method is promoted to supply a reasonable invariant pre-exponential factor, in actuality it delivers a factor that should not be used for the final solution regeneration and evaluation due to its inaccuracy. Kinetic solution evaluation with an unrefined invariant pre-exponential factor is shown to lead to erroneous mechanism selection. However, this pre-exponential factor can be refined to new, mechanism-specific estimates that have similar relative errors to the corresponding invariant activation energy. Only a single application of an equation that fits each model to the experimentally-derived component conversion signal is required to achieve this level of refinement.

Even when high resolution conversion signals generated from perfect models are analysed, there are significant but comparable uncertainties in the super correlation(s) from which the IKP are derived and in the Friedman analysis. The Friedman analysis is more useful to illustrate any significant variation of activation energy with overall conversion and is the most precise around component conversion rate maxima, whereas the super correlation(s) can still deliver reasonable IKP for noisy data and, in that case, facilitate the exclusion of at least some models based on an excessive discrepancy between their apparent kinetic parameters and the IKP. These analysis techniques were therefore used in a complementary fashion. Ultimately, apparent kinetic parameters were deemed the most suitable kinetic parameters to input into the model fitting aspect of the algorithm, since they should coincide with the IKP for the correct mechanism but have lower associated uncertainties.

Kinetic solutions are generated by a rigorously correct but more computationally intense algorithm than that of Mamleev et al. (2000a, 2000b) due to the refusal to adopt an approximate "auxiliary function". However, this new method is arguably less rigorous as it optimises the kinetic parameters at just one characteristic point. Activation energy is stepped in a prescribed direction, a new solution is computed, and from this solution the old pre-exponential factor is refined so that the kinetic parameters then constitute a pair. As TG data is normally smooth, the philosophy was that if the maximum or any other
single point in the conversion rate signal cannot induce a good match with a predicted model, then it would be just as futile to attempt to achieve such with all the data points in the computational range. Of course, this minimalistic approach will suffer if the data are poorly resolved because the random error at the chosen point will not be balanced. Complete residual sums of squares are used to deduce the best fitting model once optimisation based on the characteristic point is complete.

Reliance on derivative calculations means that this new method is unable to refine kinetic parameters for noisy data, although the relatively complex algorithm of Mamleev et al. (2000a) cannot improve upon the outcomes of the standard IKP method in this situation either. For this, and heterogeneous systems that are a challenge to model, it is very important to review the $F$-statistics and to visualise the regenerated conversion rates for every viable permutation to manually direct the optimisation. Non-linear probabilities and exclusions based on shape rather than linear $F$-statistics were found to be more useful for discrimination. Any probable mechanism must also be associated with activation energy within the 95% confidence interval of the corresponding invariant activation energy to be a candidate for selection. Optimisation tended to be more successful when based on a median conversion rate rather than the maximum rate (if available), possibly due to programming overly strict pass criteria. The facility to limit computational ranges for partially overlapped processes was shown to be critical to the progression towards an unambiguous solution. Removal of ambiguity was prioritised above the computation of very precise kinetic parameters, which appears to be an uncommon but more pragmatic approach.

Validation of the new kinetic analysis method intentionally called for the correct specification of a purely acceleratory model, since some methods (e.g. Combined Kinetic Analysis) seem unable to treat this mechanism type. These and the other less demanding mechanisms were successfully simulated from midpoint integration, as confirmed by comparison to the essentially exact analytical approximation (Orfao, 2007). Kinetic triplets that are purported to represent particular experimental data had their solutions regenerated with this algorithm, but these appeared at significantly higher or lower temperatures compared to the data they are supposed to match. Arbitrary and unreported techniques for conversion initialisation are suspected to cause this discrepancy; at the least, the correct identification of the magnitude and temperature for the first non-zero conversion datum is shown to be of critical importance. Acceleratory mechanisms drastically exaggerate any errors in initialisation. That this new method was able to return a conclusive and justifiable kinetic solution for the evaporation of water is noteworthy. This type of validation has not been seen in the literature.

**Conclusions and Recommendations**
Kinetic analyses on calcium carbonate and polypropylene thermal degradation delivered inconclusive statistics, as expected. Bockhorn et al. (1999a) agree that global kinetic parameters from non-isothermal data for polypropylene are suspect due to the complex nature of the degradation, but promote isothermal analysis as a better alternative. Realistically, a Friedman or IKP analysis supplies the same reliable model-free activation energy as that obtainable from isothermal analysis; model fitting an oversimplified function of conversion is the real problem.

Despite the reservations expressed towards indiscriminate \( n \)-order model fitting, this particular function of conversion can represent a number of different mechanism types and therefore is a good choice if all possibilities are not to be considered in a kinetic analysis. Sánchez-Jiménez et al. (2010) state that the use of an \( n \)-order mechanism for model fitting will result in the wrong kinetic parameters, however, the refinement procedure is shown to drive all probable mechanisms to the same invariant activation energy, within the 95% confidence interval. In their study, the apparent \( n \)-order mechanism is reported with an activation energy that matches the isoconversional analysis, and undermines their statement (Sánchez-Jiménez et al., 2010). The flexible Sestak-Berggren equation can be used for model fitting instead of the somewhat restricted \( n \)-order mechanism, although the statistical significance of the incorporation of another parameter should be justified.

Any mechanism that requires a complex scheme to resolve to a simple function of conversion by means of an elaborate series of assumptions is suspect. The yet to be popularised scheme for random scission certainly fits this description (Appendix A2.6), but is nevertheless included in the new method since the function of conversion that arises from the assumption that only fragments with a single carbon backbone atom are volatile is shown to match the decomposition kinetics of polybutylene terephthalate (Sánchez-Jiménez et al., 2010). The assumption of such limited volatility was not accepted and the theory was adapted to reference alkane chain boiling points. This new, more computationally expensive \( L(T) \) model no longer has a separable function of conversion and Arrhenius function of temperature; since the new method utilises numerical integration, this is of no consequence. Temperature is merely used as a switch to change which function of conversion is active. This discontinuous behaviour for variable temperature is illustrated in Table 5-1.

Another mechanism, Prout-Tompkins, that is well known but not normally identified in the literature with this type of kinetic analysis is adapted to this new method. Fair judgement of this mechanism requires the correct interpretation of the integration constant by the algorithm and user. The same constant must apply for all active processes irrespective of whether their IKP differ, which is a minor inconvenience.
The second question regarding the origins of the solid-state mechanisms, i.e. functions of conversion, is completely addressed in Appendix A2 and summarised as a stand-alone reference in Table 5-1. Each function of conversion is deduced from first principles and all mathematical manipulations and required assumptions are included in the course of the derivation. The perception that the reassessment of the validity of the list of functions of conversion is an “important consideration for the future” (Galwey, 2004) establishes these thorough and critical mechanism derivations as a direct address of a gap in the literature. The presentation in Table 5-1 is considered unique, particularly with regards to the listing of assumptions and the carefully constructed physical illustrations. Information captured in Table 5-1, along with the detailed kinetic analysis method description and supplied Visual Basic code, is designed to help accelerate the formative stages for a novice researcher.

8.1.1 Recommendations

This thesis elaborates on the new kinetic analysis method in fine detail in order to encourage others to improve either the method itself, or apply some of the ideas presented here to other similar methods. Some clear improvements can be recommended based on observations made when the method was applied to data input for this study.

The “incomplete process” aspect of the new method is perhaps more useful as an indication that any implicated TG experiment should be repeated to a higher temperature. However, the code for this aspect could be modified to treat processes such as epoxy curing (Vyazovkin et al., 2011), where incomplete conversion is realised at lower heating rates and it is impractical to extend the length of the experiment. If the implicit assumption that conversion varies between 0 and 1 is incorrect, the derived function of conversion will be distorted, except for mechanisms where a technically non-zero initial conversion has no bearing on the physical depiction (e.g. reaction order and contracting volume mechanisms). Temperature signal quality is also a significant concern and there is certainly scope to improve the rough linearised energy balances that were incorporated into this algorithm.

The facility to treat data according to the recently proposed Incremental IKP (IIKP) method (Grause et al., 2010) could be coded to supersede the Friedman analysis. If this adaptation is made, then the isoconversional principle can be properly validated when complex kinetics are addressed. Since the IIKP method essentially reformulates the IKP method to use a different compensation effect to that generated by incorrect mechanism selection, the option to select any number of different compensation effects would be a useful feature to add when adapting the code. However, incremental conversion may be the only adaptation necessary as it is shown to be the basis for a super correlation with respect to
FR type (Lesnikovich et al., 1986) and could be similarly used for FR loading. The variable that defines the nature of the super correlation is dictated by the choice of data sheets that are copied into the Excel workbook. At least this understanding can be used to extend the standard IKP method to the assessment of other compensation effects with the algorithm in its current form.

An obvious modification to this algorithm would be to add more points to the optimisation and therefore remove the focus on the alignment of functional maxima. More leeway could also be added to the shape assessment. As it stands, the algorithm reports activation energies with impossibly small uncertainties if the refinement reaches its resolution limit. A more conservative measure of uncertainty should be found.

The ability to automatically deduce a numerical representation of the function of conversion with the Sestak-Berggren equation adapted from Combined Kinetic Analysis would be useful. In the present study, these deductions had to be made manually. Automated regeneration of a heat flow signal would also be feasible from the data currently available to the algorithm, and would significantly aid in the finalisation of any complex kinetic description that otherwise does not appear unique from other viable permutations. While the pre-exponential factor is understandably deemphasised in kinetic analyses because it is so variable, it is a necessary part of the kinetic triplet for any kind of signal regeneration and needs to be at least estimated from a compensation effect.

8.2 Flame Retardant System

Only one article was cited in the literature that specifically deals with this FR system (Kaspersma et al., 2002). Statements made in this article that relate to aliphatic and aromatic bromine activity have been discredited by the present study, even on the sole basis of the literature review. A broad literature survey that covered the degradation of not only the parent compound of tetrabromobisphenol A bis(2,3-dibromopropyl ether) (TBBA-BDPE), i.e. tetrabromobisphenol A (TBBA), but flame-retarded epoxy resins and a different mixed aliphatic and aromatic brominated FR molecule used in conjunction with antimony trioxide (Sb$_2$O$_3$) proved invaluable to the interpretation of data collected in this study.

Polypropylene itself was shown to degrade under an inert atmosphere in a complex manner that could not be effectively re-simplified to a single step with a random scission scheme, even when the higher volatility of the polymer fragments at decomposition temperatures was taken into account with the L(T) function of conversion. The very prescriptive scheme of Simha and Wall (1952) assumes the undegraded polymer is made up of chains of equal length, rather than a Flory distribution of chain lengths or any other distribution that would give rise to the known polydispersity index of polypropylene of two to
six. Even if this initial specification is not critical to the final form of the function of conversion, there are many other possible reasons for this over-simplified global description to fail to match the thermal degradation of polypropylene.

TBBA-BDPE was also characterised separately and exhibited a clearly complex thermal degradation pattern ascribed to three partially overlapped independent processes. The degradation was not able to be initialised by phenol-cyclohexadienone tautomerisation as is anticipated for TBBA, and moreover, its onset temperature was below that of TBBA. Thus, it was hypothesised that the exothermic cleavage of the ether linkage was precipitated by HBr sourced from the aliphatic components of the molecule in the first instance. Rapid nucleation of brominated volatile products from this and other reactions and their evolution from the degraded TBBA-BDPE were assigned an Avrami-Erofe’ev order of three. This confident assertion was possible because of the determinism gained by the input of more than the minimum required number of TG experiments into the new kinetic analysis method, and the fact that the An mechanism derivation was understood.

The question of how polypropylene and TBBA-BDPE interact with and without Sb₂O₃ can be answered in the main by a simple physical argument. HBr, and any other volatile brominated degradation products from TBBA-BDPE, did not leave the condensed phase with the same rapidity when TBBA-BDPE was dispersed through a continuous polypropylene substrate. However, when bromine evolved from TBBA-BDPE in the presence of Sb₂O₃ at a sub-optimal Sb/Br atom ratio, it was quickly transported to the surface of the molten polymer. Given that aliphatic bromine is more thermally labile, most of this heavy, volatile SbBr₃ blanketing the condensed phase would have been comprised of aliphatic bromine. There was no evidence that Sb₂O₃ acted as a Lewis acid to extract aromatic bromine. At a higher than optimal Sb/Br atom ratio, this early loss of bromine occurred in two steps, where the second step was likely due to the extraction of more bromine from the aromatic environment as an acid complex. Cone calorimetry demonstrated that the more bromine released rapidly prior to ignition, the more effective the scavenging of radicals and the greater the ignition delay. Without Sb₂O₃, the aromatic bromine that remained in the condensed phase after ignition would have accelerated random scission before it interfered with the gas-phase chemistry and was eventually lost from the system. This summary in essence answers the question regarding the role of bromine in each chemical environment.

The condensed-phase interactions of TBBA-BDPE with a polypropylene substrate were expected to be non-trivial based on a number of literature reports. Experimental results meet this expectation as they show overt acceleration of polypropylene decomposition in the presence of TBBA-BDPE. This
acceleration should in theory favourably affect FR performance, as the reduced molecular weight of the polymer would cause it to flow away from the area of flaming combustion. Cone calorimetry showed that when the polymer was contained, a significant gas-phase FR effect was apparent in the suppression of the heat release rate. Thus, the answer to the final question of whether more emphasis should be placed on the condensed-phase action of brominated FRs would appear to be no: The vast majority of brominated FR activity at least for this system is confined to the gas phase. Timing the bromine release early enough in the combustion cycle is the main challenge.

8.2.1 Recommendations

Despite the successful marriage of the literature review with the results of simultaneous small-scale tests and cone calorimetry, some of these ideas need to be ratified with better constructed and more fundamental studies. In particular, the qualitative Fourier transform infrared spectroscopic study would benefit greatly from quantitative calibration for gas-phase species concentrations and from repetition with more realistic Sb/Br atom ratios. Closed vessels could be used to analyse the otherwise volatile TBBA-BDPE analogues, although the affects of pressure on the outcomes would need to be properly attributed. The formulations that were created with a systematic and wide range of different additive loadings could be analysed to consolidate the conclusions made here. An optimum loading of TBBA-BDPE and Sb$_2$O$_3$ could be sought.

The transition from nucleation and nucleus growth to diffusion controlled kinetics should be validated and investigated in more depth. If diffusion is as important as it appears to FR performance, electron microscopy would be useful to observe the physical impact Sb$_2$O$_3$ has on the FR system. A perceptible effect would not be surprising given that loadings of 30 – 40% TBBA-BDPE have an equivalent FR performance to less than 10% TBBA-BDPE with added Sb$_2$O$_3$. Perhaps the same rate of bromine delivery to the gas phase can be achieved by altering the physical structure of the plastic formulation, or with a different additive that does not increase the proportion of CO in the smoke. In that vein, the mechanism by which Sb$_2$O$_3$ promotes CO formation would be worthwhile to resolve.

Decomposition of the FR alone borders on a level of complexity that the new kinetic analysis method struggles to characterise. If no gains are made after the implementation of the recommendations in Section 8.1.1, it would be of more benefit to quantify the elements in the evolved volatiles and char and construct mass balances than pursue complex kinetic solutions for the other FR analogues, if the goal is to properly characterise the chemistry.
## A1 Nomenclature

This appendix lists the symbols used throughout the main body of this thesis in alphabetical order. The definition for any symbol with a subscript explicitly attached supersedes any conflicting definition for the subscript alone. Symbols specifically associated with the functions of conversion presented in Table 5-1 or only appearing in the appendices are defined in situ. There is some repetition of symbol use; this is to avoid the practice of using unconventional symbols in equations where particular symbols have become commonplace. Any ambiguity should be resolved by the accompany text.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>Pre-exponential factor (normally min$^{-1}$); Cross-sectional area (m$^2$)</td>
</tr>
<tr>
<td>$a$</td>
<td>Slope in linear regression</td>
</tr>
<tr>
<td>$a_j$</td>
<td>Ratio of the experimental conversion rate to that predicted by model, $j$ at a characteristic point (e.g. the maximum conversion rate)</td>
</tr>
<tr>
<td>$b, c$</td>
<td>Compensation parameters (variable units)</td>
</tr>
<tr>
<td>$Bi$</td>
<td>Biot number. Ratio of the rate of heat transfer to a surface to the rate of conduction through a characteristic distance $x$. May be a function of temperature $T$</td>
</tr>
<tr>
<td>$C$</td>
<td>Calibration constant for O$_2$ consumption analysis (m$^{1/2}$.kg$^{1/2}$.K$^{1/2}$)</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Heat capacity (J.mol$^{-1}$.K$^{-1}$)</td>
</tr>
<tr>
<td>$E$</td>
<td>Activation energy (kJ.mol$^{-1}$)</td>
</tr>
<tr>
<td>$F_{n_1,n_2-1}$</td>
<td>$F^2$-statistic, equivalent to the ratio of two chi-squared distributions with $n_1$ and $n_2$ degrees of freedom</td>
</tr>
<tr>
<td>$f(\alpha)$</td>
<td>Function of conversion. Cannot be a function of temperature</td>
</tr>
<tr>
<td>$g(\alpha)$</td>
<td>Integral form of the function of conversion, $f(\alpha)$</td>
</tr>
<tr>
<td>$\Delta H_R$</td>
<td>Enthalpy of reaction (kJ.mol$^{-1}$)</td>
</tr>
<tr>
<td>$h$</td>
<td>Convective heat transfer coefficient (W.m$^{-2}$.K$^{-1}$)</td>
</tr>
<tr>
<td>$\Delta h_c$</td>
<td>Net heat of combustion (kJ.kg$^{-1}$)</td>
</tr>
<tr>
<td>$k$</td>
<td>Arrhenius rate constant (same units as $A$)</td>
</tr>
<tr>
<td>$k_c$</td>
<td>Thermal conductivity (W.m$^{-1}$.K$^{-1}$)</td>
</tr>
<tr>
<td>$L$</td>
<td>Minimum length of non-volatile chain</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$m$</td>
<td>Mass/weight (kg); integer in Sestak-Berggren equation</td>
</tr>
<tr>
<td>$n$</td>
<td>Order within function of conversion; integer counter</td>
</tr>
<tr>
<td>$N$</td>
<td>Number of data points in differentiation filter</td>
</tr>
<tr>
<td>$\Delta P$</td>
<td>Orifice meter pressure differential (Pa)</td>
</tr>
<tr>
<td>$p$</td>
<td>Integer in Sestak-Berggren equation</td>
</tr>
<tr>
<td>$p(x)$</td>
<td>Temperature integral, $p(x) = \int_{\gamma}^{\infty} \frac{\exp(-x)}{x^2} dx$</td>
</tr>
<tr>
<td>$Q(x)$</td>
<td>Factor in temperature integral defining the approximation, $Q(x) = p(x) \frac{x^2}{\exp(-x)}$</td>
</tr>
<tr>
<td>$\dot{q}$</td>
<td>Heat release rate (kW)</td>
</tr>
<tr>
<td>$q$</td>
<td>Factor introduced into the Sestak-Berggren equation to enable easy initialisation</td>
</tr>
<tr>
<td>$R$</td>
<td>Ideal gas constant (kJ.mol(^{-1}).K(^{-1})); inside crucible radius (m)</td>
</tr>
<tr>
<td>$R_0$</td>
<td>Outside crucible radius (m)</td>
</tr>
<tr>
<td>$r_o$</td>
<td>Stoichiometric oxygen/fuel mass ratio</td>
</tr>
<tr>
<td>$S$</td>
<td>Variance</td>
</tr>
<tr>
<td>$s$</td>
<td>Ratio of Sestak-Berggren equation integers; recursive relationship in differentiation filter</td>
</tr>
<tr>
<td>$T$</td>
<td>Sample temperature (K); ratio of experimentally-derived and predicted temperatures at a characteristic point</td>
</tr>
<tr>
<td>$T_e$</td>
<td>Absolute temperature of gas at the orifice meter (K)</td>
</tr>
<tr>
<td>$T_\infty$</td>
<td>Bulk temperature (K)</td>
</tr>
<tr>
<td>$t$</td>
<td>Time (s)</td>
</tr>
<tr>
<td>$X$</td>
<td>Generic variable</td>
</tr>
<tr>
<td>$X_{O_2}^0$</td>
<td>Initial value of oxygen analyser reading (mol %)</td>
</tr>
<tr>
<td>$X_{O_2}$</td>
<td>Oxygen analyser reading (mol %)</td>
</tr>
<tr>
<td>$x$</td>
<td>Characteristic distance (m); argument in temperature integral approximations, i.e. $x = \frac{E}{S}$; weight fraction (with misnomer “separation point”); generic variable</td>
</tr>
</tbody>
</table>
### Greek Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>Fractional extent of conversion</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Nominal heating rate for a linear temperature program ($^\circ$C.min$^{-1}$)</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>Gamma function, $\Gamma(n) = \int_0^\infty x^{n-1}e^{-x}dx$</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Emissivity, = 1 for a perfect black-body radiator</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density (kg.m$^{-3}$)</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Stefan-Boltzmann constant, $5.67 \times 10^{-8}$ W.m$^{-2}$.K$^{-4}$</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Weighting function for non-linear optimisation based on conversion</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Random number $0 \leq \chi \leq 1$</td>
</tr>
<tr>
<td>$\psi$</td>
<td>Weighting function for non-linear optimisation based on logarithms of $g(\alpha)$</td>
</tr>
</tbody>
</table>

### Subscripts and Other Modifiers

Subscripts indicate either a particular variant of the quantity defined by the associated full-sized character (e.g. $T_m \equiv$ measured temperature), or that a variable is evaluated at a specific value defined by the subscript (e.g. $E_{\alpha} \equiv$ Activation energy at a specific conversion). Multi-dimensional variables can have multiple subscripts. When subscripts appear full size in the text, they retain their meaning.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Initial</td>
<td>$\infty$</td>
<td>Final</td>
</tr>
<tr>
<td>$i - I$</td>
<td>Data point counter; isothermal inflection point</td>
<td>$j - J$</td>
<td>Mechanism/model counter; number of rows</td>
</tr>
<tr>
<td>$p - P$</td>
<td>Process counter</td>
<td>$v - V$</td>
<td>Experiment counter</td>
</tr>
<tr>
<td>inv</td>
<td>Invariant</td>
<td>$m$</td>
<td>Measured</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>Change in</td>
<td>$\dot{x}$</td>
<td>Rate of $x$</td>
</tr>
<tr>
<td>$\bar{x}$</td>
<td>Average $x$</td>
<td>$\bar{x}$</td>
<td>$x$ for complete conversion</td>
</tr>
<tr>
<td>$x^*$</td>
<td>Specific $x$</td>
<td>$x'$</td>
<td>Derivative of $x$</td>
</tr>
</tbody>
</table>
A2 Functions of Conversion Derivations

As mentioned in Section 3.3, a consolidation of the physical origins of all functions of conversion identified in Table 5-1 is lacking in the literature. Reporting the requisite assumptions is a common omission in articles that utilise these functions. This appendix goes through every function of conversion with physical meaning listed in the most comprehensive source found (Vlaev et al., 2008), as well as the recently reported random scission scheme that has specific relevance to this study.

Terms in this appendix that are not defined in the nomenclature (Appendix A1) are defined in the context in which they appear. All contradictory definitions here supersede those in the nomenclature.

A2.1 Nucleation and Unrestricted Nucleus Growth: Power Law (Pn)

A reaction can be controlled by the formation and growth of product material (as solid or liquid phase or gas bubble) within the reacting substrate. Nucleation will occur at points in the substrate where the activation energy is minimised, known as potential nucleation sites, \( N_0 \) (Khawam and Flanagan, 2006). For single-step, first order nucleation where all sites have equal nucleation probability (i.e. the rate constant does not vary), the rate diminishes exponentially until all potential nuclei have formed:

\[
\frac{dN}{dt} = k_N (N_0(0) - N) \Rightarrow \frac{dN}{dt} = k_N N_0(0) \exp(-k_N t), \text{ for isothermal conditions}
\]

Equation 2-1 gives rise to a deceleratory function of conversion \( (\alpha) \) if \( N \) is effectively equivalent to the converted mass (no dependence on growth), with extremes of a slow linear deceleration for small \( k_N \), and an infinitely fast deceleration (instantaneous conversion) for very large \( k_N \). When growth is relevant to the overall kinetics, it is probably more appropriate to think of this as a description for the induction phase prior to nucleus growth (Pérez-Maqueda et al., 2002).

Multi-step nucleation kinetics were first derived by Bagdassarian (Allnatt and Jacobs, 1968), who proposed that \( i = p \) decomposition steps were necessary to form a growth nucleus, representing, presumably, \( p \) independent decomposition steps that generate \( p \) coalesced product molecules, or \( p \) successive decomposition steps that arrive at a certain product from which the reaction can propagate. Either interpretation can be accommodated in the defining equation (Allnatt and Jacobs, 1968):
\[
\frac{dN_i}{dt} = k_{i-1}N_{i-1} - k_iN_i
\]

However, Equation 3-1 appears too simplistic should a germ nucleus of less than \( p \) steps/molecules have the potential to regress/dissociate rather than become a stable growth nucleus: The nature of the recursive relationship demands that all nuclei that are at step/size \( i - 1 \) must become nuclei at step/size \( i \), else the rate constants would be different. The possibility of \( i \) and \( p - i \)-sized germ nuclei combining to form a growth nucleus is also omitted. This flaw is cursorily addressed in the seminal work *Chemistry of the Solid State* (Jacobs and Tompkins, 1955), where it is shown that a power law also results (i.e. Equation A2-9) if combination of germ nuclei is the sole driving mechanism, but only if dissociation is neglected and germ nuclei form at a constant rate, and are always available for combination. Redefinition of the problem would seem to be a better approach than solving an alternate problem and introducing sufficient assumptions to yield the desired result.

Neglecting the misgivings regarding Equation 3-1, it is fairly straight-forward to use Laplace transforms and the implicit initial and boundary conditions to solve for \( N_p \) in the case of unequal rate constants:

\[
N_p(t) = N_0(0)k_0k_1...k_{p-1} \sum_{l=0}^{p} \frac{\exp(-k_lt)}{\prod_{j=0}^{l}(k_j - k_l)}, \text{ for } k_j \neq k_l \text{ and isothermal conditions A2-3}
\]

If some or all of the rate constants are equal, the solution approach in the Laplace domain and the result are necessarily different, but if the exponential terms are expanded and truncated to the \( p + 1 \)th term (assuming \( k_{t,l} << 1 \)) the solutions reduce to the same basic form (Allnatt and Jacobs, 1968):

\[
N_p(t) = \frac{k_{p-1}k_{p-2}...k_1k_0N_0(0)}{p!} t^p = K t^p \quad \text{A2-4}
\]

Khawam and Flanagan (2006) present this final solution (simplified with \( k_{p-1} = k_{p-2} = ... = k_0 \)) without acknowledging the important assumption \( k_{t,l} << 1 \). Equation A2-4 is therefore only valid at the beginning of the nucleation process, which is unsurprising; an exponential decay should be retained to incorporate the fact that there are a finite number of potential nucleation sites.
The derivation that results in the purely acceleratory power law is based on the notion that the more nuclei realised from the sum total of potential nucleation sites, or the more product material formed, the faster the conversion. Consider a nucleus volume $v$ growing at a finite rate in $\lambda$ dimensions after reaching step/size $p$ at time $t_0$ (Jacobs, 1997, Khawam and Flanagan, 2006):

$$v(t_0, t) = \sigma \prod_{i=1}^{\lambda} r_i(t_0, t) = \sigma \prod_{i=1}^{\lambda} \int_{t_0}^{t} G_i(x)dx$$  \hspace{1cm} \text{(A2-5)}$$

Growth rate, $G_i(x)$, that defines the radius $r_i$ is allowed to vary in each dimension, and the shape factor $\sigma$ can be defined to suit any constant geometry ($\frac{1}{3} \pi$ for spherical growth; $\pi h$ for cylindrical (2D) growth). $G_i(x)$ is acknowledged as a function of time/size, although it must be assumed constant ($G_i(x) = k_Gi$) to arrive at the final accepted definition for the exponent in the power law. Making this assumption, the total product volume at time $t$, $V(t)$, can be interpreted as the convolution of nucleus volume and growth nuclei formation rate:

$$V(t) = \int_0^t \sigma \left[ k_G(t-t_0) \right]^{\lambda} \frac{dN_p}{dt} \bigg|_{t=t_0} dt_0$$, where $k_G$ is the geometric mean of $k_Gi$  \hspace{1cm} \text{(A2-6)}$$

Rather than cite the series solution shown without proof in *Chemistry of the Solid State*, it is possible to solve for $V(t)$ simply using the convolution theorem in the Laplace domain (Equation A2-7). For the case of multi-step nucleation:

$$V(t) = \int_0^t f(t-t_0)g(t_0)dt_0 = LT^{-1}\left(F(s)G(s)\right)$$  \hspace{1cm} \text{(A2-7)}$$

where $f(t) = \sigma \left[k_Gt \right]^{\lambda}$ and $g(t) = \frac{k_{p-1}k_{p-2}...k_1k_0N_0(0)}{(p-1)!}t^{p-1}$

Therefore, $F(s) = \frac{\sigma k_G^{\lambda} \lambda!}{s^{\lambda+1}}$ and $G(s) = \frac{k_{p-1}k_{p-2}...k_1k_0N_0(0)}{s^p}$

$$\Rightarrow V(t) = \frac{\sigma\lambda!k_G^{\lambda}k_{p-1}k_{p-2}...k_1k_0N_0(0)}{(p + \lambda)!}t^{p+\lambda}, \text{ for isothermal conditions}$$  \hspace{1cm} \text{(A2-8)}$$

This is in agreement with the equation presented by Jacobs (1997). Conversion (defined in Equation 3-6) is clearly equivalent to the ratio of the total product volume to the product volume at infinite time, $V(\infty)$, (which may or may not be equal to the initial volume of unreacted material), provided the product

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has a uniform density. This can be equated to the isothermal integral form of the conversion function,\( g(\alpha) \):

\[
\alpha = \frac{\sigma \lambda^2 k G \ell_{p-1} \ell_{p-2} \cdots \ell_1 k_0 N_0(0)}{V(\infty)(p + \lambda)!} t^{(p+\lambda)},
\]

which implies 
\( k t = g(\alpha) = \alpha^{\frac{n}{n}} \) \( A2-9 \)

where 
\[
k = \left( \frac{\sigma \lambda^2 k G \ell_{p-1} \ell_{p-2} \cdots \ell_1 k_0 N_0(0)}{V(\infty)(p + \lambda)!} \right)^{\frac{1}{n}}
\]
and 
\( n = p + \lambda \)

Single-step nucleation (Equation 2-1) yields the same result (with \( p \) taken as 1) if the exponential term is expanded and truncated to the \( n + 1 \)th term.

Note that if \( k_G = k_{p=1} = k_{p=2} = \ldots = k_1 = k_0 \), \( k \) simplifies to:

\[
k = k_0 \left( \frac{\sigma \lambda! N_0(0)}{V(\infty)(p + \lambda)!} \right)^{\frac{1}{n}}
\]

\( A2-10 \)

In fact, it is generally assumed that nuclei grow faster than they form from potential nucleation sites. If this were not the case, the entire process would be deceleratory (Allnatt and Jacobs, 1968). This cannot be discerned from Equation A2-9 specifically because of the restrictive assumption \( k_t \ll 1 \). From a kinetic analysis perspective, this means that the latter portion of any decomposition curve must be expressly excluded in order to fairly judge the fit of a power law.

The power law is normally assigned orders of 2/3, 1, 2, 3 and 4. All but the order 2/3 can be readily conceptualised. A sub-unity order basically implies that growth is not even hindered uniformly in one dimension. Decomposition according to this model approaches the shape for multidimensional contracting volume (Table 5-1), which agrees with the logic that volume contraction will limit the rate of conversion if nucleation and growth is sufficiently rapid.

**A2.2 Nucleation and Nucleus Growth: Avrami-Erofe’ev (An)**

The obvious shortcoming of the power law can be thought to arise because the inhibitory effects of nuclei coalescence and ingestion in regions of growth are ignored (Allnatt and Jacobs, 1968, Jacobs, 1997, Khawam and Flanagan, 2006). These effects naturally increase from zero to total inhibition over the course of the transition. Both Avrami and Erofe’ev utilise the same empirical modification to the
A New Adaptation of The Method of Invariant Kinetic Parameters and its Application to a Flame Retardant System

power law, the simplest possible, to create the sigmoidal response expected for nucleation and nucleus growth (Allnatt and Jacobs, 1968):

\[ d\alpha = (1 - \alpha) d\alpha_{pn}, \quad \text{where} \quad \alpha_{pn} = (kt)^{\alpha} = [g(\alpha)]^{\alpha}, \text{i.e. the power law} \]

\[ \Rightarrow g(\alpha) = [-\ln(1 - \alpha)]^{1/\alpha} \quad \text{A2-11} \]

Critically, the underlying assumption \( k_{\alpha}t << 1 \) used to develop the power law is still applicable, therefore this mechanism should correlate better to nucleation and nucleus growth kinetics at low conversions, provided the global account of inhibition is also valid. This can only possible if nucleation and nucleus growth are purely random (Allnatt and Jacobs, 1968).

Avrami arrives at the solution for \( g(\alpha) \) beginning from single-step nucleation (Equation 2-1; possible to prove with the convolution theorem), and Erofe'ev from multi-step nucleation (Equation 3-1). Both consider finite growth in three dimensions (Allnatt and Jacobs, 1968, Jacobs, 1997). It is common to see Equation A2-11 referred to as the JMAEK equation, after each of the researchers who contributed to its development (Johnson, Mehl, Avrami, Erofe'ev and Kholmogorov) (Khawam and Flanagan, 2006).

It is implied that the Avrami-Erofe'ev mechanism for single-step nucleation can be adapted should growth be diffusion controlled by simply halving the value of \( \lambda \) in the exponent (Pérez-Maqueda et al., 2003). Therefore, for instantaneous nucleation \( (k_N \text{ very large}; \text{i.e. no dependence on nucleation rate}) \), \( n \) equals 0.5, 1 and 1.5 for one-, two- and three-dimensional growth respectively. It follows that for an additional dependence on a single decomposition step, \( n \) will instead become 1.5, 2 and 2.5. The theoretical basis for this adaptation is not elaborated.

**A2.3 Nucleus Growth and Autocatalysis: Prout-Tompkins (P-T)**

Prout and Tompkins (1944) derived another popular sigmoidal description of nucleation and growth kinetics after recognising the inability of the power law to theoretically relate to potassium permanganate decomposition, and the resemblance of this decomposition curve to the symmetrical hyperbolic tangent function. Their theory ascribes acceleration of conversion rate, or autocatalysis, to the growth of highly energetic product-reactant interfaces along cracks and other imperfections. When the reaction progresses enough that product begins to encroach on already converted material, product growth is inhibited in much the same way as described in Section A2.2. Although Prout and Tompkins are
credited with this equation, their article mentions that an identical mathematical expression had already been proposed by Moles and Crespi in 1922.

In the derivation, the number of potential nucleation sites, \( N_0 \), is defined as in Equation 2-1, and is therefore representative of defect-free material. Any dependence on the rate of formation of these nuclei is eliminated (Khawam and Flanagan, 2006), which implies that growth is rate limiting; i.e. \( N_0 \) nuclei are present initially (Prout and Tompkins, 1944). It is also valid to interpret this omission as describing a negligible nucleation rate in comparison to the nucleus branching rate (Brown, 1997). Prout and Tompkins (1944) relate this well to the idea that the energetic product-reactant interface would catalyse much faster conversion than that attributable to the appearance of isolated nuclei. In either case, this means that \( N \), which represents the sum of isolated nuclei and new branches, grows well in excess of \( N_0 \).

The assumption of a first order process and a termination rate constant that varies with extent of conversion \( (k_T(\alpha)) \) implies the following equation for the branching rate:

\[
\frac{dN}{dt} = (k - k_T(\alpha))N
\]  

Incidentally, if termination is neglected and \( N \) is equated to conversion, Equation A2-12 defines the seldom reported exponential law of nucleation, with \( f(\alpha) = \alpha \) (Brown, 1997).

A relationship between \( \alpha \) and \( N \) or \( t \) must be assumed in order to integrate Equation A2-12, as the variable nature of \( k_T \) makes the problem intractable otherwise. As Retter and Vollhardt (1992) report with some scepticism, Prout and Tompkins suggest that conversion rate is proportional to the number of branches:

\[
\frac{d\alpha}{dt} = k_G N
\]  

Prout and Tompkins themselves provide inadequate reasoning for this relationship and a few of their equations suffer from dimensional inconsistencies and typographical errors. However, if the constant of proportionality is interpreted as a normalised rate of nuclei growth, Equation A2-13 essentially returns to the idea of convolving the number of nuclei with finite product growth rate in one dimension, since:
\[ \alpha(t) = \int_0^t k_G(t-t_0) \frac{dN}{dt} \bigg|_{t=t_0_0} dt_0 \quad \equiv \quad \alpha(t) = \int_0^t k_G N(t_0) dt_0 \]

Retter and Vollhardt’s valid issue with assigning this relationship between \( \alpha \) and \( N \) is that the simplicity of the implied manner of growth cannot be reconciled with Equation A2-12, i.e. that the number of nuclei branches will decrease once \( k_f(\alpha) > k \). Perhaps this concern is unfounded; it seems as though a negative branching rate in Equation A2-12 can be interpreted as the result of cancelling the linear growth of all established branches from their respective moments of termination onwards:

\[ \alpha(t) = \int_0^t k_G N(t_0) dt_0 = \int_0^t k_G N_{\text{Total}}(t_0) dt_0 - \int_{T(N_{\text{Total}}(t_0))}^{T(N_{\text{Total}}(t_0))} k_G N_{\text{Total}}(t_0) dt_0 = \int_0^{T(N_{\text{Total}}(t_0))} k_G N_{\text{Total}}(t_0) dt_0 \]

Thus, it is pertinent to consider \( N \) as the number of “active” nuclei branches.

The termination rate constant must be an increasing function of conversion with \( k_f(0) = 0 \) (as Khawam and Flanagan (2006) neglect to mention) and must cause an inflection point \( \left( \frac{d^2\alpha}{dt^2} \right)_{\alpha=\alpha_i} = 0 \) to match the empirical fact that the isothermal \( \alpha-t \) curve is sigmoidal.

Again, the simplest function that satisfies these conditions is selected (Prout and Tompkins, 1944, Retter and Vollhardt, 1992, Brown, 1997, Jacobs, 1997, Khawam and Flanagan, 2006):

\[ k_f(\alpha) = k \frac{\alpha}{\alpha_i} \quad \text{A2-14} \]

Therefore

\[ \frac{dN}{d\alpha} = \frac{k}{k_G} \left( 1 - \frac{\alpha}{\alpha_i} \right) \quad \Rightarrow \quad N = \frac{k}{k_G} \left( \alpha - \frac{\alpha_i}{2\alpha_i} \right), \]

provided

\[ N_0 = \frac{k}{k_G} \left( \alpha_0 - \frac{\alpha_0^2}{2\alpha_i} \right) \quad \text{and} \quad N_0 \neq 0, \quad \alpha_0 \neq 0 \]

Equation A2-13 can then be integrated for the isothermal case. Since Equation A2-14 prescribes symmetry about the inflection point and thus reaction completion by \( \alpha_f = 2\alpha_i \), \( \alpha_i \) is set to 0.5. The expression for \( g(\alpha) \) is:
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\[ g(\alpha) = kt = \ln\left(\frac{\alpha}{2\alpha_i - \alpha}\right) + kt_i = \ln\left(\frac{\alpha}{1 - \alpha}\right) + kt_i \]  
\[ \text{A2-15} \]

Or, as presented elsewhere:

\[ g(\alpha) = kt = \ln\left(\frac{\alpha}{1 - \alpha}\right) - c \]  
(Equation 41 in Khawam and Flanagan (2006))

or

\[ \ln\left(\frac{\alpha}{1 - \alpha}\right) = k(t - t_i) + c \]  
(Equation 6 in Skrdla (2004))

or

\[ g(\alpha) = \ln\left(\frac{\alpha}{1 - \alpha}\right) \]  
(Table 1 in Budrugeac and Segal (2001); Table 2 in Vlaev et al. (2008))

All instances of the Prout-Tompkins equation cited in literature only present the solution when \( \alpha_i = 0.5 \) except, ironically, the original article by Prout and Tompkins (this is because they use absolute pressure instead of dimensionless conversion). Many researchers make the mistake of eliminating the integration constant. Khawam and Flanagan (2006) believe that this constant has “no general criterion”, when it actually pertains to something quite specific. The constant of integration is also incorrectly assigned the dimension of time in Equation 41 of their article. Setting \( \alpha_i = 0.5 \) prior to integration may have misled Khawan and Flanagan in their conclusions regarding this constant.

Skrdla (2004) introduces a second constant \( c \) to translate the curve “vertically” but does not provide a theoretical basis for doing so. An error in interpreting Jacobs’ self-proclaimed generalised Prout-Tompkins equation (Equation A2-16) may be the cause. An additional non-zero constant is only appropriate if the \( \alpha-t \) curve is defined in terms of any point other than the inflection point (i.e. \( t_i \) in Equation 6 in Skrdla (2004) should read \( t_0 \)). Equation A2-16 is essentially identical to Equation A2-15 and retains the same restriction \( \alpha_f = 2\alpha_i \). Despite this, \( \alpha_i \) is set less than 0.5 but above the estimated “initiation” point, \( \alpha(t_0) = \alpha_0 \), to match the experimental asymmetry of the \( \alpha-t \) curve up to \( \alpha_f = 2\alpha_i \). This adaptation removes the theoretically problematic portion of the curve \( 0 \leq t < t_0 \) (Jacobs, 1997).

\[ g(\alpha) = kt = \ln\left(\frac{\alpha}{2\alpha_i - \alpha}\right) - \ln\left(\frac{\alpha_0}{2\alpha_i - \alpha_0}\right) + kt_0, \ \alpha \geq \alpha_0 \]  
\[ \text{A2-16} \]
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[Note that there is an apparent error and inconsistency in Equation 4.7 in Jacobs (1997): \( \frac{da}{dt} = k_a a^m \) should read \( k(a) = k_a a^m \) and \( \sigma' \) will be a different power of \( \sigma \) if \( a \propto \sigma^3 \).]

Equation A2-13 can be left in differential form after substituting for \( \mathcal{N} \) to supply the equation for \( f(\alpha) \):

\[
\frac{d\alpha}{dt} = k\alpha \left( 1 - \frac{\alpha}{2\alpha_i} \right) \quad \Rightarrow \quad f(\alpha) = \alpha(1 - \alpha), \quad \alpha_i = 0.5
\]

Equation A2-13

The evenly-weighted contributions of acceleration and decay are clear in this form and are characteristic of autocatalysis (Brown, 1997). Since the assignment of \( k_T(\alpha) \) is largely ambiguous, it seems that a more natural way of generating asymmetry and moving the inflection point is to allow the exponents of these contributions to vary:

\[
f(\alpha) = \alpha^m (1 - \alpha)^n
\]

\[
\Rightarrow \quad \alpha_i = \frac{m}{m + n} \quad \text{and} \quad k_T(\alpha) = k \left[ 1 - m \alpha^{m-1} (1 - \alpha)^n + n \alpha^m (1 - \alpha)^{n-1} \right]
\]

The termination rate constant \( k_T(\alpha) \) of Equation A2-18 meets all three criteria listed previously provided \( m = 1 \) and \( 0 < n \leq 1 \). If \( 0 \leq m < 1 \), the branching rate will be enhanced by \( k_T(\alpha) \) at low conversions rather than reduced. Equation A2-18, known as the Sestak-Berggren equation, is noted as the most popular function of conversion for autocatalysis examination (Jankovic et al., 2007), and in fact is flexible enough to replicate the shape of many other heterogeneous kinetic mechanisms (Section 3.3.1).

Reference should be made to isothermal data to verify the conversion and time at the inflection point and, if required, the initiation point. Any elapsed time can be difficult to interpret due to the ambiguity of the starting time, which has been recognised and addressed (Skrdla, 2004). Coupled with this difficulty is a high sensitivity to the selected value of \( \alpha_i \) (Jacobs, 1997). The appearance of \( k \) on both sides of Equation A2-15 and Equation A2-16 suggests an iterative approach to refining the selected model would be feasible. Arrhenius dependence for non-isothermal experiments has the potential to cause confusion, as all parameters in Equation A2-15 and Equation A2-16 are only valid for \( k \neq k(t) \). In the absence of corresponding real isothermal data, at least one degree of freedom is gained, severely undermining the certainty in calculated and assumed kinetic and mechanism parameters.
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A2.4 Contracting Volume: One-, Two- and Three-Dimensional (Rn)

Presuming product material nucleates and grows rapidly on or migrates quickly to the surface, the reaction rate will be controlled by the contraction of the reactant volume according to certain geometry (Allnatt and Jacobs, 1968). The shape and structure of the reactant will dictate which mechanism equation is applicable.

First, the progress of the phase boundary from \( r(0) = r_0 \) towards the centre of the reactant volume can be defined as (Khawam and Flanagan, 2006):

\[
r(t) = r_0 - k't = r_0 \left(1 - \frac{k't}{r_0}\right)
\]

This dimension needs to be related to conversion with the appropriate geometry, assuming that the reactant is structured as \( n \) particles of identical size, shape and uniform density:

1D:
\[
\alpha = \frac{n \sigma r_0 - n \sigma r}{n \sigma r_0} = 1 - \frac{r_0 - k't}{r_0} = \frac{k't}{r_0}; \quad \sigma = \text{cross-sectional area}
\]

\[\Rightarrow\]
\[
g(\alpha) = kt = \alpha
\]

2D:
\[
\alpha = \frac{n \sigma r_0^2 - n \sigma r^2}{n \sigma r_0^2} = 1 - \left(\frac{r_0 - k't}{r_0}\right)^2; \quad \sigma = \pi h \text{ for cylinder}
\]

\[\Rightarrow\]
\[
g(\alpha) = kt = 1 - \left(1 - \alpha\right)^{\frac{1}{2}}
\]

3D:
\[
\alpha = \frac{n \sigma r_0^3 - n \sigma r^3}{n \sigma r_0^3} = 1 - \left(\frac{r_0 - k't}{r_0}\right)^3; \quad \sigma = \frac{1}{2} \pi \text{ for sphere}
\]

\[\Rightarrow\]
\[
g(\alpha) = kt = 1 - \left(1 - \alpha\right)^{\frac{1}{3}}
\]

The preceding equations assume that each particle is 100% reactive, i.e. any inert material must be present as a separate substrate. Lengths in all contracting dimensions must be equivalent and decomposition must be equally probable for all particles. As required, \( kt \) varies from zero to one.

Khawam and Flanagan (2006) state that because the rate constant \((k = k'/r_0)\) is a function of the initial particle size in the contracting dimension(s), if the particle sizes vary, then the kinetic curves will be shifted in some manner. However, provided \( k' \) does not vary with particle properties, it is easy to
demonstrate using these equations that no such distortion should be anticipated. In fact, it is merely the poor definition of the rate constant in Equation A2-19 that gives rise to \( r_0 \) appearing in the denominator. It is more appropriate to focus on the likelihood that \( k' \) does vary with particle size/shape (Kral, 1989, Koga, N. and Criado, Jose M., 1998). Koga and Criado (1998) suggest that a wide particle size distribution has the effect of increasing the apparent order of a phase boundary reaction up to a maximum of unity.

**A2.5 Reaction Order: Zero, First, Second and Third (Fn)**

A homogeneous reaction such as that described by Equation 3-5 has a direct analogue in heterogenous systems. The rate at which \( n \) reaction participants form product(s) is simply governed by their densities in the substrate. While in reality these participants may be different species, for this application it is only required to express the rate in terms of non-dimensional conversion (Fatemi et al., 1986):

For \( X \rightarrow \text{Product(s)} \), \(- \frac{d[X]}{dt} = k'[X]^n \) \hspace{1cm} \text{A2-23}

Since \([X] = [X_0](1 - \alpha)\), \( \frac{d\alpha}{dt} = k'[X_0]^{n-1}(1 - \alpha)^n = k(1 - \alpha)^n \)

\[ f(\alpha) = (1 - \alpha)^n \] \hspace{1cm} \text{A2-24}

The \( n \)-order reaction mechanism was indiscriminately applied to data in the past to simplify kinetic analyses (Coats and Redfern, 1964, Urbanovici and Segal, 1984, Popescu et al., 1991, Budrugeac, 2000, Khawam and Flanagan, 2006), presumably due to both a lack of appreciation of the theoretical ramifications of doing so (Koga et al., 1991) and limited computational capability. In the current technologically and intellectually advanced climate, any unqualified simplifications of this nature should not be tolerated.

It should be noted that the first order reaction mechanism corresponds mathematically and theoretically to the Avrami-Erofe’ev equation for \( p = 1 \) and \( \lambda = 0 \) (dependence on a single decomposition reaction in the substrate, but not on growth). Furthermore, the zero order reaction mechanism is equivalent to the one-dimensional contracting volume expression and also to the power law should \( p = 0 \) and \( \lambda = 1 \) (no dependence on number of decomposition steps and growth in one dimension). Purely mathematically, of course, the only meaningful distinction between \( p \) and \( \lambda \) is confined to the pre-exponential factor (Equation A2-10) and thus they can be considered interchangeable.
To extend upon this, if the Rn conversion functions were expressed in terms of \( f(\alpha) = (1 - \alpha)^n \), they would have fractional orders according to \( n_{Fn} = 1 - \frac{1}{n_{Rn}} \), where \( n_{Rn} \) is the number of contracting dimensions. Some authors disagree on the form of the Fn conversion functions (Ravindran et al., 1977, Rose et al., 1994, Richard-Campisi et al., 1996), but it is unclear why; most of the alternate expressions proposed are essentially equivalent to the Rn set as the orders are fractional. Rose et al. (1994) do not arrive at the correct \( g(\alpha) \) as they neglect the definite nature of the integral.

**A2.6 Random Scission: Minimum length of Non-Volatile Chain (L)**

Rate laws describing random scission were developed in detail many years ago (Simha and Wall, 1952). Despite their obvious applicability to polymer decomposition and appearance in a seminal article by Ozawa (1965), these equations have apparently been adapted to non-specific heterogenous kinetic analyses only recently (Sánchez-Jiménez et al., 2010, Grause et al., 2010, Perejón et al., 2011) and have not yet attained widespread application in this context. This reluctance may be due to underconfidence in the theoretical development or the relative inaccessibility/difficulty of the derivation (Boyd, 1967). Mathematical complexity of the scission equations certainly forces the introduction of many assumptions if this mode of decomposition is to be expressed as a simple function of conversion.

Simha and Wall (1952) consider the following scenario. At high temperature, random homolytic cleavage of carbon-carbon bonds in the backbone of a linear polymer initiates decomposition. Unsaturated monomers are then repeatedly eliminated from the shortening radical chains and volatilise, until the radical chains transfer their unpaired electron elsewhere or terminate. Electron transfer can occur through the elimination of a portion of the polymer chain under attack, complicating the decomposition with non-monomeric unsaturated compounds. Greater reactivity of the attacking radical and stability of the intermediate will clearly promote this type of transfer (Simha and Wall, 1952). Simha and Wall (1952) deliberately simplify their analysis by assuming that termination only occurs via radical disproportionation, i.e. abstraction of a \( \beta \)-atom (usually hydrogen) from one radical by another. This complete scheme is represented in Figure A2-1.
Ignoring radical combination as a parallel termination step seems to be a particularly tenuous simplification given that the rates of disproportionation and combination are comparable (Kelley and Klein, 1974), and the combination rate is reportedly significantly larger in many cases (Gibian and Corley, 1973, Bockhorn et al., 1999a, Setser et al., 2004). It should be kept in mind that as the amount of available atoms $\beta$ to the radical centre increases, the ratio of the rates of disproportionation to combination increases, following the progression primary $>$ secondary $>$ tertiary with respect to the $\beta$-atom environment (Kelley and Klein, 1974). Steric effects are very influential on this ratio (Kelley and Klein, 1974), and furthermore, it has been reported that the ratio of disproportionation to combination rates in the gas and liquid phases decreases subtly as temperature increases (Gibian and Corley, 1973).
If the assumption of negligible combination is made, an average kinetic chain length can be deduced provided the “usual” assumption of steady overall radical numbers holds \( \overline{R} = \sum_{j=1}^{\infty} R_j \), where \( j \) is the number of atoms forming the backbone of radical \( R_j \):

\[
\frac{d\overline{R}}{dt} = 2k_i \overline{P} - k_i \overline{R}^2 = 0 \quad \Rightarrow \quad \overline{P} = \frac{k_i \overline{R}^2}{2k_i}
\]

where \( \overline{P} \equiv \text{Total number of polymer fragments} \)

Equation A2-25 is clearly invalid at the beginning and end of the scission process. Note that the concept of steady radical numbers is only synonymous with steady radical concentration if reaction volume is also constant. MacCallum (1971) implies that a number basis is more frequently used for the steady-state hypothesis, and while Simha and Wall (1952) specifically state “concentration”, it does not appear to be critical to their equation development because of the implicit assumption of constant volume.

Average kinetic chain length \( \left( \frac{1}{\varepsilon} - 1 \right) \) is defined as the ratio of propagation rate to the sum of termination and transfer rates and can be thought of as the average normalised zip length from initiation to transfer or termination (Simha and Wall, 1952, Boyd, 1967):

\[
\frac{1}{\varepsilon} - 1 = \frac{k_p \overline{R}}{k_i \overline{R}^2 + k_p \overline{R} \overline{P}} = \frac{k_p}{k_i \overline{R} + k_p k_i \overline{R}^2} = \frac{k_p}{k_i \overline{R} \left( 1 + \frac{\sigma}{2} \right)}; \quad \sigma = \frac{k_p \overline{R}}{k_i}
\]

Intramolecular hydrogen rearrangement and \( \beta \)-scission (analogous to intermolecular transfer) can also contribute to the transfer of unpaired electrons, which ultimately means that the estimate for average kinetic chain length (Equation A2-26) is at its lower limit (Simha and Wall, 1952).

These parameters can be utilised in rigorous rate equations where the multitude of chain lengths and increased opportunity for reaction with longer chains are appropriately taken into account. The simplest case where all carbon backbone bonds are equally reactive and only primary carbon radicals can be formed (if \( X_i \) in Figure A2-1 represents a single atom) is considered. If the bonds to any pendant groups are more labile than the bonds forming the polymer backbone, such is the case with polyvinyl chloride or acetate, a different mathematical treatment is required (Simha and Wall, 1952).
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According to the scheme proposed by Simha and Wall and the basic collision theory exemplified in Equation 3-5, it is logical to write (Simha et al., 1950, Simha and Wall, 1952, Boyd, 1959):

\[
\frac{dP_n}{dt} = -k_i(n-3)P_n - k_v(n-3)P_n \sum_{j=1}^{\infty} R_j + k_v R_n \sum_{j=1}^{\infty} (j-3)P_j + k_v \sum_{j=1}^{\infty} R_j \sum_{j=2}^{\infty} P_j + k_v R_n \sum_{j=1}^{\infty} R_j
\]

\[
\frac{dR_n}{dt} = 2k_i \sum_{j=n+2}^{\infty} P_j - k_v R_n + k_v R_{n+2} - k_v R_n \sum_{j=4}^{\infty} (j-3)P_j + k_v \sum_{j=1}^{\infty} R_j \sum_{j=2}^{\infty} P_j - k_v R_n \sum_{j=1}^{\infty} R_j
\]

\[
\therefore \frac{1}{k_i} \frac{dP_n}{dt} = -(1 + \sigma)(n-3)P_n + \frac{\sigma R_n}{R} \sum_{j=4}^{\infty} (j-3)P_j + \sigma \sum_{j=2}^{\infty} P_j + \frac{k_v R_n}{k_i} \overline{R}
\]

\[
\frac{1}{k_i} \frac{dR_n}{dt} = (2 + \sigma) \sum_{j=n+2}^{\infty} P_j + \frac{k_v}{k_i} R_{n+2} - \frac{\sigma R_n}{R} \sum_{j=4}^{\infty} (j-3)P_j - \frac{k_v R_n}{k_i} \overline{R}
\]

In these equations and in Simha and Wall’s derivation, \( n \) refers to the number of atoms in the carbon backbone, not the number of condensed monomer units (degree of polymerisation) as is presented elsewhere (Boyd, 1959). It is also assumed that these units are two carbons in length. An unrealistic consequence of defining \( n \) as the degree of polymerisation is that initiation and transfer reactions that lead to chains of non-integer multiples of monomer units are implicitly disallowed. Maintaining \( n \) as the number of carbon atoms is therefore preferred.

It may be thought that Simha and Wall (1952) use the multiplier \( n - 3 \) in the equations above to exclude the possibility of initiation and transfer at the terminal bonds, since the total number of available bonds is \( n - 1 \) for a saturated chain. However, this multiplier is in fact interpreted simplistically as the median number of available hydrogens, given that either end of the chain can be unsaturated (Figure A2-1) (i.e. \( \max n - 2 \), which yields monomer as the smallest fragment; \( \min n - 4 \) (Simha et al., 1950).

Simha and Wall also limit the polymer length at \( n = N \) and rewrite the infinite summations accordingly. Fixing the value for maximum chain length and the imperative to avoid the production of sub-monomer fragments compel Simha and Wall to deliberately concatenate the expressions for \( P_n \) and \( P_{n+1} \) and \( R_n \) and \( R_{n+1} \), since otherwise there is a technical distinction between the equations for odd and even \( n \). This effectively imposes the same limitation as if \( n \) was defined as the degree of polymerisation. They define the following approximation and specify \( n \) as even and assume \( N \) as odd:
Now, if the assumption of steady radical numbers is applied to each chain length:

\[
R_n = \frac{(2 + \sigma)k_i \sum_{j=n+2}^{N} P_j + k_p R_{n+2}}{k_p + \frac{\sigma k_i}{R} \sum_{j=4}^{N} (j-3)P_j + k_i R}
\]

The term associated with transfer in the denominator of Equation A2-30 can be substituted with Equation A2-25:

\[
\frac{\sigma k_i}{R} \sum_{j=4}^{N} (j-3)P_j \approx \frac{\sigma k_i}{R} P = \frac{\sigma}{2} k_i R
\]

\[
R_n = \frac{(2 + \sigma)k_i \sum_{j=n+2}^{N} P_j + k_p R_{n+2}}{k_p + k_i R \left(1 + \frac{\sigma}{2}\right)}
\]

\[
R_n = \frac{(2 + \sigma)k_i}{k_p + k_i R \left(1 + \frac{\sigma}{2}\right)} \left(\sum_{j=0}^{(N-n-2)/2} \left(\frac{k_p}{k_p + k_i R \left(1 + \frac{\sigma}{2}\right)}\right)^j \sum_{k=n+2}^{N} P_k\right)
\]

Using the definition from Equation A2-26:

\[
R_n = (2 + \sigma)(1 - \varepsilon) \frac{k_i}{k_p} \sum_{j=0}^{(N-n-2)/2} \left(1 - \varepsilon\right)^j \sum_{k=n+2}^{N} P_k
\]

It follows that:

\[
R_n + R_{n+1} = (2 + \sigma)(1 - \varepsilon) \frac{k_i}{k_p} \left[ \sum_{j=0}^{(N-n-2)/2} \left(1 - \varepsilon\right)^j \sum_{k=n+2}^{N} P_k + \sum_{j=0}^{(N-n-3)/2} \left(1 - \varepsilon\right)^j \sum_{k=n+2}^{N} P_k \right]
\]
And by applying Equation A2-29:

\[ R_n + R_{n+1} = (2 + \sigma)(1 - \varepsilon)\frac{k_l}{k_p} \left( \frac{N-n+3}{2} \right)^{1/2} \sum_{j=0}^{N-1} \frac{Q_k}{k_{p,j+2}} \left( 1 - \varepsilon \right)^j \]

The summation for \( Q_k \) needs to be rewritten such that only the even indices are considered, necessitating the introduction of a factor of two:

\[ R_n + R_{n+1} = 2(2 + \sigma)(1 - \varepsilon)\frac{k_l}{k_p} \left[ \sum_{j=0}^{(N-n-3)/2} Q_{n+2,j+2} + (1 - \varepsilon) \sum_{j=1}^{(N-n-3)/2} Q_{n+2,j+2} + \ldots + (1 - \varepsilon)^{(N-n-3)/2} Q_{N-1} \right] \]

Simha and Wall (1952) substitute according to:

\[ \sum_{j=0}^{(N-n-3)/2} Q_{n+2,j+2} + (1 - \varepsilon) \sum_{j=1}^{(N-n-3)/2} Q_{n+2,j+2} + \ldots + (1 - \varepsilon)^{(N-n-3)/2} Q_{N-1} \approx \frac{1}{\varepsilon} \sum_{j=0}^{(N-n-3)/2} \left[ 1 - \left( \frac{1}{4}\varepsilon \right)(1 - \varepsilon)^j \right] Q_{n+2,j+2} \]

It is stated that Equation A2-36 is a good approximation provided \( 0 < \varepsilon << 1 \) (propagation rate high compared to termination and transfer rates) (Simha et al., 1950). [This substitution is reminiscent of the identity \( 1 + (1 - \varepsilon) + (1 - \varepsilon)^2 + \ldots + (1 - \varepsilon)^j = \frac{1}{\varepsilon} \left[ 1 - (1 - \varepsilon)(1 - \varepsilon)^j \right] \).]

\[ \therefore R_n + R_{n+1} = 2(2 + \sigma)\frac{k_l}{k_p} \left( \frac{N-n-3}{2} \right)^{1/2} \sum_{j=0}^{(N-n-3)/2} \left[ 1 - \left( \frac{1}{4}\varepsilon \right)(1 - \varepsilon)^j \right] Q_{n+2,j+2} \]

After substituting Equation A2-31 into Equation A2-27, the result for the appearance rate of polymer fragments becomes:

\[ \frac{1}{k_i} \frac{dP_n}{dt} = -(1 + \sigma)(n-3)P_n + \frac{k_i R}{k_i} \left( 1 + \frac{\sigma}{2} \right) R_n + \sigma \sum_{j=n+2}^{N} P_j \]

Concatenating this with the next equation in the series, ignoring the difference in the factor in the first term on the right hand side, substituting with Equation A2-37 and simplifying:
\[
\frac{1}{k_i} \frac{dQ_n}{dt} = -(1 + \sigma)(n - 3)Q_n + 2(2 + \sigma) \sum_{j=0}^{(N-n+1)/2} [1 - (1 - \epsilon)(1 - \epsilon)^j] Q_{n+2j} + \sigma \sum_{j=0}^{N-1} Q_j
\]

\[
\therefore \quad \frac{1}{k_i} \frac{dQ_n}{dt} = -(1 + \sigma)(n - 3)Q_n + 2 \sum_{j=0}^{(N-n+1)/2} (2 + \sigma) [1 - (1 - \epsilon)(1 - \epsilon)^j] + \sigma Q_{n+2j+2}
\]

A2-39

Simha and Wall start the summation in Equation A2-39 at \( j = 1 \) and express the term for \( Q_{n+2} \) separately. They also appear to subtract \( \frac{\sigma}{2} Q_{n+2} \) for unclear reasons. Equation A2-40 is a reproduction of their Equation 2a (Simha and Wall, 1952):

\[
\frac{1}{k_i} \frac{dQ_n}{dt} = -(1 + \sigma)(n - 3)Q_n + 2 \left( \frac{K_0 - \sigma}{4} \right) Q_{n+2} + 2 \sum_{j=1}^{(N-n+1)/2} K_j Q_{n+2j+2}
\]

where \( K_j = (2 + \sigma) [1 - (1 - \epsilon)(1 - \epsilon)^j] + \sigma \)

A2-40

If the average kinetic chain length is short (\( \epsilon \) close to one) and Equation A2-36 is still an adequate approximation, Equation A2-39 simplifies to:

\[
\frac{1}{k_i} \frac{dQ_n}{dt} = -(1 + \sigma)(n - 3)Q_n + 4(1 + \sigma) \sum_{j=0}^{(N-n+1)/2} Q_{n+2j+2}
\]

or

\[
\frac{dQ_n}{dt} = -k(n - 3)Q_n + 4k \sum_{j=0}^{(N-n+1)/2} Q_{n+2j+2} \quad \therefore \quad k = k_i + k_p R
\]

A2-41

Then, if \( Q_n \) is reverted to \( P_n \) and the multiplier \( n - 3 \) is replaced with \( n - 1 \) (justified previously), the equation becomes that utilised in an earlier article by Simha and Wall (1951):

\[
\frac{dP_n}{dt} = -k(n - 1)P_n + 2k \sum_{j=n+1}^{N} P_j
\]

A2-42

Either description for polymer fragmentation (Equation A2-41 or Equation A2-42) needs to be developed into a function of conversion to be of use. Volatility is chosen as the basis for conversion, restricting the application to thermogravimetric analyses (Sánchez-Jiménez et al., 2010). Polymer chains equal to or longer than \( L \) backbone atoms and radicals of all lengths are considered non-volatile (at least until further reaction), while polymer chains of less than \( L \) atoms in length are treated as volatilising instantly.
A New Adaptation of The Method of Invariant Kinetic Parameters and its Application to a Flame Retardant System (Boyd, 1967). This discontinuity is introduced despite the fact that the changes in relative magnitudes of evaporation and reaction rates with chain length would be gradual (Simha and Wall, 1951).

Mathematically, Equation A2-41 or Equation A2-42 must be appended with an appropriately defined, chain length-dependent evaporation rate to suit this theory. Since the final form for $f(\alpha)$ presented by Ozawa (1965), Sánchez-Jiménez (2010) and Gao (2003) is that derived from Equation A2-42, this will be exemplified. It is worth mentioning that all these authors cite Simha and Wall (1952) rather than Simha and Wall (1951) upon presentation of $f(\alpha)$, which is somewhat misleading.

\[
\frac{dP_n}{dt} = -k(n-1)P_n + 2k \sum_{j=n+1}^{N} P_j - k_{e,n} P_n \quad \text{A2-43}
\]

where $k_{e,n} = 0$ for $n \geq L$ and $k_{e,n} \gg k(n-1)$ for $n < L$, representing the evaporation rate constant.

Equation A2-43 has an intuitive series solution for the isothermal case that requires an initial distribution to be assumed to finalise the constants of integration, $h_j a_{n,j}$ (Simha and Wall, 1951):

\[
P_n = \sum_{i=0}^{N} h_i a_{n,i} e^{-(k(i-1)+k_{e,j})t} \quad \text{A2-44}
\]

where $[k(i-1)+k_{e,j}-k_{e,n}]a_{i,j} + 2k \sum_{j=n+1}^{i} a_{i,j} = 0$ and $a_{i,j} = 0$ for $i < l$.

Simha and Wall (1951) take the most basic approach and set a uniform chain length of $N$ initially ($P_N(0) = P_N0$; $P_n(0) = 0$ for $0 < n < N$), arguing that a distribution complicates the derivation while not adding anything “fundamentally new”. The opposite may be true if a later article, Boyd (1959), is to be used as a guide. Notably, assuming a distribution of chain lengths would mean that distinguishing between odd and even chain lengths is patently unnecessary and the approximation of Equation A2-36 can be omitted in the case of long average kinetic chain length. The most apt distribution to assume in the context of the depolymerisation scheme presented by Simha and Wall is the Flory distribution, or “most probable” distribution for random linear polymerisation (Boyd, 1959, 1967). Monomer is actually the most prolific species if the polymer abides by a Flory distribution, which is in stark contrast to Simha and Wall’s assumption.
Evaluation of Equation A2-43 for the volatile fraction is easily accomplished (Simha and Wall, 1951), but unnecessary for this application. For the non-volatile fraction, Equation A2-44 can be reduced to:

\[ P_n = \sum_{i=0}^{N} h_i a_{n,i} e^{-k(i-1)t} \]  

\[ \text{A2-45} \]

where \( k(l-i)a_{i,j} + 2k \sum_{r=1}^{j} a_{r,j} = 0 \) and \( a_{i,j} = 0 \) for \( l < i \), for \( L \leq n \leq N \)

Consider the substitution \( i = l - 1 \):

\[ ka_{l-1,i} + 2ka_{i,j} = 0 \quad \Rightarrow \quad a_{l-1,i} = -2a_{i,j} \]

Similarly, for \( i = l - 2 \):

\[ 2ka_{l-2,i} + 2(a_{l-1,i} + a_{i,j}) = 0 \quad \Rightarrow \quad a_{l-2,i} = a_{i,j} \]

It follows that all other coefficients \( a_{i,j} \) in this progression are zero. To illustrate the origin of the final equation cited in literature, Simha and Wall’s initial conditions are adopted:

\[ P_N(0) = h_N a_{N,N} = P_{N0}; \]
\[ P_{N-1}(0) = h_{N-1} a_{N-1,N-1} + h_N a_{N-1,N} = 0 \quad \Rightarrow \quad h_{N-1} a_{N-1,N-1} = 2h_N a_{N,N} = 2P_{N0} \]
\[ P_{N-2}(0) = h_{N-2} a_{N-2,N-2} + h_{N-1} a_{N-2,N-1} + h_N a_{N-2,N} = 0 \quad \Rightarrow \quad h_{N-2} a_{N-2,N-2} = 3P_{N0} \]

The general result for \( P_n(0) = 0 \) can be derived beginning from the observable recursive dependencies of the coefficients:

\[ P_{n-2}(0) = h_{n-2} a_{n-2,n-2} + h_{n-1} a_{n-2,n-1} + h_n a_{n-2,n} = 0 \]
\[ \therefore \quad P_{n-2}(0) = h_{n-2} a_{n-2,n-2} - 2h_{n-1} a_{n-1,n-1} + h_n a_{n,n} = 0 \]
\[ \Rightarrow \quad P_{n-2}(0) = (N - n + 3)P_{N0} - 2(N - n + 2)P_{N0} + (N - n + 1)P_{N0} = 0 \]

or

\[ P_n(0) = (N - n + 1)P_{N0} - 2(N - n)P_{N0} + (N - n - 1)P_{N0} = 0, \quad L \leq n < N \]

Introducing the specified relationship to time from Equation A2-45:
The problem under consideration is to determine the rate of bond rupture, which can be described by the following equation:

\[ \frac{dx}{dt} = k(1 - x) \quad \Rightarrow \quad x = 1 - e^{-kt}, \text{ for isothermal conditions} \]  

Assuming the rate of bond rupture is directly proportional to the fraction of polymer backbone bonds remaining in the non-volatilised material, \( 1 - x \) (Simha and Wall, 1951, 1952, Sánchez-Jiménez et al., 2010):

\[ \frac{dx}{dt} = k(1 - x) \quad \Rightarrow \quad x = 1 - e^{-kt}, \text{ for isothermal conditions} \]  

This relationship can be substituted into Equation A2-46:

\[ P_n(t) = P_{N0}e^{-(n-1)kt} - 2(N - n)P_{N0}e^{-nk} + (N - n - 1)e^{-2kt} \]

\[ \therefore P_n(t) = P_{N0}e^{-(n-1)kt} \left[ (N - n + 1) - 2(N - n)e^{-kt} + (N - n - 1)e^{-2kt} \right] \]  

Noting that \( P_n(x) = P_{N0}(1 - x)^{N-1} \)

Finally, given the assumed initial conditions, the conversion to volatile material is equivalent to:

\[ \alpha = 1 - \frac{\sum_{n=L}^{N}nP_n}{NP_{N0}} \]  

The summation is tedious to evaluate, but can be achieved by first rearranging Equation A2-48:

\[ P_n = \frac{P_{N0}x}{1-x} \left[ 2 + (N-1)x \right] \left[ 1-x \right]^n - \frac{P_{N0}x^2}{1-x} n(1-x)^n \]

\[ \therefore \sum_{n=L}^{N}nP_n = \frac{P_{N0}x}{1-x} \left[ 2 + (N-1)x \right] \sum_{n=L}^{N-1} n(1-x)^n - \frac{P_{N0}x^2}{1-x} \sum_{n=L}^{N-1} n^2(1-x)^n + NP_{N0}(1-x)^{N-1} \]

Applying the identities:

\[ \sum_{n=0}^{N-1} n(1-x)^n = \frac{1-x}{x^2} \left[ 1 - N(1-x)^{N-1} + (N-1)(1-x)^N \right] \]
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\[ \sum_{n=0}^{N-1} n^2 (1 - x)^n = \frac{1 - x}{x^2} \left[ (1 + (1 - x) - N^2 (1 - x)^{N-1} + 2(N - 1)^2 + 2(N - 1) - 1)(1 - x)^N - (N - 1)^2 (1 - x)^{N+1} \right] \]

\[ \sum_{n=L}^{N} f(n) = \sum_{n=0}^{N-1} f(n) - \sum_{n=0}^{L-1} f(n) \]

Ultimately, all the terms involving \((1 - x)^{N-1}\) in the combined summations resolve to \(-NP_{N0}(1 - x)^{N-1}\) and therefore cancel out the opposing term in Equation A2-50. The remaining terms simplify to:

\[ \sum_{n=L}^{N} nP_{n} = P_{N0}(1 - x)^{L-1}\left[N + x(N - L)(L - 1)\right] \]

\[ \Rightarrow \quad \alpha = 1 - (1 - x)^{L-1}\left[1 + x \frac{(N - L)(L - 1)}{N}\right] \quad A2-51 \]

Yet another assumption, \(N >> L\), reduces Equation A2-51 to:

\[ \alpha = 1 - (1 - x)^{L-1}\left[1 + x(L - 1)\right] \quad A2-52 \]

\[ \therefore \quad \frac{d\alpha}{dt} = \left[(L - 1)(1 - x)^{L-2}(1 + x(L - 1)) - (1 - x)^{L-1}(L - 1)\right] \frac{dx}{dt} \]

\[ \Rightarrow \quad \frac{d\alpha}{dt} = k(L - 1)(1 - x)^{L-1} xL \]

i.e. \(f(x(\alpha)) = (L - 1)(1 - x)^{L-1} xL \quad A2-53\)

Regrettably, Equation A2-53 can only be transformed into an explicit function of conversion for \(L = 2\) (volatile monomers) (Sánchez-Jiménez et al., 2010). The result is easily shown to be:

\[ f(\alpha) = 2(\alpha^{\frac{1}{2}} - \alpha) ; \quad \alpha = x^2 \quad A2-54 \]

Composite solutions for higher \(L\) values are easy to obtain but ultimately make these equations less attractive to the average researcher. The applicability of this mechanism to non-isothermal experiments is limited given that the parameter \(L\) is clearly an increasing function of temperature, and \(f(x(\alpha))\) cannot be a function of the rate constant to be admissible for non-isothermal kinetic analyses that utilise a temperature integral approximation. This complication is merely alluded to by Gao (2003) in their
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discussion of the apparent activation energy increase with conversion. Sánchez-Jiménez et al. (2010) and Perejón (2011) make no mention of this in their non-isothermal analyses.

If \( L \) can be described by a function of temperature, it makes sense to equate it to a representative set of known normal boiling points. Reported boiling points for linear alkanes (Bailey and Bailey, 2000) precisely conform to a logarithmic function of chain length (Figure A2-2). The regression equation can be rearranged to make \( L(T) \) the subject, where \( L(T) \) is one more than the number returned by the regression and is rounded down to the nearest integer:

\[
T = 286.46 \ln(L + 2) - 285.28
\]

\[ \Rightarrow \quad L(T) = \left[ 2.7e^{0.0035T} - 2 \right] \]

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\[
T = 286.46 \ln(L + 2) - 285.28
\]

\[ \Rightarrow \quad L(T) = \left[ 2.7e^{0.0035T} - 2 \right] \]

Grause et al. (2010) use a different adaptation of Simha and Wall’s equation for \( L = 2 \) where, it seems, conversion is equated directly to the fraction of bonds broken:

\[
\frac{d\alpha}{dt} = k(1 - \alpha)(1 + \alpha)
\]
No derivation or reference is cited for this variant. It is presumed Equation A2-56 is an invalid interpretation, or at least is incorrect in the context of thermogravimetric analysis.

Polymer decompositions have commonly been modelled as simple \( n \)-order reactions, which are inadequate at describing the abnormally long induction periods during which the polymer fragments are non-volatile (Bockhorn et al., 1999a, Bockhorn et al., 1999b, Chrissafis, 2009, Sánchez-Jiménez et al., 2010). Random scission schemes can address this failing. As a further illustration, Equation A2-52 can be rearranged to:

\[
x(L - 1) = \frac{1 - \alpha}{(1 - x)^{L-1}} - 1
\]

This can be substituted into Equation A2-53 to transform the conversion function to:

\[
f(\alpha, x) = L \left[ (1 - \alpha) - (1 - x)^{L-1} \right]
\]

Equation A2-57 clearly shows that as the fraction of backbone bonds broken approaches one, the conversion function resembles that of a first order reaction more and more (Gao et al., 2003). Deviation from the first order reaction conversion function is obviously more pronounced the greater the value of \( L \). At \( L = 1 \), the two conversion functions appear identical; however, conversion naturally stagnates at zero as no chain lengths are volatile in that case.

Functions of conversion for any \( L \) give rise to sigmoidal \( \alpha-t \) curves (Table 5-1) and are reminiscent of the Avrami-Erofe’ev mechanisms. The two mechanism types have very similar shapes for small \( L \) and values of \( n_{An} \) near to one.

### A2.7 Diffusion and Anti-Diffusion: One-, Two- and Three-Dimensional (\( Dn, Dn^* \))

If a second or higher order reaction is driving a transformation, then the participating species must first migrate through inert material or a growing product layer to the reaction site. Products from a reaction, including nuclei or volatiles, may need to escape through the substrate to facilitate further decomposition, as would be the case for reversible reactions (Vyazovkin and Wight, 1997). In either case, if hindrance to transportation is significant, then diffusion will be rate limiting. An expanding condensed product will clearly diminish the rate of reaction as conversion increases. The literature is
contradictory regarding whether rate limiting diffusion in the solid state is a commonly encountered phenomenon or not (Galwey and Brown, 1998, Khawam and Flanagan, 2006).

Consider a concentration $C(r)$ of species $A$ diffusing in $\lambda$ equivalent dimensions (dictating linear, cylindrical and spherical coordinates, and shape factor $\sigma$ as for the contracting volume expressions). By performing a shell mass balance across a small length $\Delta r$ in the active dimension:

$$
\lambda \sigma r^{\lambda-1} N(r) - \lambda \sigma (r + \Delta r)^{\lambda-1} N(r + \Delta r) = \int_r^{r+\Delta r} \lambda \sigma r^{\lambda-1} dr = \frac{\partial C}{\partial t} \left[ \sigma (r + \Delta r)^{\lambda} - \sigma r^{\lambda} \right]
$$

$$
\Rightarrow \quad \lambda \sigma \left[ r^{\lambda-1} N(r) - (r + \Delta r)^{\lambda-1} N(r + \Delta r) \right] \approx \frac{\partial C}{\partial t} \lambda \sigma r^{\lambda-1} \Delta r \quad \text{(ignoring terms with } \Delta r^i, i > 1)
$$

Taking the limit as $\Delta r \to 0$:

$$
- \frac{1}{r^{\lambda-1}} \frac{\partial}{\partial r} \left( r^{\lambda-1} N(r) \right) = \frac{\partial C}{\partial t} \quad \text{A2-58}
$$

As $N(r)$ is the mass flux at position $r$, it can be related to the concentration gradient with an appropriate adaptation of Fick’s Law, applicable in all three coordinate systems:

$$
N(r) = -D \frac{\partial C}{\partial r} \quad \text{A2-59}
$$

The multiplier $D$ follows Arrhenius dependence. Substituting Equation A2-59 into Equation A2-58 and considering the steady-state solution:

$$
\frac{\partial}{\partial r} \left( r^{\lambda-1} D \frac{\partial C}{\partial r} \right) = 0
$$

$$
\Rightarrow \quad \frac{\partial C}{\partial r} = \frac{k'}{r^{\lambda-1}} \quad \text{A2-60}
$$

The assumption of steady-state implies that the concentration gradient takes a negligible amount of time to equilibrate as the dimensions change. Equation A2-60 can be integrated for one, two and three active dimensions and the boundary conditions applied ($C(r_1) = C_1$ and $C(r_2) = 0$ [due to effectively immediate reaction or departure of $A$ at this interface]) to give:
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1D: \[
\frac{\partial C}{\partial r} = k' \quad \Rightarrow \quad C = k' r + c \quad \Rightarrow \quad C = C_1 \left[ \frac{r - r_2}{r_1 - r_2} \right]
\]
\[\therefore \quad \frac{\partial C}{\partial r} = \frac{C_1}{r_1 - r_2} \quad \text{A2-61}\]

2D: \[
\frac{\partial C}{\partial r} = \frac{k'}{r} \quad \Rightarrow \quad C = k' \ln r + c \quad \Rightarrow \quad C = C_1 \left[ \frac{\ln r - \ln r_2}{\ln r_1 - \ln r_2} \right]
\]
\[\therefore \quad \frac{\partial C}{\partial r} = \frac{C_1}{r \ln \left( \frac{r_1}{r_2} \right)} \quad \text{A2-62}\]

3D: \[
\frac{\partial C}{\partial r} = \frac{k'}{r^2} \quad \Rightarrow \quad C = -\frac{k'}{r} + c \quad \Rightarrow \quad C = C_1 \left[ \frac{r_1 (r - r_2)}{r(r_1 - r_2)} \right]
\]
\[\therefore \quad \frac{\partial C}{\partial r} = \frac{C_1 r_1 r_2}{r^2 (r_1 - r_2)} \quad \text{A2-63}\]

Should the diffusion barrier consist of a condensed product, the barrier depth \((x = r_2 - r_1; r_2 \text{ fixed})\) can be related to conversion in an analogous manner to that shown for the contracting volume mechanisms. However, in this case the stoichiometry and different molar volumes of reactant and product need to be considered (Christie et al., 1978, Michèle et al., 2011). Say for \(aA \rightarrow pP\):

Set \[
z = \frac{p M_p}{\rho_p} \cdot \frac{\rho_A}{a M_A}, M_x = \text{molecular weight of } x \quad \text{A2-64}
\]
\[
\alpha = \frac{n \sigma_2^{\frac{1}{z}} - n \sigma_1^{\frac{1}{z}}}{zn \sigma_2^{\frac{1}{z}}} \quad \Rightarrow \quad \alpha = \frac{1}{z} \left[ 1 - \left( \frac{r_2 - x}{r_2} \right)^{\frac{1}{z}} \right] \quad \text{A2-65}
\]
\[\therefore \quad x = r_2 \left( 1 - (1 - z \alpha)^{\frac{1}{z}} \right) \quad \text{A2-66}
\]
and also \[
r_1 = r_2 \left( 1 - z \alpha \right)^{\frac{1}{z}} \quad \text{A2-67}
\]

Application of Fick’s Law (Equation A2-59) and substitution of the concentration gradient evaluated at \(r = r_2\) gives the mass flux at the far side of the interface. Now, for \(aA \rightarrow pP\) and effectively instantaneous conversion of \(A\) transported to interface \(r_2\), the left-hand side of Equation A2-59 is equivalent to:
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After substituting for $r_1$ using Equation A2-67, the final general expression for mass flux becomes:

$$N(r_2) = \frac{aM_A \rho_p r_2 z}{\lambda p M_p} \frac{d \alpha}{d t} = \frac{r_2 \rho_A}{\lambda} \frac{d \alpha}{d t}$$

The following rate equations result:

1D:

$$N(r_2) = -D \frac{C_1}{(r_1 - r_2)} \Rightarrow r_2 \rho_A \frac{d \alpha}{d t} = D \frac{C_1}{r_2 \left[1 - (1 - \alpha r_2)\right]} \Rightarrow \frac{d \alpha}{d t} = \frac{DC_1}{r_2^2 \rho_A} \left(z \alpha\right)^{-1}$$

$$f(\alpha) = (z \alpha)^{-1}$$

2D:

$$N(r_2) = -D \frac{C_1}{r_2 \ln \left(r_1 / r_2\right)} \Rightarrow \frac{r_2 \rho_A}{2} \frac{d \alpha}{d t} = -D \frac{C_1}{r_2 \ln \left(1 - z \alpha \right)^{1/2}}$$

$$\Rightarrow \frac{d \alpha}{d t} = \frac{2DC_1}{r_2^2 \rho_A} \left[- \ln \left(1 - z \alpha \right)^{1/2}\right]^{-1}$$

$$f(\alpha) = \left[- \ln \left(1 - z \alpha \right)^{1/2}\right]^{-1}$$

3D:

$$N(r_2) = -D \frac{C_1 r_1}{r_2 (r_1 - r_2)} \Rightarrow \frac{r_2 \rho_A}{3} \frac{d \alpha}{d t} = D \frac{C_1 (1 - z \alpha)^{1/2}}{r_2 \left[1 - (1 - z \alpha)^{1/2}\right]}$$

$$\Rightarrow \frac{d \alpha}{d t} = \frac{3DC_1}{r_2^2 \rho_A} \left[(1 - z \alpha)^{1/2} - 1\right]^{-1}$$

$$f(\alpha) = \left[(1 - z \alpha)^{1/2} - 1\right]^{-1}$$

The latter two forms of $f(\alpha)$ above, provided $z = 1$, are labelled the Valensi and Ginstling–Brounshtein diffusion equations respectively after those who first derived them (Khawam and Flanagan, 2006, Vlaev et al., 2008). Critically, ignoring the possibility that $aM_A / \rho_A \neq pM_p / \rho_p$ has the implication that the product layer grows inwards from a fixed outer surface position and 100% conversion corresponds to the product layer reaching the centre. Christie et al. (1978) proposed a modified version of the Ginstling–Brounshtein equation that takes into account a difference in molar volume in a different
manner to that presented above, although a rigorous theoretical development is not shown (Christie et al., 1978). Provided the product is denser than the reactant ($z < 1$) Equation A2-70 to Equation A2-72 can suffice and $r_1$ will be somewhat greater than zero at complete conversion. Of course, if the product is not as dense, then $r_2$ will be forced to increase with time once the available space has been filled within the particles. Furthermore, this theoretical construction implies that the same forms of $f(\alpha)$ will arise if the diffusion of a product gas limits the rate. If that is the case, Equation A2-69 will simply need the reactant stoichiometric coefficient and molar volume to be interchanged with those of the product gas ($z$ unchanged). The assumptions of constant internal concentration ($C_1$) and density seem much less applicable to a product gas, however.

A common diffusion model that was discredited more than 60 years ago still appears in the literature. Jander derived a three-dimensional diffusion model in 1927, but made the gross simplification of substituting Equation A2-69 into Equation A2-61 instead of Equation A2-63. Ginstling–Brounshtein corrected this theoretical flaw in 1950. However, almost universally, the three-dimensional Jander equation is presented as the primary model for spherical diffusion (Khawam and Flanagan, 2006, Sarker et al., 2006, Min et al., 2007), whereas the Ginstling–Brounshtein equation is often not associated with any geometry or, in one example, is actually mislabelled as applying to cylindrical symmetry (Vlaev et al., 2008). This deficiency cannot be excused as the Jander description differs markedly from the correct theory (Mamleev et al., 2000a, Khawam and Flanagan, 2006, Michèle et al., 2011) and the kinetic problem is too ill-defined to accommodate even small theoretical errors. It has been recommended not to apply the Jander equation to conversions greater than 15% (Christie et al., 1978), but given the existence of a superior, equally useable replacement, it is hard to understand why it should be included in the listing of diffusion models at all. Realistically the Jander equation has no corresponding physical significance. The Jander equation’s persistence in the literature is facilitated by the fact that even when an article acknowledges its theoretical inadequacy, its suitability as a model to describe experimental data is often still tested. It is also interesting to note that the popularised two-dimensional model is that of Valensi (Equation A2-71), not the cylindrical model that can be derived using Jander’s approach. This peculiarity certainly does not reflect well on the consistency of the literature. Even articles written by one of the most prolific and well-regarded authors within the field of kinetic analysis, Sergey Vyazovkin, presents only one unlabelled equation for three-dimensional diffusion, which is the Jander equation (e.g. (Vyazovkin et al., 2011)).

Modified versions of Jander’s three-dimensional model have not gained the same popularity as the Jander equation itself. For these, the diffusion rate “constant” is specified as proportional to the
remaining reactant or the inverse of time by Zhuravlev, Lesokhin and Templeman (Dickinson and Heal, 1999) and Kroger and Zeigler (Malecki and Doumerc, 1986) respectively, which gives rise to strongly deceleratory functions of conversion. Dickinson and Heal (1999) express some similar frustrations regarding the frequent errors that appear in the literature and attempt to show derivations from first principles of these alternate diffusion equations. Unfortunately they begin with the parabolic law of diffusion \( x^2 = kt \), not a mass balance, and therefore create the false impression that the Jander and related equations (including three original variants) are fundamentally valid. It is suspected that the origins of the Zhuravlev and Kroger equations are not appreciated in the relatively small number of articles in which they appear.

“Anti”-diffusion is mentioned in the literature (Dickinson and Heal, 1999, Vlaev et al., 2008, Li, D. et al., 2012) and describes the outward growth of the diffusion-limiting product layer from \( r_1 \). The continuous phase surrounding the particles must necessarily be diffusing to the inner boundary, just as the dispersed phase must be diffusing to the outer surface of the particles in the standard diffusion case described previously. Realistically, as diffusion is towards the centre of the particles, it is very unlikely that this process relates to a product gas. For anti-diffusion, Equation A2-65 is replaced by:

\[
\alpha = \frac{1}{z} \left[ \left( \frac{r_1 + x}{r_1} \right)^{\frac{1}{z}} - 1 \right] \quad \text{A2-73}
\]

\[
\therefore \quad x = r_1 \left( (1 + z \alpha)^{\frac{1}{z}} - 1 \right); \quad 0 \leq x \leq r_1 \left( (1 + z)^{\frac{1}{z}} - 1 \right) \quad \text{A2-74}
\]

and also
\[
r_2 = r_1 \left( 1 + z \alpha \right)^{\frac{1}{z}} \quad \text{A2-75}
\]

Provided the mass flux is evaluated at the stationary inner boundary and the sign reversed to account for the change in direction, and the concentration boundary conditions are interchanged, the anti-diffusion equations become:

1D: \( f(\alpha) = (z \alpha)^{\frac{1}{z}} \) \quad \text{A2-76}

2D: \( f(\alpha) = \left[ \ln(1 + z \alpha)^{\frac{1}{z}} \right]^{-1} \) \quad \text{A2-77}

3D: \( f(\alpha) = \left[ 1 - \left( 1 + z \alpha \right)^{\frac{1}{z}} \right]^{-1} \) \quad \text{A2-78}
Note that Vlaev et al. (2008) apparently neglect to reverse the sign for the three-dimensional case; the implied negative values for \( f(\alpha) \) are nonsensical.

Two more reasonable permutations that have not been cited in the literature involve the additional complexity of evaluating the mass flux at the moving boundary. Physically, for either standard or anti-diffusion, this would mean that the product is deposited such that the reaction interface grows into the stationary reactant. It is easily shown that in this case the mass flux at the active boundary (Equation A2-68) is equal to:

\[
N(r_z) = \frac{a M_d P r_z z}{\lambda^2 p M_p} \left( \lambda + z \alpha \right) (1 + z \alpha)^{\frac{1-2\lambda}{\lambda}} \frac{d\alpha}{dt} \quad \text{for diffusion of dispersed phase} \tag{A2-79}
\]

Therefore by substituting Equation A2-79 into Equation A2-61, Equation A2-62 and Equation A2-63 respectively:

1D: \[ f(\alpha) = (z\alpha)^{-1} \tag{A2-80} \]

2D: \[ f(\alpha) = \left[ -\ln(1-z\alpha)^{\frac{1}{2}} (2 + z\alpha)(1 + z\alpha)^{-\frac{1}{2}} \right]^{-1} \tag{A2-81} \]

3D: \[ f(\alpha) = \left[ \left( (1-z\alpha)^{-\frac{1}{3}} - 1 \right) (3 + z\alpha)(1 + z\alpha)^{-\frac{2}{3}} \right]^{-1} \tag{A2-82} \]

And similarly:

\[
N(r_z) = \frac{-a M_d P r_z z}{\lambda^2 p M_p} (\lambda - z \alpha)(1 - z \alpha)^{\frac{1-2\lambda}{\lambda}} \frac{d\alpha}{dt} \quad \text{for diffusion of continuous phase} \tag{A2-83}
\]

\[
\Rightarrow \quad 1D: \quad f(\alpha) = (z\alpha)^{-1} \tag{A2-84} \\
2D: \quad f(\alpha) = \left[ \ln(1 + z\alpha)^{\frac{1}{2}} (2 - z\alpha)(1 - z\alpha)^{-\frac{1}{2}} \right]^{-1} \tag{A2-85} \\
3D: \quad f(\alpha) = \left[ \left( 1 - (1+z\alpha)^{-\frac{1}{3}} \right) (3 - z\alpha)(1 - z\alpha)^{-\frac{2}{3}} \right]^{-1} \tag{A2-86} 
\]

If \( \lambda = 1 \) (linear diffusion), then \( f(\alpha) \) does not change regardless of the conceptual model. Figure A2-3 shows that if the physical scenario abides by this alternative description \( (z = 1) \), a marked decrease in the reaction rate for all two- and three-dimensional diffusion controlled processes would be expected.
Moreover, the legitimacy of claiming the differentiation of one-, two- and three-dimensional diffusion controlled processes is even more questionable with the addition of this alternate theory.

Figure A2-3: All discussed functions of conversion for diffusion, including those that relate to diffusion to a moving interface (marked with an apostrophe)

Finally, it is worth pointing out that all the diffusion equations presented are specific to the situation where there exists growing diffusive resistance from a product layer. These models do not appear to allow for diffusion through inert material or a depleting reactant.

**A2.8 Concluding Remarks**

Conversion is an indiscriminate measure of change in a condensed-phase material. As a consequence, the parameters and form of the necessarily separable rate equation (i.e. \( \frac{d\alpha}{dT} = k(T)f(\alpha) \)) are also indiscriminate. The Arrhenius parameters derived here are either composed of inseparable constants resulting from a complex theoretical development (Pn, An, L, Dn and Dn*), or are more probabilistic and global in nature (P-T, Rn and Fn). Arriving at a simple separable equation in each case does seem to be of paramount concern. The purpose of retaining a high level of complexity at intermediate stages of the derivation is undermined by making convenient simplifications.
All nucleation and nucleus growth theories demonstrate inadequacies near $t = 0$. Jacobs (1997) suggests that the rate constant at very low conversion may be fundamentally identical to that for the majority of the conversion, but is altered by the actual shape of these very small nuclei, with the effect of dilating the induction period. This is not verified physically but does match indirect experimental observation well (Jacobs, 1997). Specifying the transition point to either a power law, Avrami-Erofe’ev or Prout-Tompkins kinetics will always be somewhat ambiguous.

The family of nucleation and growth mechanisms and those describing contracting volume are derived specifically for isothermal conditions as the mechanism arrived at is $g(\alpha) = kt; f(\alpha)$ is determined from Equation 3-7 and is assumed transferable to non-isothermal analyses. All other derivations evaluate $f(\alpha)$ directly. Random scission and diffusion derivations require steady-state assumptions to be made regarding the radical concentration/number and reactant concentration gradient respectively. In the case of random scission, steady-state is clearly impossible at the start and end of reaction, whereas it is conceivable that the concentration gradient may not change over the entire course of the decomposition if Fick’s Law remains applicable and the core concentration of reactant is fixed. Reaction order mechanisms are by far the simplest conceptually and therefore the most likely to precisely fit real decomposition curves should they be active.

Geometry, number of nuclei etc. are idealised and considered unchanging. At the least, imperfect/distributed or tortuous growth/contraction in one, two or three dimensions would give rise to non-integer orders. The simple theoretical basis used to arrive at the equations for contracting volume, for example, is ultimately very prescriptive. Gradual transitions from one order to another would also be difficult to detect.

While these derivations account for all known functions of conversion, they do not appear to be exhaustive in terms of physical possibilities. It should be feasible to derive entirely new mechanisms based on theoretical hypotheses or independent experimental observations and test their validity. Future developments should be more oriented towards accuracy rather than computational simplicity. More accurate equations may already be available in obscure references, such as the generalised Avrami equation valid not just for $k,t << 1$ that was labelled as too inconvenient to use at the time (Allnatt and Jacobs, 1968).
A3 Temperature Correction Equation Derivations

A3.1 Sample Centreline Temperature from Surface Temperature

Consider a radial energy balance over a cylindrical shell of thickness $\Delta r$, length $L$, inner surface area $A = 2\pi r L$ and volume $V_{\Delta r}$:

$$\rho V_{\Delta r} C_p \frac{\partial T}{\partial t} = \dot{q} \bigg|_r - \dot{q} \bigg|_{r+\Delta r} - \rho V_{\Delta r} \frac{\partial \alpha}{\partial t} \Delta H_R$$  \hspace{1cm} A2-87

where $\dot{q} = -k_c A \frac{\partial T}{\partial r}$

$$\therefore \quad \rho V_{\Delta r} C_p \frac{\partial T}{\partial t} = -k_c 2\pi r L \frac{\partial T}{\partial r} \bigg|_r + k_c 2\pi (r + \Delta r) L \frac{\partial T}{\partial r} \bigg|_{r+\Delta r} - \rho V_{\Delta r} \frac{\partial \alpha}{\partial t} \Delta H_R$$  \hspace{1cm} A2-88

Now, $V_{\Delta r} = \pi (r + \Delta r)^2 L - \pi r^2 L \approx 2\pi r \Delta r L$. Divide Equation A2-88 by $2\pi \Delta r L = \frac{V_{\Delta r}}{r}$:

$$\rho r C_p \frac{\partial T}{\partial t} = -k_c r \frac{\partial T}{\partial r} \bigg|_r + k_c (r + \Delta r) \frac{\partial T}{\partial r} \bigg|_{r+\Delta r} - \rho r \frac{\partial \alpha}{\partial t} \Delta H_R$$  \hspace{1cm} A2-89

Take the limit as $\Delta r \to 0$:

$$\rho r C_p \frac{\partial T}{\partial t} = k_c \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) - \rho r \frac{\partial \alpha}{\partial t} \Delta H_R$$

Rearrange to

$$\frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) = \frac{\rho r}{k_c} \left( C_p \frac{\partial T}{\partial t} + \frac{\partial \alpha}{\partial t} \Delta H_R \right)$$  \hspace{1cm} A2-90

Simplify partial time differentials to constant rates derived from measured data:

$$\Rightarrow \quad \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) \approx \frac{\rho r}{k_c} \left( C_p \frac{\Delta T_m}{\Delta t} + \frac{\Delta \alpha}{\Delta t} \Delta H_R \right)$$

$$\therefore \quad r \frac{\partial T}{\partial r} \approx \frac{\rho r^2}{2k_c} \left( C_p \frac{\Delta T_m}{\Delta t} + \frac{\Delta \alpha}{\Delta t} \Delta H_R \right) + C; \ C = \text{integration constant}$$
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\[
\frac{\partial T}{\partial r} \approx \frac{\rho r}{2k} \left( C_p \frac{\Delta T_m}{\Delta t} + \frac{\Delta \alpha}{\Delta t} \Delta H_R \right) + \frac{C}{r}
\]

\[
T(r) \approx \frac{\rho r^2}{4k} \left( C_p \frac{\Delta T_m}{\Delta t} + \frac{\Delta \alpha}{\Delta t} \Delta H_R \right) + C \ln r + D; \quad D = \text{integration constant}
\]

A2-91

Since \( T(0) \) is finite, \( C = 0 \). At the sample surface boundary, Equation A2-91 becomes:

\[
T(R) \approx \frac{\rho R^2}{4k} \left( C_p \frac{\Delta T_m}{\Delta t} + \frac{\Delta \alpha}{\Delta t} \Delta H_R \right) + D
\]

\[
\Rightarrow \quad D \approx T(R) - \frac{\rho R^2}{4k} \left( C_p \frac{\Delta T_m}{\Delta t} + \frac{\Delta \alpha}{\Delta t} \Delta H_R \right)
\]

A2-92

Therefore, at the centreline:

\[
T(0) \approx T(R) - \frac{\rho R^2}{4k} \left( C_p \frac{\Delta T_m}{\Delta t} + \frac{\Delta \alpha}{\Delta t} \Delta H_R \right)
\]

A2-93

To accommodate multiple reactions in a homogenous sample, Equation A2-93 can be rewritten as:

\[
T(0) \approx T(R) - \frac{\rho R^2}{4k} \left( C_p \frac{\Delta T_m}{\Delta t} + \sum_{p=1}^{P} \frac{\Delta \alpha_{R,p}}{\Delta t} \frac{x_p (m_{e_p} - m_{e_p})}{m_0} \right)
\]

A2-94

where \( T_m(t) = T_m(t_0) + \frac{T_m(t_i) - T_m(t_0)}{t_i - t_0} (t - t_0) = T_m(t_0) + \frac{\Delta T_m}{\Delta t} (t - t_0) \) for \( T_m = T(R) \)

A2-95

Substituting Equation A2-95 into Equation A2-94 gives the final result for \( T = T(0) \):

\[
T(t) \approx T_m(t_0) + \left( t - t_0 \right) - \frac{C_p \rho R^2}{4k} \frac{\Delta T_m}{\Delta t} - \frac{(m_{e_p} - m_{e_p}) \rho R^2}{4k m_0} \sum_{p=1}^{P} \Delta H_{R,p} x_p \frac{\Delta \alpha_{R,p}}{\Delta t}
\]

A2-96

A3.2 Bulk Sample Temperature from Furnace Temperature

Consider energy accumulating in the diminishing sample from external heat flux, neglecting any effects of the crucible. Furnace wall and atmosphere are assumed to be at the same temperature, i.e. that measured by the thermocouple:
\[ \bar{m}_i C_p \frac{dT}{dt} = hA(T_m - T) + \sigma \varepsilon A(T_m^4 - T^4) - \sum_{p=1}^{P} \frac{d\alpha_p}{dt} \Delta H_{R,p} \frac{x_p (m_0 - m_{\infty})}{m_0} \bar{m}_i \] \hspace{1cm} A2-97

The subscript \( i \) corresponds to row number and thus indicates a signal. Temperature and conversion are known as signals and the subscripts are omitted for clarity. Linearise radiation term:

\[ \sigma \varepsilon A(T_m^4 - T^4) \approx \sigma \varepsilon A(T_{m,ss}^4 - T_{ss}^4) + 4\sigma \varepsilon A\left[T_{m,ss}^3 (T_m - T_{m,ss}) - T_{ss}^3 (T - T_{ss})\right] \] \hspace{1cm} A2-98

Now, define steady-state temperature \( T_{m,ss} = T_{ss} \) as the measured temperature at the end of the \( i \)th time step, \( T_m(t_i) \).

\[ \therefore \sigma \varepsilon A(T_m^4 - T^4) \approx 4\sigma \varepsilon A\left[T_m(t_i)\right]^3 (T_m - T) \] \hspace{1cm} A2-99

Therefore Equation A2-97 can be rewritten as:

\[ \bar{m}_i C_p \frac{dT}{dt} \approx \left[h + 4\sigma \varepsilon \left[T_m(t_i)\right]^3 \right] A(T_m - T) - \sum_{p=1}^{P} \frac{d\alpha_p}{dt} \Delta H_{R,p} \frac{x_p (m_0 - m_{\infty})}{m_0} \bar{m}_i \] \hspace{1cm} A2-100

In the case of axial heat transfer only:

\[ \bar{m}_i C_p \frac{dT}{dt} \approx \left[h + 4\sigma \varepsilon \left[T_m(t_i)\right]^3 \right] \pi R^2 (T_m - T) - \sum_{p=1}^{P} \frac{d\alpha_p}{dt} \Delta H_{R,p} \frac{x_p (m_0 - m_{\infty})}{m_0} \bar{m}_i \] \hspace{1cm} A2-101

In the case of radial heat transfer only, \( A_i = 2\pi R_0 L_i \) and must be considered a signal. If density remains constant then sample depth is:

\[ L_i = \frac{\bar{m}_i}{\pi \rho R^2} \quad \Rightarrow \quad A_i = \frac{2\bar{m}_i R_0}{\rho R^2} \]

\[ \therefore \bar{m}_i C_p \frac{dT}{dt} \approx \left[h + 4\sigma \varepsilon \left[T_m(t_i)\right]^3 \right] \frac{2\bar{m}_i R_0}{\rho R^2} (T_m - T) - \sum_{p=1}^{P} \frac{d\alpha_p}{dt} \Delta H_{R,p} \frac{x_p (m_0 - m_{\infty})}{m_0} \bar{m}_i \] \hspace{1cm} A2-102

Both Equation A2-101 and Equation A2-102 can be generalised as:
\[
\tau \frac{dT}{dt} \approx (T_m - T) - \sum_{p=1}^{P} K_p \frac{d\alpha_p}{dt}, \quad \text{where} \quad \tau = \frac{\bar{m} C_p}{[h + 4\sigma \varepsilon T_m(t_i)] A} \\
\text{and} \quad K_p = \frac{\Delta H_{p,p} \alpha_p (m_0 - m_n) \bar{m}_i}{[h + 4\sigma \varepsilon T_m(t_i)] A m_0}
\]

Equation A2-103 is linear provided all terms in \( \tau \) and \( K_p \) are constant. Transform to the Laplace domain:

\[
\tau (sT(s) - T(t_0)) = T_m(s) - T(s) - \sum_{p=1}^{P} K_p \left( s \alpha_p(s) - \alpha_p(t_0) \right)
\Rightarrow
T(s) \approx \frac{T_m(s)}{s \tau + 1} + \frac{T(t_0)}{s \tau + 1} - \sum_{p=1}^{P} \frac{K_p}{s \tau + 1} \left( s \alpha_p(s) - \alpha_p(t_0) \right)
\]

Now, considering Equation A2-95, the measured signals transform to:

\[
T_m(s) = \frac{T_m(t_0)}{s} + \frac{\Delta T_m}{\Delta t} \frac{1}{s^2} = \frac{1}{s} \left( T_m(t_0) + \frac{\Delta T_m}{\Delta t} \frac{1}{s} \right)
\]

and similarly,

\[
\alpha_p(s) = \frac{1}{s} \left( \alpha_p(t_0) + \frac{\Delta \alpha_p}{\Delta t} \frac{1}{s} \right)
\]

Substituting Equation A2-105 and Equation A2-106 into Equation A2-104:

\[
T(s) = \frac{T_m(t_0)}{s \tau + 1} + \frac{\Delta T_m}{\Delta t} \frac{1}{s^2 \tau + 1} + \frac{T(t_0)}{s \tau + 1} - \sum_{p=1}^{P} \frac{K_p}{s \tau + 1} \frac{\Delta \alpha_p}{\Delta t} \frac{1}{s}
\Rightarrow
T(s) = \frac{T_m(t_0)}{s \tau + 1} + \frac{\Delta T_m}{\Delta t} \left( \frac{1}{s^2} - \frac{\tau}{s \tau + 1} \right) + \frac{T(t_0)}{s \tau + 1} - \sum_{p=1}^{P} \frac{K_p}{s \tau + 1} \frac{\Delta \alpha_p}{\Delta t} \frac{1}{s}
\]

Inverting to the time domain:

\[
T(t) = T_m(t_0) \left( 1 - e^{-\Delta t(t_0) \tau} \right) + \frac{\Delta T_m}{\Delta t} (t - t_0) - \frac{\Delta T_m}{\Delta t} \left( 1 - e^{-\Delta t(t_0) \tau} \right) + T(t_0) e^{-\Delta t(t_0) \tau} - \sum_{p=1}^{P} K_p \frac{\Delta \alpha_p}{\Delta t} \left( 1 - e^{-\Delta t(t_0) \tau} \right)
\]

i.e.

\[
T(t) = \frac{\Delta T_m}{\Delta t} (t - t_0) + \left( T_m(t_0) - \frac{\Delta T_m}{\Delta t} - \sum_{p=1}^{P} K_p \frac{\Delta \alpha_p}{\Delta t} \right) \left( 1 - e^{-\Delta t(t_0) \tau} \right) + T(t_0) e^{-\Delta t(t_0) \tau}
\]
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A4 Setaram Labsys TG-DTA/DSC Calibration

This appendix describes and evaluates the calibrations for the two 1600°C probes used in the Labsys.

A comprehensive set of data for the metals in Table A2-1 was collected with the first probe under 33 mL/min nitrogen at 2, 10 and 20°C/min (Figure A2-4 and Figure A2-5). The same metal samples were repeatedly melted and resolidified and ranged in weight from 13.7 mg (In) to 62.3 mg (Zn). The prime reference for weight was an external electronic balance that displayed weight in grams to four decimal places. Melting onset temperatures and heat flow peak integrations (area in μV.s; linear baselines) were estimated using Setaram’s Setsoft software. Only the silver standard was not properly evaluated as three repeats at 20°C/min confirmed that its integrated and normalised heat flow signal inexplicably opposed the downward trend in sensitivity (two repeats coincided at $K_{Ag,20} = 212 \mu V/W$ cf. Figure A2-5). Omitting silver from the calibration was justified by the lower degradation temperature range of the FR system. Any integration that appeared unreliable was repeated. Onset temperatures were found to agree to one decimal place for the two repeats at 20°C/min for indium and tin and the three repeats at 10°C/min for lead. The only discrepancy in onset temperature (0.7°C) was recorded for zinc at 2°C/min.

Table A2-1: Relevant thermal properties of the metal standards supplied with the Labsys (Setaram, 2004)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Melting Point (°C)</th>
<th>Heat of Fusion (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indium</td>
<td>156.598</td>
<td>28.51 ± 0.19</td>
</tr>
<tr>
<td>Tin</td>
<td>231.94</td>
<td>60.21 ± 0.19</td>
</tr>
<tr>
<td>Lead</td>
<td>327.47</td>
<td>23.00 ± 0.06</td>
</tr>
<tr>
<td>Zinc</td>
<td>419.56</td>
<td>107.4 ± 1.3</td>
</tr>
<tr>
<td>Aluminium</td>
<td>660.33</td>
<td>401.3 ± 1.6</td>
</tr>
<tr>
<td>Silver</td>
<td>961.780</td>
<td>104.8*</td>
</tr>
</tbody>
</table>

* Uncertainty not reported

As onset temperatures were collected for a sufficient number of metals and heating rates, thermal lag from the sample to the measurement thermocouple fixed to the underside of the crucible support plate was fitted to a two-dimensional function of measured temperature and heating rate (Setaram, 2004):

$$T_v - T_{mv} = B_0 + B_1 T_{mv} + B_2 \beta_v$$

Equation 2-1 with these coefficients was used to transform all temperature data subsequently acquired with the Labsys (excepting later calibration data).
The nuances of the data were obviously not well represented by the two-dimensional linear regression (Figure A2-4). Increasing the heating rate translated but also skewed the thermal lag to lower values. A distinct upward trend in thermal lag with temperature, peaking at lead, followed by a downward trend was consistent across the three heating rates, even at 2°C/min where the uncertainty in measured temperature was presumed greater. The only other regression equation supported by the software appends Equation 2-1 with a term proportional to the square of the heating rate, not measured temperature as the data would suggest, and was deemed unsuitable. Note that the thermal lag represented in Figure A2-4 only ranged from -0.47 to 5.07°C; while the regression was a poor fit, it would not have altered the measured thermal lag of any metal by more than 1.4°C. Moreover, in all cases the regression matched the melting points in Table A2-1 better than if no temperature correction was applied; except for aluminium at 20°C/min (well above the decomposition range of the FR system).
The Labsys manual implies that thermal lag should be independent of the probe and therefore the same temperature correction should have been valid for the second probe, provided the crucible type and the nature and flow rate of the gas were not changed. Transducer sensitivity is stated to be a function of the probe as well as sample shape and mass, but not heating rate (Setaram, 2004). The second probe was therefore commissioned with a sensitivity calibration and validation of the temperature correction under 33 mL/min nitrogen for all five metals at 20°C/min, tin also at 10°C/min and indium at all three heating rates (Figure A2-5). Sample weights were kept more consistent (46.8 – 61.8 mg), although it was demonstrated that neither onset temperature nor sensitivity differed significantly for indium of weights 13.6 mg and 49.6 mg. Another sensitivity calibration was carried out eight months later with the same probe under 100 mL/min nitrogen, where each metal standard (47.1 – 61.8 mg) was melted at 10°C/min in duplicate (except zinc where greater variability encouraged a third replication) (Figure A2-5).

Figure A2-5: Calculated transducer sensitivity for the first five metal standards listed in Table A2-1 and the regressions applied as calibrations (solid lines). Error bars combine the 0.5 mg uncertainty in sample weight with the uncertainties reported in Table A2-1. Alumina crucibles of 110 μL were used for all calibrations.

The close match of the dotted black linear trendline to the solid dark purple linear trendline in Figure A2-5 implies a trivial dependence of the sensitivity calibration on gas flow rate and age of the probe, relative to the residual errors. The anticipated lack of response of the differential scanning calorimetric signal to deliberate fluctuations in regulator pressure (i.e. flow rate) was verified in situ. Calibration constants were selected from a quadratic regression for the second probe under 100 mL/min nitrogen
due to an appreciable reduction in the residual sum of squares. The manual states that the sensitivity calibration should be fitted to a quartic polynomial (Setaram, 2004); however, doing so for any of the data sets in Figure A2-5 led to patently ridiculous results.

Systematic increases in the measured melting onset temperatures (i.e. reduced thermal lag) with the second probe under both 33 mL/min and 100 mL/min nitrogen (perceptible in Figure A2-5) effectively invalidated the previous temperature correction. Statistically insignificant differences in thermal lag were observed between the two flow rates for the second probe and hence all results are plotted together in Figure A2-6. At 20ºC/min, the measured onset temperature for aluminium differed by +9.5ºC from that recorded with the first probe, whereas the other metals exhibited more modest increases of 2.1 – 3.2ºC. These examples represent the greatest discrepancies; the overall trend of thermal lag with heating rate retained approximately the same slope. Thermal lags were distributed above and below zero (no temperature correction) and not the regression plane of Equation 2-1 (Figure A2-6). All calibrations raised doubts about the reliability of quantitative high temperature data.

Figure A2-6: Thermal lag for probe #2 under 33 or 100 mL/min N₂. Metal standards and heating rates were identical to those shown in Figure A2-4. All data at 10ºC/min correspond to 100 mL/min N₂ except the two points for In and Sn of greatest thermal lag. Planes representing the previous regression (Figure A2-4) and zero thermal lag are shown.
A5 Method Adaptation in VBA

In the interests of completeness, the algorithm realising the new kinetic analysis method as it appears in the Visual Basic for Applications editor is presented in this appendix prefaced by instructions for the user to follow. Minimal error handling for inappropriate user input was written into the code as it was intended for private use only. In contrast, substantial effort was made to improve the ability of the algorithm to cope with poor data and the often unforeseen ways in which errors arose and propagated.

A5.1 Preparation Instructions

The steps listed here should result in the delivery of a kinetic solution with complete sets of statistics to describe an input of three or more sets of TG data:

1. Open an Excel workbook containing raw TG data
2. Copy and paste/organise all TG data sets for the same sample material into separate spreadsheets in this workbook
3. Ensure that:
   a. Each sheet of TG data has time, temperature and weight signals
   b. These signals are assigned the same columns in every sheet (e.g. Column A for time, Column B for temperature etc.)
   c. The data set begins at the same row in every sheet. Leave at least $2 + 3 \times \text{HighProcess}$ rows above the start of data
   d. Time is in mins, temperature is in °C, weight is in mg
   e. The data sheets are consecutive and there are no sheets to their left (unless the sheet is named “Summary”)
4. Open a workbook that contains all subroutines listed in Section A5.2
5. Open the Visual Basic Editor via the “Tools” drop-down menu (or from the “View” tab in Excel 2007/2010)
6. Expand the “Modules” folder associated with the workbook containing the subroutines in the top left window of the Editor
7. Copy all four modules to the new workbook by dragging and dropping each module from the “Modules” folder to the area directly below the “VBAPerent (.xls)” heading
8. Close the workbook from which the modules were copied
9. Double click on “Module31” (the third module) in the Visual Basic Editor
10. Scroll up to the top of the main window
11. Indicate which columns the time, temperature and weight data appear on each sheet (A = 1, B = 2 etc.) by setting the constants `Time`, `Temp` and `Weight` accordingly.
12. Set `MaxSheets` to the maximum number of data sheets in the workbook.
13. Set `MaxData` to the maximum number of rows in any one data sheet.
14. Set `RowOffset` to the row number where the data starts.
15. Set `ColOffset` to the column number that will define the left-most column in which data shall be written by the subroutines. Ensure no critical information appears to the right of this column as it will be overwritten.
16. Set `UserInputRow` to the row number where the heating rate will be entered. This must be above row `RowOffset`, and preferably the first row.
17. Set `UserInputCol` to the column number where the onset temperature(s) will be entered.
18. Set `AETableRow` to the row number that will define the top of the table of apparent Arrhenius parameters. This also must be above row `RowOffset`.
19. Set `AETableCol` to the column number that will define the left-hand side of the table of apparent Arrhenius parameters.
20. Determine how many independent decomposition processes are implied by the data (refer to the weight loss/derivative weight loss curve). This number will need to apply to all data sheets. Set `HighProcess` to match this number.
21. Set `HighMech` to the match the number of different mechanisms that will be considered for the analysis. The mechanisms can be changed within the subroutines “SetUp()” and “MechAssignment()” at the points indicated in the code. Alterations may necessitate changes to the constants `FirstOrder` and `ProutTompkins`.
22. To exclude the random scission mechanism with variable $L$, set $Scission = 0$. Even if this mechanism is excluded, the same locally-initialised constant at the beginning of the subroutine “ModelFitting()” must be set to its mechanism number ($Scission = 17$ as default).
23. Set `XPrecision` to the conversion resolution desired.
24. Set `Sig` to a conversion value deemed significant that will determine if processes overlap.
25. Set `Estep` to the largest step size to be used to increment activation energy for the optimisation in “ModelFitting()”.
26. Set `FilterN` to the length of the Savitzky-Golay filter used for differentiation.
27. Set physical constants $Cp$ (sample heat capacity; J/molK), $epsilon$ (emissivity), $h$ (heat transfer coefficient; W/m²K), $Ri$ (inside crucible radius; mm), $Ro$ (outside crucible radius; mm), $rho$ (sample density; kg/m³) and $Conduct$ (sample thermal conductivity; W/mK) if temperature lag is to be computed.
28. Set Reaction1, Reaction2 etc. to the heat of reaction(s) (kJ/kg) of the decomposing substance(s). A positive value indicates an endothermic process.

29. Set IsoconvMax to the maximum overall conversion to be used for the Friedman analysis, and NoPoints to the number of data points to be computed between zero and IsoconvMax.

30. Set LowerCompLimit1, LowerCompLimit2 etc. to the desired lower limit of calculation in terms of degree of conversion for each process.

31. Set UpperCompLimit1, UpperCompLimit2 etc. to the desired upper limit of calculation in terms of degree of conversion for each process.

32. In the subroutine “CompRequirements()”, ensure that HighProcess set(s) of Reaction, LowerCompLimit and UpperCompLimit is/are active by commenting lines of code as necessary.

33. Select the first sheet of data. Enter the heating rate applicable to that data sheet in °C/min in the cell denoted by [UserInputRow, UserInputCol + 1].

34. Define onset temperature ($T_i$) and completion temperature ($T_f$) for each decomposition process in cells [UserInputRow + Process, UserInputCol] and [UserInputRow + Process, UserInputCol + 2] respectively. E.g. If Process 1 is active between 150°C and 250°C and the heating rate is entered into cell D1, type 150 in cell C2 and 250 in cell E2.

35. If the baseline for weight is to be computed from a temperature higher than that at the start of data, enter this temperature in cell [UserInputRow + 1, UserInputCol – 1].

36. Repeat steps 33 to 35 for each sheet of data. Enter the information into the same rows and columns as for the first sheet. Save the file.

37. Select a cell in each spreadsheet (If a chart is selected, the code will generate a runtime error).

38. If required, reduce the data sets so they each take up a manageable number of rows. Do this by selecting the appropriate data sheet and calling the subroutine “Reduce()” (Ctrl + r) and typing the desired factor of reduction into the pop-up window. If unsure, skip this step.

39. Run subroutine “ModelFree()” (Ctrl + w).

40. Inspect the results of the IKP and Friedman analyses. If the results are acceptable, run subroutine “ModelFitting()” (Ctrl + p). If they are not, change aspects of the input and re-run “ModelFree()” until satisfied enough to run “ModelFitting()”.

41. If deemed of interest, plot conversion and conversion rate predictions for different data sheets by running subroutine “SolutionGraph()” (Ctrl + j).

42. If deemed of interest, plot the linear regressions used to generate the apparent kinetic parameters and IKP by running subroutines “ApparentGraph()” (Ctrl + g; relevant data sheet must be active) and “CEGraph()” (Ctrl + h).

43. For multiple overlapping processes, repeat steps 39 to 42 until the solution converges.
A5.2 Visual Basic Code

This reproduction of the code used for validation with water includes all subroutines and functions in the order in which they should be called. Optional subroutines and functions and those called from multiple locations are listed last. All comments are coloured purple, including temporarily disabled lines of code.

```vbnet
Public i As Integer
Public N As Integer
Public Q As Integer
Public TempRef As Integer
Public Repeat As Integer
Public WholeRange As Integer
Public Core As Integer
Public CalcTemp As Integer
Public Cylindrical As Integer
Public SampleT As Integer
Public Graph As Integer
Public dalphadt As Integer
Public Alpha As Integer
Public Const Time As Integer = 5
Public Const Temp As Integer = 1
Public Const Weight As Integer = 4
Public Const MaxSheets As Integer = 5
Public Const MaxData As Integer = 1500
Public Const RowOffset As Integer = 15
Public Const ColOffset As Integer = 8
Public Const UserInputRow As Integer = 1
Public Const UserInputCol As Integer = 3
Public Const AETableRow As Integer = 6
Public Const AETableCol As Integer = 4
Public Const FirstOrder As Integer = 9
Public Const ProutTompkins As Integer = 10
Public Const HighProcess As Integer = 1
Public Const HighMech As Integer = 22
Public Const Scission As Integer = 17
Public Const XPrecision As Double = 0.000001
Public Const Sig As Double = 0.001
Public Const EStep As Double = 0.02
Public Const FilterN As Integer = 11
Public Const Cylindrical As Integer = 4.2
Public Const sigma As Double = 0.00000005669
Public Const epsilon As Double = 0.96
Public Const h As Double = 10
Public Const Ri As Double = 2.5
Public Const Ro As Double = 2.7
Public Const rho As Double = 950
Public Const Conduct As Double = 0.6
Public Const Reaction1 As Double = 2260
Public Const Reaction2 As Double = 150
Public Const Reaction3 As Double = 150
Public Const IsoconvMax As Double = 0.95
Public Const NoPoints As Integer = 20
Public Const LowerCompLimit1 As Double = 0.155
Public Const UpperCompLimit1 As Double = 0.24
Public Const LowerCompLimit2 As Double = 0.8
Public Const UpperCompLimit2 As Double = 0.9
Public Const LowerCompLimit3 As Double = 0.3
Public Const UpperCompLimit3 As Double = 0.7
Public CellHeight As Double
Public OverallNoise As Double
Public Noisemg As Double
Public StoredData As Boolean
Public Reaction(HighProcess - 1) As Double
Public LowerCompLimit(HighProcess - 1) As Double
Public UpperCompLimit(HighProcess - 1) As Double
Public InDataSet(HighProcess - 1, MaxSheets - 1) As Boolean
Public IKPEExist(HighProcess - 1) As Boolean
Public ExpBondFraction(HighProcess - 1, MaxSheets - 1, MaxData - 1) As Double
Public IsoconversionRow(NoPoints - 1, MaxSheets - 1) As Integer
Public SevereOverlap(MaxSheets - 1) As Boolean
```
Sub ModelFree()
' Shortcut: Ctrl + w
' Calls procedure(s) to calculate invariant kinetic parameters
' Calls procedure to calculate activation energy as a function of conversion
' as per the Friedman method
' Presents results on 'Summary' sheet

Dim Process As Integer
Dim Slope As Double
Dim Intercept As Double
Dim Einv(HighProcess - 1) As Double
Dim Ainv(HighProcess - 1) As Double
Dim X As Range
Dim Y As Range
Dim Chart As String
Dim No(HighProcess - 1) As Integer
Dim B As Double
Dim Continue As Boolean

Application.ScreenUpdating = False
SampleT = ColOffset + 2 + 2 * HighMech + 2 + HighMech + 1
Graph = SampleT + 2
dalphadt = Graph + HighProcess + 1
Alpha = dalphadt + HighProcess + 1

' Collection of user requirements for computations
Repeat = MsgBox("Do you want to use the current spreadsheet values for this iteration?", vbYesNo + vbQuestion + vbDefaultButton2, "Second or Greater Iteration")
If Repeat = vbYes Then
    TempRef = vbYes
Else
    N = InputBox("Enter the number of sheets of experimental data to use for kinetic analysis", "Number of Data Sets", MaxSheets)
    TempRef = MsgBox("Would you like to refine the user-defined onset and completion temperatures before analysis?", vbYesNo + vbQuestion, "Temperature Range Refinement")
End If
Q = MsgBox("Would you like to compute a new temperature signal?", vbYesNo + vbQuestion + vbDefaultButton2, "Temperature Lag")
If Q = vbYes Then
    Core = MsgBox("Estimate sample centreline temperature? & Chr(13) & "(If 'No', the lumped heat capacity assumption will be invoked for measured furnace temperature)", vbYesNo + vbQuestion, "Temperature Lag")
    If Core = vbYes Then
        Cylindrical = MsgBox("Assume radial heat transfer only? & Chr(13) & "(If 'No', heat transfer will be calculated through exposed surface only)", vbYesNo + vbQuestion, "Temperature Lag")
    End If
    CalcTemp = MsgBox("Would you like to use the calculated temperature as the sample temperature? & Chr(13) & "(If 'No', temperature data will not be altered)", vbYesNo + vbQuestion + vbDefaultButton2, "Temperature Lag")
End If

' Delete (1st iteration) or move and rename (2nd and subsequent iterations)
'Summary' sheet(s)

If WorksheetExists("Summary") = True Then
    Application.DisplayAlerts = False
    Continue = True
    i = 0
    Do
        If WorksheetExists("Summary(" & i & ")") = True Then
            If Repeat = vbYes Then
                Sheets("Summary(" & i & ")").Delete
            Else
                Continue = False
            End If
        End If
        i = i + 1
    Loop While Continue
If Repeat = vbYes Then
    Sheets("Summary").Select
    With ActiveSheet
        .Name = "Summary(" & i & ")"
    End With
End If
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```vba
.Move After:=Sheets(N + 1)
End With
Else
Sheets("Summary").Delete
End If
Application.DisplayAlerts = True
End If
Sheets.Add
ActiveSheet.Name = "Summary"
Sheets("Summary").Move Before:=Sheets(1)
ActiveSheet.Zoom = 75
CellHeight = ActiveSheet.Cells(1, 1).Height

' Labelling of compensation parameters, bv and cv
Cells(1, HighMech + 6).Select
With Selection
.FormulaR1C1 = "Compensation Parameters for Apparent Kinetic Parameters Copied Left"
.Font.Bold = True
End With
For Process = 1 To HighProcess
Cells(2, HighMech + 7 + 2 * (Process - 1)).Select
With Selection
.FormulaR1C1 = "bv" & Process
.Font.Bold = True
.HorizontalAlignment = xlCenter
End With
Cells(2, HighMech + 8 + 2 * (Process - 1)).Select
With Selection
.FormulaR1C1 = "cv" & Process
.Font.Bold = True
.HorizontalAlignment = xlCenter
End With
Next

' Runs SetUp() for all sheets on first iteration to prepare the experimental data,
' set mechanism orders and insert labels
' Runs Apparent() to generate apparent kinetic parameters and determine rows for
' isoconversional analysis
For i = 1 To N
Worksheets(i + 1).Select
LastRow = Cells(RowOffset, Time).End(xlDown).Row
If Repeat = vbYes Then
Else
Call SetUp
End If
Call Apparent

' Takes the results of Apparent() and copies them to 'Summary' sheet
B = Cells(UserInputRow, UserInputCol + 1)
Range(Cells(AETableRow, AETableCol - 1), Cells(AETableRow + 2 + 3 * (HighProcess - 1),
AETableCol + HighMech + 1)).Select
Selection.Copy
Sheets("Summary").Select
Cells(i + 3 * (i - 1) * HighProcess, 1).Select
ActiveSheet.Paste

' Labelling of heating rate, printing of XFractions and italicising computational
' temperature range on 'Summary' sheet
Cells(2 + i, HighMech + 6).Select
With Selection
.FormulaR1C1 = B & Chr(186) & "C/min"
.Font.Bold = True
.HorizontalAlignment = xlRight
End With
For Process = 1 To HighProcess
Cells(1 + 3 * (i - 1) * HighProcess + 1 + 3 * (Process - 1), HighMech + 4).Select
With Selection
.FormulaR1C1 = "X" & Process
.Font.Bold = True
.HorizontalAlignment = xlCenter
End With
Cells(1 + 3 * (i - 1) * HighProcess + 2 + 3 * (Process - 1), HighMech + 4).Select
With Selection
.FormulaR1C1 = Sheets(i + 1).Cells(LastRow + 4, Alpha + Process)
.HorizontalAlignment = xlLeft
```

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With Selection
    .FormulaR1C1 = "Ainv (min-1)"
    .Font.Bold = True
    .HorizontalAlignment = xlCenter
End With
ActiveCell.Characters(Start:=10, Length:=2).Font.Superscript = True
Cells(5 + N, HighMech + 10).Select
With Selection
    .FormulaR1C1 = Chr(177) & "95% CI (ln A)"
    .Font.Bold = True
    .HorizontalAlignment = xlCenter
End With
Columns(HighMech + 3).EntireColumn.AutoFit
Columns(HighMech + 7).EntireColumn.AutoFit
Columns(HighMech + 8).EntireColumn.AutoFit
Columns(HighMech + 9).EntireColumn.AutoFit
Columns(HighMech + 10).EntireColumn.AutoFit

' Graphical presentation of relationship between compensation parameters across all heating rates for each valid process
' If a process is deemed invalid, a warning message is displayed

For Process = 1 To HighProcess
    If IKPEXist(Process - 1) Then
        Set X = Range(Cells(3, HighMech + 7 + 2 * (Process - 1)), Cells(2 + N, HighMech + 7 + 2 * (Process - 1)))
        Set Y = Range(Cells(3, HighMech + 8 + 2 * (Process - 1)), Cells(2 + N, HighMech + 8 + 2 * (Process - 1)))
        Charts.Add
        ActiveChart.ChartType = xlXYScatter
        ActiveChart.SetSourceData Source:=Union(X, Y), PlotBy:=xlColumns
        ActiveChart.Location Where:=xlLocationAsObject, Name:="Summary"
        With ActiveChart
            .HasTitle = True
            .Axes(xlCategory, xlPrimary).HasTitle = True
            .Axes(xlValue, xlPrimary).HasTitle = True
        End With
        With ActiveChart.Axes(xlCategory)
            .HasMajorGridlines = False
            .HasMinorGridlines = False
        End With
        With ActiveChart.Axes(xlValue)
            .HasMajorGridlines = False
            .HasMinorGridlines = False
        End With
        Chart = Replace(ActiveChart.Name, "Summary ", "")
    End If
Next Process

Slope = Application.WorksheetFunction.Slope(Y, X)
Intercept = Application.WorksheetFunction.Intercept(Y, X)
Einv(Process - 1) = -Slope
Ainv(Process - 1) = Exp(Intercept)
Cells(5 + N + Process, HighMech + 6).Select
With Selection
    .NumberFormat = "0"
End With
Sub SetUp()

    ' Run only on first iteration
    ' Performs calculations that relate to experimental variables and assigns mechanism orders
    ' All labelling and formatting is consigned to this subroutine (apart from that required for
    ' the 'Summary' sheet)
    ' Sheet with experimental data of choice must be selected

    Dim LastRow As Integer
    Dim i As Integer
    Dim StartTemp As Integer
    Dim Slope As Double
    Dim Intercept As Double
    Dim Baseline As Integer

    LastRow = Cells(RowOffset, Time).End(xlDown).Row
    ActiveSheet.Cells.Select
    With Selection
        .Interior.ColorIndex = xlColorIndexNone
        .ColumnWidth = 8.43
        .NumberFormat = "General"
    End With

    Range(Cells(RowOffset - 3, ColOffset), Cells(65536, 256)).Select
    With Selection
        .Clear
        .UnMerge
    End With

End Sub

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.R1C1 = Einv(Process - 1)
End With
Cells(5 + N + Process, HighMech + 9).Select
With Selection
    .NumberFormat = "0.00E+00"
    .FormulaR1C1 = Ainv(Process - 1)
End With

' Calculation and presentation of the corresponding 95% confidence intervals
' If the process cannot be found in one or more sheets, CIs will need to be
' calculated manually as Excel requires contiguous data
If No(Process - 1) = N Then
    Cells(5 + N + Process, HighMech + 8).Select
    With Selection
        .NumberFormat = "0"
        .FormulaLocal = "=INDEX(LINEST(" & Y.AddressLocal(False, False) & "," & X.AddressLocal(False, False) & ",1,1,2,1)*TINV(0.05," & N - 2 & ")"
    End With
    Cells(5 + N + Process, HighMech + 10).Select
    With Selection
        .NumberFormat = "0.0"
        .FormulaLocal = "=INDEX(LINEST(" & Y.AddressLocal(False, False) & "," & X.AddressLocal(False, False) & ",1,1,2,2)*TINV(0.05," & N - 2 & ")"
    End With
Else
    Cells(5 + N + Process, HighMech + 8).Select
    With Selection
        .FormulaR1C1 = "?"
        .HorizontalAlignment = xlRight
    End With
    Cells(5 + N + Process, HighMech + 10).Select
    With Selection
        .FormulaR1C1 = "?"
        .HorizontalAlignment = xlRight
    End With
End If
OK = MsgBox("Einv is " & Format(Einv(Process - 1), 0) & Chr(177) & Format(Cells(5 + N + Process, HighMech + 8).Value, 0) & " J/mol and Ainv is ~" & Format(Ainv(Process - 1), "Scientific") & " min-1", vbInformation, "Invariant Kinetic Parameters for Process " & Process)
Else
    OK = MsgBox("Not enough sheets of useable data to calculate invariant kinetic parameters", vbCritical, "Invariant Kinetic Parameters for Process " & Process)
End If
Next
StoredData = True
Application.ScreenUpdating = True
End Sub
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Estimation of noise based on maximum excursion from (linear) baseline before initiation of first process. A temperature can be input to the left of the first onset temperature (cell (UserInputRow + 1, UserInputCol - 1)) from which the baseline will be computed; if this cell is empty, the default is the initial temperature.

If Cells(UserInputRow + 1, UserInputCol - 1) = “” Then
Baseline = RowOffset
Else
Baseline = RowAssignment(Temp, RowOffset, LastRow, Cells(UserInputRow + 1, UserInputCol - 1), Range(Cells(RowOffset, ColOffset), Cells(Baseline - 1, ColOffset))) = “1"
End If
StartTemp = RowAssignment(Temp, Baseline, LastRow, Cells(UserInputRow + 1, UserInputCol), 0)

If StartTemp = Baseline Then
Noisemg = 0
Else
Slope = Application.WorksheetFunction.Slope(Range(Cells(Baseline, Weight), Cells(StartTemp, Weight)), Range(Cells(Baseline, Time), Cells(StartTemp, Time)))
Intercept = Application.WorksheetFunction.Intercept(Range(Cells(Baseline, Weight), Cells(StartTemp, Weight)), Range(Cells(Baseline, Time), Cells(StartTemp, Time)))
Noisemg = 0
For i = Baseline To StartTemp
If Abs(Cells(i, Weight) - (Slope * Cells(i, Time) + Intercept)) > Noisemg Then
Noisemg = Abs(Cells(i, Weight) - (Slope * Cells(i, Time) + Intercept))
End If
Next
End If

OverallNoise = Noisemg / (Application.WorksheetFunction.Max(Range(Cells(Baseline, Weight), Cells(LastRow, Weight))) - Application.WorksheetFunction.Min(Range(Cells(Baseline, Weight), Cells(LastRow, Weight)))) - 2 * Noisemg
If OverallNoise < XPrecision Then
Noisemg = 0
OverallNoise = 0
End If
Cells(LastRow + 2, ColOffset + 1).Select
With Selection
.NumberFormat = "0.00%"
.FormulaR1C1 = OverallNoise
End With

Calculation of noise-corrected experimental degree of conversion. This relates to the reactive portion of weight and remains constant.

Range(Cells(Baseline, ColOffset), Cells(LastRow, ColOffset)) = "=(RC" & Weight & ") - (Min(R" & Baseline & "C" & Weight & ":R" & LastRow & "C" & Weight & "))/" & OverallNoise & " + 2" & Noisemg & ")

Filling in temperature and inverse temperature data in case of either no temperature lag incorporation requested; or if the lumped heat capacity verification is graphed but the centreline temperature is not used for the analysis.

If Q = vbNo Or CalcTemp = vbNo Then
Range(Cells(RowOffset, Temp), Cells(LastRow, Temp)).Select
Selection.Copy
Selection.Copy
With ActiveSheet.Paste
.Cells(RowOffset, SampleT).Select
.Range(Cells(RowOffset, ColOffset + 2 + 2 * HighMech + 1), Cells(LastRow, ColOffset + 2 + 2 * HighMech + 1)) = "=1/(RC" & Temp & ") + 273.16)"
.Range(Cells(RowOffset, ColOffset + 2 + 2 * HighMech + 2), Cells(LastRow, ColOffset + 2 + 2 * HighMech + 2)) = "=1/(RC" & SampleT & ") + 273.16)"

Labeling of mechanisms and assignment of orders. Must be edited if the list of mechanisms appearing in MechAssignment() is changed in any way.

For Mech = 1 To 22
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Range(Cells(RowOffset - 2, ColOffset + 1 + 2 * Mech), Cells(RowOffset - 2, ColOffset + 2 + 2 * Mech)).Select
With Selection
  .Font.Bold = True
  .HorizontalAlignment = xlCenter
  .VerticalAlignment = xlBottom
  .NumberFormat = "@"
  .MergeCells = True
End With
Select Case Mech
Case 1 To 4
  If Mech = 4 Then
    j = "2/3"
  Else
    j = 5 - Mech
  End If
  ActiveCell.FormulaR1C1 = "P" & j
Case 5 To 9
  If Mech = 9 Then
    j = 1
  Else
    If Mech = 8 Then
      j = "3/2"
    Else
      j = 9 - Mech
    End If
  End If
  ActiveCell.FormulaR1C1 = "A" & j & ", F1"
End If
Case 10
  j = 2.6
  ActiveCell.FormulaR1C1 = "P-T"
Case 11 To 13
  j = Mech - 10
  If j = 1 Then
    ActiveCell.FormulaR1C1 = "R" & j & ", P1, F0"
  Else
    ActiveCell.FormulaR1C1 = "R" & j
  End If
End If
Case 14 To 15
  j = Mech - 12
  ActiveCell.FormulaR1C1 = "F" & j
Case 16
  ActiveCell.FormulaR1C1 = "L2"
Case 17
  ActiveCell.FormulaR1C1 = "L(T)"
Case 18
  ActiveCell.FormulaR1C1 = "D1(*)"
Case 19
  ActiveCell.FormulaR1C1 = "D2"
Case 20
  ActiveCell.FormulaR1C1 = "D2*"
Case 21
  ActiveCell.FormulaR1C1 = "D3"
Case 22
  ActiveCell.FormulaR1C1 = "D3*"
End Select
If Mech < 16 Then
  Cells(RowOffset - 3, ColOffset + 1 + 2 * Mech).Select
  If Mech = 10 Then
    ActiveCell.FormulaR1C1 = "c ="
  Else
    ActiveCell.FormulaR1C1 = "n ="
  End If
  With Selection
    .HorizontalAlignment = xlRight
    .VerticalAlignment = xlBottom
    .MergeCells = False
  End With
  Cells(RowOffset - 3, ColOffset + 2 + 2 * Mech).Select
  Selection.HorizontalAlignment = xlLeft
  ActiveCell.FormulaR1C1 = Evaluate(j)
End If
Next
' Non-specific labelling
For Mech = 1 To HighMech
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Cells(RowOffset - 1, ColOffset + 1 + 2 * Mech).Select
With ActiveCell
  .FormulaR1C1 = "f_j"
  .Characters(Start:=2, Length:=1).Font.Subscript = True
End With
Cells(RowOffset - 1, ColOffset + 2 + 2 * Mech).Select
With ActiveCell
  .FormulaR1C1 = "g_j"
  .Characters(Start:=2, Length:=1).Font.Subscript = True
End With
Next
Range(Cells(RowOffset - 1, ColOffset + 3), Cells(RowOffset - 1, ColOffset + 2 + HighMech * 2)).Select
With Selection
  .HorizontalAlignment = xlCenter
  .VerticalAlignment = xlBottom
  .MergeCells = False
End With

' AETable: Refers to the where the table of apparent Arrhenius parameters will be presented
' AETableRow = Top-most row; AETableCol = Left-most column. Table is 2*HighProcess + 1 rows tall and HighMech columns wide

' Drawing borders for table of apparent Arrhenius parameters
Range(Cells(AETableRow, AETableCol), Cells(AETableRow + 2 + 3 * (HighProcess - 1), AETableCol + (HighMech - 1))).Select
Selection.UnMerge
Selection.Borders(xlDiagonalDown).LineStyle = xlNone
Selection.Borders(xlDiagonalUp).LineStyle = xlNone
With Selection.Borders(xlEdgeLeft)
  .LineStyle = xlContinuous
  .Weight = xlMedium
  .ColorIndex = xlAutomatic
End With
With Selection.Borders(xlEdgeTop)
  .LineStyle = xlContinuous
  .Weight = xlMedium
  .ColorIndex = xlAutomatic
End With
With Selection.Borders(xlEdgeBottom)
  .LineStyle = xlContinuous
  .Weight = xlMedium
  .ColorIndex = xlAutomatic
End With
With Selection.Borders(xlEdgeRight)
  .LineStyle = xlContinuous
  .Weight = xlMedium
  .ColorIndex = xlAutomatic
End With
Selection.Borders(xlInsideVertical).LineStyle = xlNone
Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
Range(Cells(AETableRow, AETableCol), Cells(AETableRow + 2 + 3 * (HighProcess - 1), AETableCol + (HighMech - 1))).Select
Selection.Borders(xlDiagonalDown).LineStyle = xlNone
Selection.Borders(xlDiagonalUp).LineStyle = xlNone
With Selection.Borders(xlEdgeLeft)
  .LineStyle = xlContinuous
  .Weight = xlMedium
  .ColorIndex = xlAutomatic
End With
With Selection.Borders(xlEdgeTop)
  .LineStyle = xlContinuous
  .Weight = xlMedium
  .ColorIndex = xlAutomatic
End With
With Selection.Borders(xlEdgeBottom)
  .LineStyle = xlDouble
  .Weight = xlThick
  .ColorIndex = xlAutomatic
End With
With Selection.Borders(xlEdgeRight)
  .LineStyle = xlContinuous
  .Weight = xlMedium
  .ColorIndex = xlAutomatic
End With
Selection.Borders(xlInsideVertical).LineStyle = xlNone
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For Mech = 1 To HighMech
    Cells(AETableRow, AETableCol + Mech - 1).Select
    With Selection
        .Font.Bold = True
        .HorizontalAlignment = xlCenter
        .VerticalAlignment = xlBottom
        .NumberFormat = "@"
        .MergeCells = False
    End With
    ActiveCell.FormulaR1C1 = Cells(RowOffset - 2, ColOffset + 1 + 2 * Mech).FormulaR1C1
Next
For Process = 1 To HighProcess
    Cells(AETableRow + 1 + 3 * (Process - 1), AETableCol - 1).Select
    ActiveCell.FormulaR1C1 = "Ej" & Process
    With Selection
        .Font.Bold = True
        .HorizontalAlignment = xlRight
        .VerticalAlignment = xlBottom
        .MergeCells = False
    End With
    Cells(AETableRow + 2 + 3 * (Process - 1), AETableCol - 1).Select
    ActiveCell.FormulaR1C1 = "ln Aj" & Process
    With Selection
        .Font.Bold = True
        .HorizontalAlignment = xlRight
        .VerticalAlignment = xlBottom
        .MergeCells = False
    End With
End With
' Additional labels
Cells(RowOffset - 2, ColOffset).Select
ActiveCell.FormulaR1C1 = "1-alpha"
With Selection
    .Font.Bold = True
    .HorizontalAlignment = xlCenter
    .VerticalAlignment = xlBottom
    .WrapText = False
    .ShrinkToFit = True
End With
Cells(RowOffset - 2, ColOffset + 1).Select
ActiveCell.FormulaR1C1 = "alpha"
With Selection
    .Font.Bold = True
    .HorizontalAlignment = xlCenter
    .VerticalAlignment = xlBottom
    .WrapText = False
    .ShrinkToFit = True
End With
Cells(RowOffset - 2, SampleT).Select
If CalcTemp = vbYes Then
    ActiveCell.FormulaR1C1 = "T(estimated)"
Else
    ActiveCell.FormulaR1C1 = "T(raw)"
End If
With Selection
    .Font.Bold = True
    .HorizontalAlignment = xlCenter
    .VerticalAlignment = xlBottom
    .WrapText = False
    .ShrinkToFit = True
End With
If Q = vbYes And CalcTemp = vbNo Then
    Cells(RowOffset - 2, SampleT + 1).Select
    ActiveCell.FormulaR1C1 = "T(estimated)"
With Selection
    .Font.Bold = True
    .HorizontalAlignment = xlCenter
End With
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Sub Apparent()
' Computes apparent Arrhenius kinetic parameters for all defined processes and mechanisms and
' presents results in a table
' Sheet with experimental data of choice must be selected
Const R As Double = 8.314
Dim XStartRow(HighProcess - 1) As Integer
Dim XEndRow(HighProcess - 1) As Integer
Dim StartRow(HighProcess - 1) As Integer
Dim EndRow(HighProcess - 1) As Integer
Dim Mech As Integer
Dim XAxis As Integer
Dim YAxis As Integer
Dim Process As Integer
Dim InvPT(HighProcess - 1, 1) As Double
Dim SheetName As String
Dim X As Range
Dim Y As Range
Dim Slope As Double
Dim Intercept As Double
Dim B As Double
Dim LastRow As Integer
Dim MaxWeight As Double
Dim MinWeight As Double
Dim i As Integer
Dim j As Integer
Dim k As Integer
Dim L As Integer
Dim SampleTemp As String
Dim XFraction(HighProcess - 1) As Double
Dim Unconverged As Boolean
Dim ProcessAlpha(HighProcess - 1) As String
Dim Order(HighProcess - 1) As Integer
Dim XStartRowMin As Integer
Dim XStartRowMinNext As Integer
Dim XEndRowMax As Integer
Dim Continue As Boolean
Dim XSum As Double
Dim RowStart As Integer
Dim RowEnd As Integer
Dim Looping As Boolean
Dim Count As Integer
Dim DownTrend As Integer
Dim Maximum As Double
Dim Neutral As Integer

End Sub
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Dim UpTrend As Integer
Dim MaxTemp As Integer
Dim AlphaFraction(HighProcess - 1) As Double
Dim SigRowLow(HighProcess - 1) As Integer
Dim SigRowHigh(HighProcess - 1) As Integer
Dim Noise As Double
Dim NoiseJump As Integer
Dim NeutralStreak As Integer
Dim Exclude As String
Dim Residue As Boolean
Dim ConvCol As Integer
Dim AverageWeight As String
Dim UA As String
Dim torr As String
Dim Kalpha(HighProcess - 1) As String
Dim ReactionSum As String
Dim AlphaRate As String
Dim FinalAlphaRate As String
Dim FinalReactionSum As String
Dim FinalTempRate As String
Dim TempRate As String
Dim TempCol As Integer
Dim Z As Range
Dim Qu As String
Dim SlopePrevious As Double
Dim RangeStart(HighProcess - 1) As Integer
Dim RangeEnd(HighProcess - 1) As Integer
Dim FNumerator As Double
Dim FDenominator As Double
Dim FStat(HighMech - 1) As Double
Dim FStatBest As Double
Dim FStatBestMech As Integer
Dim NonUniqueStart As Integer
Dim NonUniqueEnd As Integer
Dim NonUniqueRange As Boolean

Call CompRequirements
SheetName = ActiveSheet.Name
LastRow = Cells(RowOffset, Time).End(xlDown).Row
SevereOverlap(Worksheets(SheetName).Index - 2) = False

' UserInput:
' Structure is three columns wide; heating rate in middle column and process start and end temps in first and last column respectively
' Structure is HighProcess + 1 rows tall; heating rate in first row and process start and end temps in rows below
' UserInputRow = Row where heating rate is input; UserInputCol = Column where process start temperatures are input
' Collection of nominal heating rate and process start and end temperatures from the spreadsheet

For Process = 1 To HighProcess
    InvPT(Process - 1, 0) = 1 / (273 + Cells(UserInputRow + Process, UserInputCol))
    InvPT(Process - 1, 1) = 1 / (273 + Cells(UserInputRow + Process, UserInputCol + 2))
Next

B = Cells(UserInputRow, UserInputCol + 1)

' Setting overall conversion column or resetting it in case a process was defined as incomplete in previous iteration
' Collection of OverallNoise, XFraction and process ranges from previous iteration

Range(Cells(RowOffset, ColOffset + 1), Cells(LastRow, ColOffset + 1)) = "=1-RC[-1]"
If Repeat = vbYes Then
    For Process = 1 To HighProcess
        XFraction(Process - 1) = Cells(LastRow + 4, Alpha + Process).Value
        XStartRow(Process - 1) = RowAssignment(dalphadt + Process, LastRow, RowOffset, XPrecision, 0)
        XEndRow(Process - 1) = RowAssignment(dalphadt + Process, RowOffset, LastRow, 1 - XPrecision, 0)
    Next
Else
    For Process = 1 To HighProcess
        OverallNoise = Cells(LastRow + 2, ColOffset + 1)
    Next

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XEndRow(Process - 1) = RowAssignment1(ColOffset + 2 + 2 * HighMech + 2, RowOffset, LastRow, InvPT(Process - 1, 1), 0)
XStartRow(Process - 1) = RowAssignment1(ColOffset + 2 + 2 * HighMech + 2, XEndRow(Process - 1), RowOffset, InvPT(Process - 1, 0), 0)
Next

' Definition of initial conversion function(s) as equivalent to normalised corrected overall experimental conversion between user-defined start and end temperatures. No consideration of overlap
' Conversion functions are distorted further from their true shapes the greater the overlap with other processes
' Approximation of XFractions based on normalised differences between maximum and minimum weights in the prescribed conversion ranges
XSum = 0
For Process = 1 To HighProcess
  If TempRef = vbYes Then
    ConvCol = dalphadt + Process
  Else
    ConvCol = Alpha + Process
  End If
  If XStartRow(Process - 1) = RowOffset Then
    Else
      Range(Cells(RowOffset, ConvCol), Cells(XStartRow(Process - 1) - 1, ConvCol)) = "0"
  End If
  MaxWeight = Application.WorksheetFunction.Max(Range(Cells(XStartRow(Process - 1), Weight), Cells(XEndRow(Process - 1), Weight))) - Noisemg
  MinWeight = Application.WorksheetFunction.Min(Range(Cells(XStartRow(Process - 1), Weight), Cells(XEndRow(Process - 1), Weight))) + Noisemg
  If MaxWeight > MinWeight Then
    Range(Cells(XStartRow(Process - 1), ConvCol), Cells(XEndRow(Process - 1), ConvCol)) = "(" & MaxWeight & "+-RC & Weight & ")/(" & MaxWeight & "-" & MinWeight & ")"
    If XEndRow(Process - 1) < LastRow Then
      InDataSet(Process - 1, Worksheets(SheetName).Index - 2) = 1
      Range(Cells(XEndRow(Process - 1) + 1, ConvCol), Cells(LastRow, ConvCol)) = "1"
    Else
      InDataSet(Process - 1, Worksheets(SheetName).Index - 2) = 0
    End If
    XFraction(Process - 1) = MaxWeight - MinWeight
    XSum = XSum + XFraction(Process - 1)
  Else
    InDataSet(Process - 1, Worksheets(SheetName).Index - 2) = -1
    Range(Cells(XStartRow(Process - 1), ConvCol), Cells(LastRow, ConvCol)) = "0"
    OK = MsgBox("Process " & Process & " cannot be found in sheet " & SheetName & " in the specified temperature range", vbCritical, "Warning")
    End If
  Next
  For Process = 1 To HighProcess
    XFraction(Process - 1) = XFraction(Process - 1) / XSum
    Cells(LastRow + 4, Alpha + Process).Value = XFraction(Process - 1)
  Next
End If

' Recalculation of component conversion (ProcessAlpha) from overall experimental conversion and previous solution
' Uses corrected sets of component conversion if they are available so that the process makeup is self-consistent
' If XFraction is zero for a particular process, conversion is still calculated in case another process can be found in a different temperature range
If TempRef = vbYes Then
  For Process = 1 To HighProcess
    ProcessAlpha(Process - 1) = "RC" & ColOffset + 1
    For j = 1 To HighProcess
      If j < Process Then
        ProcessAlpha(Process - 1) = ProcessAlpha(Process - 1) & "+&" & XFraction(j - 1)
      Else
        If j > Process Then
          ProcessAlpha(Process - 1) = ProcessAlpha(Process - 1) & "+" & dalphadt + j & "+&" & XFraction(j - 1)
        End If
      End If
    Next
    End If
Next
If XFraction(Process - 1) = 0 Then
  ProcessAlpha(Process - 1) = "(" & ProcessAlpha(Process - 1) & ")"
Else
    ProcessAlpha(Process - 1) = "(" & ProcessAlpha(Process - 1) & ")/" & XFraction(Process - 1)
End If
Next
'
' If XFraction is zero it is reset to unity temporarily to avoid runtime errors
'
' Individual conversion columns are printed as unreferenced values before process
' ranges are sought within them

XSum = 0
For Process = 1 To HighProcess
    If XFraction(Process - 1) = 0 Then
        XFraction(Process - 1) = 1
    End If
    Range(Cells(RowOffset, dalphadt + Process), Cells(LastRow, dalphadt + Process)).Select
    Selection = "= ProcessAlpha(Process - 1) + "
    Selection.Copy
    Selection.PasteSpecial Paste:=xlPasteValues
    NonUniqueRange = False
    Count = 0
    RangeStart(Process - 1) = RowOffset
    RangeEnd(Process - 1) = RowOffset
    L = 1
    i = RowOffset
    Looping = True
    Do
        j = i + 1
        Continue = True
        DownTrend = 0
        Neutral = 0
        UpTrend = 0
        Maximum = Application.WorksheetFunction.Min(Range(Cells(i, dalphadt + Process), Cells(LastRow, dalphadt + Process)))
        ' Noting whether another process initiates/terminates during the search for
        ' the end point of a process
        ' Amplification of noise according to the weight fraction (most conservative
        ' approach; valid only where processes do not overlap)
        Do
            NoiseJump = L
            For k = 1 To HighProcess
                If k < Process Then
                    If j >= RangeStart(k - 1) And j <= RangeEnd(k - 1) Then
                        L = L + 1
                    End If
                Else
                    If k > Process Then
                        If j >= XStartRow(k - 1) And j <= XEndRow(k - 1) Then
                            L = L + 1
                        End If
                    End If
                End If
            Next
            Noise = OverallNoise / XFraction(Process - 1)
            ' Reset starting row if another process terminates and conversion changes
            ' have been insignificant compared to noise
            If NoiseJump > L And (Neutral + DownTrend) > 10 And Noise > XPrecision Then
                UpTrend = 0
                Neutral = 0
                DownTrend = 0
            End If
        End Do
    End If
Next
'
' An active conversion range is defined to start where conversion is first
' within the computational limit/noise of the first significant increment
' in conversion
' UpTrend increases and Neutral and DownTrend are reset each
' time conversion increases significantly
If Cells(j, dalphadt + Process) > Maximum + XPrecision + Noise Then
    Maximum = Cells(j, dalphadt + Process)
    If UpTrend = 0 Then
        UpTrend = 1
        Neutral = 0
        DownTrend = 0
    End If
End If

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```vba
RowStart = j - Neutral - DownTrend - 1
End If
Neutral = 0
DownTrend = 0
UpTrend = UpTrend + 1
Else
    ' Specify whether conversion has stagnated or decreased
    If Cells(j, dalphadt + Process) >= Maximum - XPrecision - 2 * Noise
        Then
            Neutral = Neutral + 1
        Else
            DownTrend = DownTrend + 1
        End If
    End If

    ' The search for a valid data range is terminated in one of three ways:
    *Conversion has trended down on more than five occasions without a
    significant increase in conversion
    *Conversion has not increased significantly for a large number of rows
    *The end of data is reached (A measure of completion is calculated in
    this case)

    If DownTrend = 5 Or Neutral + DownTrend > 50 Or j = LastRow Then
        RowEnd = j - (L - NoiseJump)
        If j = LastRow Then
            NeutralStreak = Neutral + DownTrend
        End If
    End If

    Continue = False
End If
j = j + 1
Loop While Continue

i = j

' A valid range is compared to the ranges ultimately selected for previously
' calculated processes before proceeding
' If multiple ranges of conversion are found that do not coincide with ranges
' for previous processes, the section of data encompassing the greatest
' conversion increase is selected as operative

If UpTrend > 5 Then
    Continue = True
    For k = 1 To Process - 1
        If RowStart = RangeStart(k - 1) And RowEnd = RangeEnd(k - 1) Then
            Continue = False
        End If
    Next
    If Continue Then
        If Cells(RowEnd, dalphadt + Process) - Cells(RowStart, dalphadt + Process) > Cells(RangeEnd(Process - 1), dalphadt + Process) - Cells(RangeStart(Process - 1), dalphadt + Process) Or Count = 0 Then
            RangeStart(Process - 1) = RowStart
            RangeEnd(Process - 1) = RowEnd
            Count = Count + 1
        End If
    Else
        NonUniqueRange = True
        NonUniqueStart = RowStart
        NonUniqueEnd = RowEnd
    End If
End If
If i >= LastRow Then
    Looping = False
End If
Loop While Looping

' If only non-unique conversion ranges are found for a particular process, the
' user is given the option to continue the calculation with 100% overlap
' If no conversion ranges can be found at all, the user is given the option to
' continue the calculation with the user-defined temperature ranges

If Count = 0 Then
    If NonUniqueRange Then
        Exclude = MsgBox("Process ", Process & ", cannot be assigned a unique range in sheet ", & SheetName & ".", vbYesNo + vbCritical, "Warning")
    End If
End If
```

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RangeStart(Process - 1) = NonUniqueStart
RangeEnd(Process - 1) = NonUniqueEnd
End If
Else
Exclude = MsgBox("Process " & Process & ", sheet " & SheetName & ". " & Chr(13) & "Do you wish to exclude it from the computation?", vbYesNo + vbCritical, "Warning")
If Exclude = vbNo Then
RangeStart(Process - 1) = XStartRow(Process - 1)
RangeEnd(Process - 1) = XEndRow(Process - 1)
End If
Else
Exclude = vbNo
End If
If Exclude = vbYes Then
Range(Cells(RowOffset, Alpha + Process), Cells(LastRow, Alpha + Process)) = "0"
InDataSet(Process - 1, Worksheets(SheetName).Index - 2) = -1
RangeEnd(Process - 1) = LastRow
Else
' Calculation of maximum and minimum conversion over selected range,
' considering noise
' Re-approximation of XFraction assuming no overlap only on first iteration
' (too crude for subsequent solutions)
' Redefinition and placement of conversion
MaxWeight = Application.WorksheetFunction.Max(Range(Cells(RangeStart(Process - 1), dalphadt + Process), Cells(RangeEnd(Process - 1), dalphadt + Process))) - OverallNoise / XFraction(Process - 1)
MinWeight = Application.WorksheetFunction.Min(Range(Cells(RangeStart(Process - 1), dalphadt + Process), Cells(RangeEnd(Process - 1), dalphadt + Process))) + OverallNoise / XFraction(Process - 1)
If Repeat = vbYes Then
Else
XSum = XSum + XFraction(Process - 1)
End If
Range(Cells(RangeStart(Process - 1), Alpha + Process), Cells(RangeEnd(Process - 1), Alpha + Process)).Select
Selection = "=(RC" & dalphadt + Process & "-" & MinWeight & ")/(" & MaxWeight & "-" & MinWeight & ")"
Selection.Copy
Selection.PasteSpecial Paste:=xlPasteValues
If RangeStart(Process - 1) > RowOffset Then
Range(Cells(RowOffset, Alpha + Process), Cells(RangeStart(Process - 1) - 1, Alpha + Process)) = "0"
End If

' Judgement of whether a process is incomplete
If RangeEnd(Process - 1) = LastRow And NeutralStreak < 10 Then
InDataSet(Process - 1, Worksheets(SheetName).Index - 2) = 0
Else
InDataSet(Process - 1, Worksheets(SheetName).Index - 2) = 1
If RangeEnd(Process - 1) < LastRow Then
Range(Cells(RangeEnd(Process - 1) + 1, Alpha + Process), Cells(LastRow, Alpha + Process)) = "I"
End If
End If
Next

' Respecification of XStartRow and XEndRow
For Process = 1 To HighProcess
If InDataSet(Process - 1, Worksheets(SheetName).Index - 2) = -1 Then
XStartRow(Process - 1) = LastRow
XEndRow(Process - 1) = LastRow
Else
If InDataSet(Process - 1, Worksheets(SheetName).Index - 2) = 0 Then
XEndRow(Process - 1) = LastRow
Else

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XEndRow(\text{Process - 1}) = \text{RowAssignment}(\text{Alpha} + \text{Process}, \text{RangeStart(\text{Process - 1})}, \text{RangeEnd(\text{Process - 1})}, 1 - \text{XPrecision}, 0)

\text{End If}

XStartRow(\text{Process - 1}) = \text{RowAssignment}(\text{Alpha} + \text{Process}, \text{RangeEnd(\text{Process - 1})}, \text{RangeStart(\text{Process - 1})}, \text{XPrecision}, 0)

\text{End If}

\text{Next}

' Normalisation and reprinting of XFraction estimate on first iteration

If Repeat = vbYes Then

Else

For Process = 1 To HighProcess

XFraction(\text{Process - 1}) = XFraction(\text{Process - 1}) / XSum

Cells(LastRow + 4, Alpha + Process).Value = XFraction(\text{Process - 1})

\text{Next}

\text{End If}

\text{End If}

' Definition of ranges where processes are deemed significant

' Assignment of process order on the basis of XStartRow

For Process = 1 To HighProcess

If LowerCompLimit(\text{Process - 1}) < \text{Sig} Then

\text{SigRowLow(\text{Process - 1}) = RowAssignment(Alpha + \text{Process}, XStartRow(\text{Process - 1}), XEndRow(\text{Process - 1}), LowerCompLimit(\text{Process - 1}), 0)}

Else

\text{SigRowLow(\text{Process - 1}) = RowAssignment(Alpha + \text{Process}, XStartRow(\text{Process - 1}), XEndRow(\text{Process - 1}), \text{Sig}, 0)}

\text{End If}

If UpperCompLimit(\text{Process - 1}) > 1 - \text{Sig} Then

\text{SigRowHigh(\text{Process - 1}) = RowAssignment(Alpha + \text{Process}, XEndRow(\text{Process - 1}), XStartRow(\text{Process - 1}), UpperCompLimit(\text{Process - 1}), 0)}

Else

\text{SigRowHigh(\text{Process - 1}) = RowAssignment(Alpha + \text{Process}, XEndRow(\text{Process - 1}), XStartRow(\text{Process - 1}), 1 - \text{Sig}, 0)}

\text{End If}

\text{Order(\text{Process - 1}) = HighProcess}

\text{XStartRowMin = XStartRow(0)}

\text{XStartRowMinNext = XStartRow(0)}

For i = 1 To HighProcess

For j = 1 To i - 1

\text{If Order(\text{j - 1}) = Process - 1 Then Continue = False}

\text{End If}

\text{Next}

\text{If Continue Then}

\text{If XStartRow(\text{Process - 1}) <= XStartRowMin Then}

\text{XStartRowMin = XStartRow(\text{Process - 1})}

\text{k = Process}

\text{Else}

\text{XStartRowMinNext = XStartRow(\text{Process - 1})}

\text{End If}

\text{End If}

\text{Next}

\text{XStartRowMin = XStartRowMinNext}

\text{Order(i - 1) = k - 1}

\text{Next}

' Assigning XEndRowMax as the maximum XEndRow (not necessarily of last process)

\text{XEndRowMax = XEndRow(0)}

\text{For Process = 2 To HighProcess}

\text{If XEndRow(\text{Process - 1}) > XEndRowMax Then}

\text{XEndRowMax = XEndRow(\text{Process - 1})}

\text{End If}

\text{Next}

' Recalculation of conversion (overall and for the affected process) should process not finish before end of data (includes processes that cannot be found in the temperature range after temperature refinement)

' Uses averaged unaffected estimates for XFraction from processed worksheets

' If more than one data set is incomplete or at least one data set is always incomplete, conversion is not recalculated

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Continue = False
Count = 0
For Process = 1 To HighProcess
If InDataSet(Process - 1, Worksheets(SheetName).Index - 2) = 0 Or (InDataSet(Process - 1, Worksheets(SheetName).Index - 2) = -1 And TempRef = vbYes) And XFraction(Process - 1) < 1 Then
    Continue = True
    Count = Count + 1
End If
If InDataSet(Process - 1, Worksheets(SheetName).Index - 2) = -1 And TempRef = vbNo Then
    Count = Count + 1
End If
Next
If Continue And Count = 1 Then
    Count = 0
    For i = 0 To Worksheets(SheetName).Index - 3
        Worksheets(i + 2).Select
        LastRow = Cells(RowOffset, Time).End(xlDown).Row
        For Process = 1 To HighProcess
            If InDataSet(Process - 1, i) = 1 Then
                Continue = False
            Else
                Continue = True
                Count = Count + 1
            End If
        Next
        If Continue Then
            For Process = 1 To HighProcess
                AlphaFraction(Process - 1) = AlphaFraction(Process - 1) + Cells(LastRow + 4, Alpha + Process)
            Next
            Count = Count + 1
        End If
    Next
    Worksheets(SheetName).Select
    LastRow = Cells(RowOffset, Time).End(xlDown).Row
    If Count > 0 Then
        For Process = 1 To HighProcess
            AlphaFraction(Process - 1) = AlphaFraction(Process - 1) / Count
            For i = XStartRow(Process - 1, 1) To XEndRow(Process - 1)
                Cells(i, Alpha + Process) = Cells(i, Alpha + Process) * ((1 - AlphaFraction(Process - 1)) / (1 - XFraction(Process - 1)) - (1 - AlphaFraction(Process - 1))) / AlphaFraction(Process - 1)
            Next
            XStartRow = RowAssignment(Alpha + Process, XStartRow(Process - 1, 1), Sig, 0)
            XEndRow = RowAssignment(Alpha + Process, XStartRow(Process - 1, 1), 1 - Sig, 0)
            If RowAssignment(Alpha + Process, LastRow, XStartRow(Process - 1, 1), 1 - XPrecision - OverallNoise / XFraction(Process - 1, 1) < LastRow Then
                InDataSet(Process - 1, Worksheets(SheetName).Index - 2) = 1
            End If
        Next
        MaxWeight = Application.WorksheetFunction.Max(Range(Cells(XStartRow(Order(0)), Weight), Cells(XEndRowMax, Weight)))
        MinWeight = Application.WorksheetFunction.Min(Range(Cells(XStartRow(Order(0)), Weight), Cells(XEndRowMax, Weight)))
        Range(Cells(RowOffset, ColOffset + 1), Cells(XEndRowMax, ColOffset + 1)) = "=" & MaxWeight & "/" & MinWeight & " & AlphaFraction(Process - 1) & "/(1" & XFraction(Process - 1) & ")"
        End If
        Cells(LastRow + 4, Alpha + Process).Value = AlphaFraction(Process - 1)
    Next
End If
End If

* Specification of limited ranges for calculation of apparent kinetic parameters
* StartRow and EndRow adjust accordingly should conversion values imply processes overlap more than specified computational limits
* If overlap is too severe (less than 10 non-overlapping rows; covers more than 50% of requested range), computational limits are left unchanged and this fact is recorded
* If furnace temperature decreases within the determined range of conversion, EndRow is limited to the row where the maximum temperature occurs
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MaxTemp = RowAssignment(Temp, RowOffset, LastRow, Application.WorksheetFunction.Max(Range(Cells(RowOffset, Temp), Cells(LastRow, Temp))) - XPrecision, 0)
For i = 1 To HighProcess
    Process = Order(i - 1) + 1
    If (InDataSet(Process - 1, Worksheets(SheetName).Index - 2) = -1) = False Then
        StartRow(Process - 1) = RowAssignment(Alpha + Process, XStartRow(Process - 1), LowerCompLimit(Process - 1), 1)
        EndRow(Process - 1) = RowAssignment(Alpha + Process, XStartRow(Process - 1), XEndRow(Process - 1), UpperLimit(Process - 1), InDataSet(Process - 1, Worksheets(SheetName).Index - 2))
        If i < HighProcess Then
            If (InDataSet(Order(i), Worksheets(SheetName).Index - 2) = -1) = False Then
                StartRow(Process - 1) = RowAssignment(Alpha + Process, XStartRow(Process - 1), XEndRow(Process - 1), Alpha + Process)
                StartRow(Process - 1) = SigRowLow(Order(i), Alpha + Process) - Cells(StartRow(Process - 1), Alpha + Process) + (LowerCompLimit(Process - 1) + UpperCompLimit(Process - 1)) / 2 Then
                    StartRow(Process - 1) = SigRowLow(Order(i), Alpha + Process)
                    UpperCompLimit(Process - 1) = Cells(StartRow(Process - 1) + 1, Alpha + Process)
                    If StartRow(Process - 1) < SigRowHigh(Order(i)) Then
                        StartRow(Process - 1) = SigRowHigh(Order(i)) - 10 And
                        (Cells(SigRowLow(Order(i)), Alpha + Process) - Cells(SigRowHigh(Order(i)), Alpha + Process)) > (LowerCompLimit(Process - 1) + UpperCompLimit(Process - 1)) / 2 Then
                            StartRow(Process - 1) = SigRowHigh(Order(i), Alpha + Process)
                            LowerCompLimit(Process - 1) = Cells(StartRow(Process - 1) - 1, Alpha + Process)
                            If StartRow(Process - 1) > MaxTemp Then
                                StartRow(Process - 1) = MaxTemp
                                UpperCompLimit(Process - 1) = Cells(StartRow(Process - 1) + 1, Alpha + Process)
                    End If
                End If
                If i > 1 Then
                    For j = 1 To i - 1
                        If (InDataSet(Order(j - 1), Worksheets(SheetName).Index - 2) = -1) = False Then
                            If StartRow(Process - 1) < SigRowHigh(Order(j - 1)) Then
                                If EndRow(Process - 1) > SigRowHigh(Order(j - 1)) + 10 And
                                    (Cells(SigRowLow(Order(j - 1)), Alpha + Process) - Cells(SigRowHigh(Order(j - 1)), Alpha + Process)) > (LowerCompLimit(Process - 1) + UpperCompLimit(Process - 1)) / 2 Then
                                        StartRow(Process - 1) = SigRowHigh(Order(j - 1), Alpha + Process)
                                        LowerCompLimit(Process - 1) = Cells(SigRowLow(Order(j - 1)), Alpha + Process)
                                    Else
                                        SevereOverlap(Worksheets(SheetName).Index - 2) = True
                                    End If
                                End If
                            End If
                        End If
                    Next
                End If
                If EndRow(Process - 1) > MaxTemp Then
                    EndRow(Process - 1) = MaxTemp
                    UpperCompLimit(Process - 1) = Cells(EndRow(Process - 1) + 1, Alpha + Process)
            End If
        End If
    End If
Next

' Printing of computational limits and active temperature ranges
For Process = 1 To HighProcess
    If (InDataSet(Process - 1, Worksheets(SheetName).Index - 2) = -1) = False Then
        If Cells(XEndRow(Process - 1), Alpha + Process) < UpperCompLimit(Process - 1) And
            Cells(XEndRow(Process - 1), Alpha + Process) > LowerCompLimit(Process - 1) And
            Cells(XEndRow(Process - 1), Alpha + Process) > LowerCompLimit(Process - 1) Then
            UpperCompLimit(Process - 1) = Cells(XEndRow(Process - 1), Alpha + Process) + XPrecision
            End If
        Cells(LastRow + 2, Alpha + Process) = LowerCompLimit(Process - 1)
        Cells(LastRow + 3, Alpha + Process) = UpperCompLimit(Process - 1)
        Cells(AETableRow + 2 + 3 * (Process - 1), AETableCol + HighMech + 1) = Format(Cells(StartRow(Process - 1), Temp), 0) & "°" & Format(Cells(EndRow(Process - 1), Temp), 0) & Chr(186) & "°C"
        Else
            Cells(LastRow + 2, Alpha + Process) = ""
            Cells(LastRow + 3, Alpha + Process) = ""
            Cells(AETableRow + 2 + 3 * (Process - 1), AETableCol + HighMech + 1) = ""
            End If
        Cells(AETableRow + 1 + 3 * (Process - 1), AETableCol + HighMech + 1) = Format(Cells(XStartRow(Process - 1), Temp), 0) & "°" & Format(Cells(XEndRow(Process - 1), Temp), 0) & Chr(186) & "°C"
Next

' Calculation of overall experimental d(alpha)/dt and dT/dt. T taken as sample temperature
' (calculated subsequently)
' Search for and store rows for subsequent isoconversional analysis

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Call Derivative(ColOffset + 1, Time, XStartRow(Order(0)), XEndRowMax, Graph)
Call Derivative(SampleT, Time, RowOffset, LastRow, ColOffset + 2)
Call IsoRow(XStartRow(Order(0)), XEndRowMax, Worksheets(SheetName).Index - 1)

' Calculation of sample temperature if temperature lag incorporation is requested
' XFraction is deliberately retained such that the computation is accurate even if a
' process is recalculated as incomplete
' Utilises a dynamic energy balance and requires constant inputs for sample density
' (radial heat transfer only), heat capacity, inside crucible radius and reaction
' enthalpies, and:
' If the lumped heat capacity assumption is to be tested, thermal conductivity (yields
' centreline sample temperature); or
' If measured temperature is taken as atmospheric and refractory temperature, outside
' crucible radius (radial heat transfer only), convective heat transfer coefficient and
' emissivity (yields uniform sample temperature)
' Note that convective or radiative heat transfer can be "turned off" by setting the
' appropriate constants to zero
' Thermal resistivity and heat capacity of crucible are considered negligible

If Q = vbYes Then
   MaxWeight = Application.WorksheetFunction.Max(Range(Cells(RowOffset, Weight),
   Cells(LastRow, Weight))) - Noisemg
   MinWeight = Application.WorksheetFunction.Min(Range(Cells(RowOffset, Weight),
   Cells(LastRow, Weight)))
   ' Set the row range (j >= 0) that the simplified linear driving forces of measured
   ' temperature and conversion are calculated over
   ' A larger range smoothes noise; a smaller range is more accurate for good data
   ' Specify whether computations should accommodate a residue
   Residue = False
   j = 3
   ' Expressions for total sample weight for each row (no smoothing)
   ' Correct average weight so it would be zero at the minimum weight if weight loss is
   ' complete before LastRow and there is no residue
   AverageWeight = "(R[-1]C" & Weight & "+RC" & Weight & ")/2"
   If XEndRowMax < LastRow Then
      If Residue = False Then
         AverageWeight = "(" & AverageWeight & "+ MinWeight & ")"
      End If
      MinWeight = MinWeight - Noisemg
   Else
      Residue = False
   End If
   ' Definition of linear driving forces (reaction heat and measured temperature)
   For Process = 1 To HighProcess
      FinalAlphaRate = "Slope(R" & LastRow - j & ")C & Alpha + Process & ",R" & LastRow & ")C & Alpha + Process"
      Kalpha(Process - 1) = XFraction(Process - 1) * Reaction(Process - 1)
      If Process = 1 Then
         ReactionSum = Kalpha(Process - 1) * AlphaRate
         FinalReactionSum = Kalpha(Process - 1) * AlphaRate
      Else
         ReactionSum = ReactionSum + Kalpha(Process - 1) * AlphaRate
         FinalReactionSum = FinalReactionSum + Kalpha(Process - 1) * AlphaRate
      End If
   Next
   TempRate = "Slope(R[-1]C" & Temp & ",R[-1]C" & Time & ",R" & j & ")C & Temp & ",R" & LastRow & ")C & Temp"
   FinalTempRate = "Slope(R" & LastRow - j & ")C & Temp & ",R" & LastRow & ")C & Temp"
   ' If it is requested, estimate "worst-case" centreline temperature if the sample
   ' surface temperature matches the measured temperature
   ' Sample temperature used for analysis is either set as the calculated temperature or
   ' left unaltered
   ' Assume sample is initially in thermal equilibrium with the furnace
   If CalcTemp = vbYes Then
      TempCol = SampleT
   End If
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Else

TempCol = SampleT + 1
End If
Cells(RowOffset, TempCol) = "=RC" & Temp
If Core = vbYes Then
If Residue Then
Range(Cells(RowOffset + 1, TempCol), Cells(LastRow - j - 1, TempCol)) = "=R[1]C" & Temp & "+(RC" & Time & "-R[-1]C" & Time & "-" & Cp & "*" & rho & "*" & Ri ^ 2 &
"/(60*1000*4*" & Conduct & "))*" & TempRate & "-(" & MaxWeight & "-" & MinWeight & ")*" & rho
& "*" & Ri ^ 2 & "/(60*1000*4*" & Conduct & "*" & MaxWeight & ")*" & ReactionSum
Else
Range(Cells(RowOffset + 1, TempCol), Cells(LastRow - j - 1, TempCol)) = "=R[1]C" & Temp & "+(RC" & Time & "-R[-1]C" & Time & "-" & Cp & "*" & rho & "*" & Ri ^ 2 &
"/(60*1000*4*" & Conduct & "))*" & TempRate & "-" & rho & "*" & Ri ^ 2 & "/(60*1000*4*" &
Conduct & ")*" & ReactionSum
End If
Else
If Cylindrical = vbYes Then
UA = "60*2*" & AverageWeight & "*" & Ro & "/(" & rho & "*" & Ri ^ 2 & ")" &
"*(" & h & "+4*" & sigma & "*" & epsilon & "*(RC" & Temp & "+273.16)^3)"
Else
UA = "60/1000*" & Application.WorksheetFunction.Pi() * Ri ^ 2 & "*(" & h &
"+4*" & sigma & "*" & epsilon & "*(RC" & Temp & "+273.16)^3)"
End If
If Residue Then
ReactionSum = "(" & MaxWeight & "-" & MinWeight & ")*" & AverageWeight & "*("
& ReactionSum & ")/((" & UA & ")*" & MaxWeight & ")"
FinalReactionSum = "(" & MaxWeight & "-" & MinWeight & ")*" & AverageWeight &
"*(" & FinalReactionSum & ")/((" & UA & ")*" & MaxWeight & ")"
Else
ReactionSum = AverageWeight & "*(" & ReactionSum & ")/(" & UA & ")"
FinalReactionSum = AverageWeight & "*(" & FinalReactionSum & ")/(" & UA & ")"
End If
torr = "(" & AverageWeight & "*" & Cp & "/(" & UA & "))"
Range(Cells(RowOffset + 1, TempCol), Cells(LastRow - j - 1, TempCol)) = "=" &
TempRate & "*(RC" & Time & "-R[-1]C" & Time & ")+(R[-1]C" & Temp & "-" & torr & "*" & TempRate
End If
' If/when weight reduces to zero, set zero temperature lag
' Otherwise, fix the linear driving forces for j less rows than LastRow so temperature
' follows a first order approach to steady-state
If XEndRowMax < LastRow Then
Range(Cells(XEndRowMax + 1, TempCol), Cells(LastRow, TempCol)) = "=RC" & Temp
Else
If Core = vbYes Then
If Residue Then
Range(Cells(LastRow - j, TempCol), Cells(LastRow, TempCol)) = "=R" &
LastRow - j - 1 & "C" & Temp & "+(RC" & Time & "-R" & LastRow - j - 1 & "C" & Time & "-" & Cp
& "*" & rho & "*" & Ri ^ 2 & "/(60*1000*4*" & Conduct & "))*" & FinalTempRate & "-(" &
MaxWeight & "-" & MinWeight & ")*" & rho & "*" & Ri ^ 2 & "/(60*1000*4*" & Conduct & "*" &
MaxWeight & ")*" & FinalReactionSum
Else
Range(Cells(LastRow - j, TempCol), Cells(LastRow, TempCol)) = "=R" &
LastRow - j - 1 & "C" & Temp & "+(RC" & Time & "-R" & LastRow - j - 1 & "C" & Time & "-" & Cp
& "*" & rho & "*" & Ri ^ 2 & "/(60*1000*4*" & Conduct & "))*" & FinalTempRate & "-" & rho &
"*" & Ri ^ 2 & "/(60*1000*4*" & Conduct & ")*" & FinalReactionSum
End If
Else
Range(Cells(LastRow - j, TempCol), Cells(LastRow, TempCol)) = "=" &
FinalTempRate & "*(RC" & Time & "-R" & LastRow - j - 1 & "C" & Time & ")+(R" & LastRow - j - 1
& "C" & Temp & "-" & torr & "*" & FinalTempRate & "-" & FinalReactionSum & ")*(1-exp(-(RC" &
Time & "-R" & LastRow - j - 1 & "C" & Time & ")/" & torr & "))+R" & LastRow - j - 1 & "C*exp((RC" & Time & "-R" & LastRow - j - 1 & "C" & Time & ")/" & torr & ")"
End If
End If
' Generation of graph
Set X = Range(Cells(RowOffset, Time), Cells(LastRow, Time))
Set Y = Range(Cells(RowOffset, Temp), Cells(LastRow, Temp))
Set Z = Range(Cells(RowOffset, TempCol), Cells(LastRow, TempCol))
Charts.Add
With ActiveChart
.ChartType = xlXYScatterSmoothNoMarkers
.SetSourceData Source:=Union(X, Y, Z), PlotBy:=xlColumns

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Cells(AETableRow + 1 + 3 * (Process - 1), AETableCol + Mech - 1) = -Slope * R
Cells(AETableRow + 2 + 3 * (Process - 1), AETableCol + Mech - 1).Select
If Slope < 0 Then
    Intercept = Application.WorksheetFunction.Intercept(Y, X)
    ActiveCell.FormulaR1C1 = Intercept - Application.WorksheetFunction.Ln(R / (B * Cells(AETableRow + 1 + 3 * (Process - 1), AETableCol + Mech - 1)))
    FNumerator = 0
    FDenominator = 0
    For i = StartRow(Process - 1) To EndRow(Process - 1)
        FNumerator = FNumerator + (Cells(i, Yaxis) - Application.WorksheetFunction.Average(Range(Cells(StartRow(Process - 1), Yaxis), Cells(EndRow(Process - 1), Yaxis)))) * (Cells(i, ColOffset + 2 + 2 * HighMech + 1) - Application.WorksheetFunction.Average(Range(Cells(StartRow(Process - 1), ColOffset + 2 + 2 * HighMech + 1), Cells(EndRow(Process - 1), ColOffset + 2 + 2 * HighMech + 1))))
        FDenominator = FDenominator + (Cells(i, Yaxis) - (Slope * Cells(i, ColOffset + 2 + 2 * HighMech + 1) + Intercept)) ^ 2
    Next
    FStat(Mech - 1) = Slope * (EndRow(Process - 1) - StartRow(Process - 1) - 1) * FNumerator / FDenominator
    If FStat(Mech - 1) > FStatBest Then
        FStatBest = FStat(Mech - 1)
        FStatBestMech = Mech
    End If
Else
    ActiveCell.Value = ""
    Count = Count + 1
End If
Next

If all mechanisms yield positive slopes and therefore incalculable pre-
exponential factors, remove process from calculation
Highlight mechanism with the best F-statistic and those mechanisms within an
order of magnitude

If Count = HighMech Then
    InDataSet(Process - 1,Worksheets(SheetName).Index - 2) = -1
Else
    For Mech = 1 To HighMech
        Cells(AETableRow + 1 + 3 * (Process - 1), AETableCol + Mech - 1),
        Cells(AETableRow + 2 + 3 * (Process - 1), AETableCol + Mech - 1).Select
        If Mech = FStatBestMech Then
            Selection.Interior.ColorIndex = 6
        Else
            If FStat(Mech - 1) > FStat(FStatBestMech - 1) * 0.1 Then
                Selection.Interior.ColorIndex = 36
            Else
                Selection.Interior.ColorIndex = xlColorIndexNone
            End If
        End If
    Next
End If

If a row cannot be determined for the specified conversion, the affected row is set to
MaxData to facilitate its exclusion in the subsequent analysis

Sub IsoRow(Start As Integer, Finish As Integer, i As Integer)
' Searches for and stores rows for isoconversional analysis for data sheet i for the whole
' range of weight loss
' If a row cannot be determined for the specified conversion, the affected row is set to
' MaxData to facilitate its exclusion in the subsequent analysis

Dim j As Integer
Dim Isoconversion As Double
Dim Temp As Integer

For j = Start To Finish
    Isoconversion = Cells(i, j).Value
    If Isoconversion = "" Then
        Cells(i, j) = MaxData
        InDataSet(i,Worksheets(SheetName).Index - 2) = -1
        Exit Sub
    End If
Next
End Sub
For j = 1 To NoPoints
    Isoconversion = j * IsoconvMax / NoPoints
    IsoTemp = RowAssignment(ColOffset + 1, Start, Finish, Isoconversion, 0)
    If Cells(IsoTemp, ColOffset + 1) < Isoconversion Or IsoTemp < Start + (FilterN - 1) / 2 Or IsoTemp > Finish - (FilterN - 1) / 2 Then
        IsoconversionRow(j - 1, i - 1) = MaxData
    Else
        If Abs(Cells(IsoTemp, ColOffset + 1) - Isoconversion) < Abs(Cells(IsoTemp - 1, ColOffset + 1) - Isoconversion) Then
            IsoconversionRow(j - 1, i - 1) = IsoTemp
        Else
            IsoconversionRow(j - 1, i - 1) = IsoTemp - 1
        End If
    End If
Next
End Sub

Sub Friedman()
' Computes all steps required to yield activation energy as a function of conversion in accordance with the Friedman isoconversional method
' Results are graphed with error bars indicating the 95% confidence intervals in activation energies

    Const R = 8.314
    Dim PrintStart As Integer
    Dim X As Range
    Dim Y As Range
    Dim ErrorBarRange As Range
    Dim Slope As Double
    Dim Count As Integer
    Dim Chart As String


    ' Labelling on 'Summary' sheet
    Range(Cells(PrintStart - 2, 1), Cells(PrintStart - 2, 6)).Select
    With Selection
        .HorizontalAlignment = xlCenter
        .Font.Bold = True
        .Font.Size = 14
        .MergeCells = True
        .FormulaR1C1 = "FRIEDMAN ISOCONVERSIONAL ANALYSIS"
    End With

    For i = 1 To NoPoints
        Range(Cells(PrintStart, (i - 1) * 3 + 2), Cells(PrintStart, (i - 1) * 3 + 3)).Select
        With Selection
            .HorizontalAlignment = xlCenter
            .Font.Bold = True
            .Font.Size = 14
            .MergeCells = True
            .FormulaR1C1 = "1/T"
        End With
        Cells(PrintStart + 1, (i - 1) * 3 + 2).Select
        ActiveCell.FormulaR1C1 = "ln dalpha/dt"
        With Selection
            .HorizontalAlignment = xlLeft
            .Font.Bold = True
        End With
        Next
    End If
End Sub
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With Selection
  .HorizontalAlignment = xlLeft
  .Font.Bold = True
  .Font.Size = 14
End With
Cells(PrintStart + N + 3, 1).Select
ActiveCell.FormulaR1C1 = Chr(177) & "95% CI (J/mol)"
With Selection
  .HorizontalAlignment = xlLeft
End With
For i = 1 To N
  Cells(PrintStart + 1 + i, 1) = Cells(2 + i, HighMech + 6)
Next
Columns(1).EntireColumn.AutoFit

' Compute activation energy and 95% confidence interval for each conversion (if possible)
' from previously determined rows of data of the relevant columns
' Exclude any data points not found within data range, and sheets where a range for the
' process could not be set

For j = 1 To NoPoints
  Count = 0
  For i = 1 To N
    If IsoconversionRow(j - 1, i - 1) = MaxData Then
      Else
        Cells(PrintStart + 1 + i, (j - 1) * 3 + 2) = Sheets(i + 1).Cells(IsoconversionRow(j - 1, i - 1), ColOffset + 2 + 2 * HighMech + 1)
        Cells(PrintStart + 1 + i, (j - 1) * 3 + 3) = "=LN(" & Sheets(i + 1).Cells(IsoconversionRow(j - 1, i - 1), Graph) & ")"
        Count = Count + 1
    End If
  Next
  Set X = Range(Cells(PrintStart + 1 + 1, (j - 1) * 3 + 2), Cells(PrintStart + 1 + Count, (j - 1) * 3 + 2))
  Set Y = Range(Cells(PrintStart + 1 + 1, (j - 1) * 3 + 3), Cells(PrintStart + 1 + Count, (j - 1) * 3 + 3))
  If Count = N Then
    Slope = Application.WorksheetFunction.Slope(Y, X)
    Range(Cells(PrintStart + N + 2, (j - 1) * 3 + 2), Cells(PrintStart + N + 2, (j - 1) * 3 + 3)).Select
    With Selection
      .HorizontalAlignment = xlCenter
      .NumberFormat = "0"
      .MergeCells = True
      .FormulaR1C1 = -Slope * R
    End With
    Range(Cells(PrintStart + N + 3, (j - 1) * 3 + 2), Cells(PrintStart + N + 3, (j - 1) * 3 + 3)).Select
    With Selection
      .HorizontalAlignment = xlCenter
      .NumberFormat = "0"
      .MergeCells = True
      .FormulaLocal = "=INDEX(LINEST(" & Y.AddressLocal(False, False) & ",X," & Slope & ")", 2)"
    End With
  End If
Next

' Graphical presentation

Set X = Range(Cells(PrintStart, 2), Cells(PrintStart, (NoPoints - 1) * 3 + 2))
Set Y = Range(Cells(PrintStart + N + 2, 2), Cells(PrintStart + N + 2, (NoPoints - 1) * 3 + 2))
Set ErrorBarRange = Range(Cells(PrintStart + N + 3, (NoPoints - 1) * 3 + 2), Cells(PrintStart + N + 3, (NoPoints - 1) * 3 + 2))
Charts.Add
ActiveChart.ChartType = xlXYScatter
ActiveChart.SetSourceData Source:=Union(X, Y), PlotBy:=xlRows
ActiveChart.Location Where:=xlLocationAsObject, Name:="Summary"
With ActiveChart
  .HasTitle = True
  .ChartTitle.Characters.Text = "Friedman Plot"
  .Axes(xlCategory, xlPrimary).HasTitle = True
  .Axes(xlValue, xlPrimary).HasTitle = True
  .Axes(xlValue, xlPrimary).AxisTitle.Characters.Text = "Ea (J/mol)"
End With
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Sub ModelFitting()
' Shortcut: Ctrl + p
' Calculates and refines kinetic parameters, generates F-Statistics and relative probabilities
' for models and presents probabilities as a column graph
' Calls SolutionGraph() to generate charts to compare selected permutation(s) with
' experimental data

Const Scission As Integer = 17
Const R As Double = 8.314
Dim LastRow As Integer
Dim j As Integer
Dim k As Integer
Dim m As Integer
Dim Process As Integer
Dim Mech As Integer
Dim InvPT(HighProcess - 1, 1) As Double
Dim XStartRow(HighProcess - 1, MaxSheets - 1) As Integer
Dim XEndRow(HighProcess - 1, MaxSheets - 1) As Integer
Dim StartRow(HighProcess - 1, MaxSheets - 1) As Integer
Dim EndRow(HighProcess - 1, MaxSheets - 1) As Integer
Dim Sum(HighProcess - 1, MaxSheets - 1, HighMech ^ HighProcess - 1) As Double
Dim Sj(HighProcess - 1, MaxSheets - 1, HighMech ^ HighProcess - 1) As Double
Dim Sjave(HighProcess - 1, HighMech ^ HighProcess - 1) As Double
Dim Smin(HighProcess - 1) As Double
Dim OtherProcess As Integer
Dim Residual As Double
Dim Remainder As Double
Dim Viable(HighMech ^ HighProcess - 1) As Boolean
Dim PermutMech(HighProcess - 1) As Integer
Dim Permutation(HighProcess - 1) As Integer
Dim Fj(HighProcess - 1, HighMech - 1) As Double
Dim PjRev As Double
Dim Pj(HighProcess - 1, HighMech - 1) As Double
Dim Formulaf As String
Dim Formula(HighMech - 1) As String
Dim Formula1(HighMech - 1) As String
Dim AlphaOverall As String
Dim dalphadtOverall As String
Dim XFraction(HighProcess - 1, MaxSheets - 1) As Double
Dim XPrevious(HighProcess - 1) As Double
Dim Variance(2) As Double
Dim Experimental(2) As Double
Dim Xf(2) As Double
Dim Xmin As Integer
Dim Continue As Boolean
Dim Insignificant As Boolean
Dim Halve As Boolean
Dim RateEquation As String
Dim Unconverged As Boolean
Dim Unconverged1 As Boolean
Dim AlphaKinetic As Double
Dim AlphaKinetic1 As Double
Dim AlphaLessThan1 As Boolean
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Dim CompStart(MaxSheets - 1) As Integer
Dim CompEnd(MaxSheets - 1) As Integer
Dim Rate(HighProcess - 1, HighMech - 1, MaxSheets - 1, MaxData - 1) As String
Dim AlphaMech(HighProcess - 1, HighMech - 1, MaxSheets - 1, MaxData - 1) As Double
Dim FindFormula As Integer
Dim TotalNonActive As Integer
Dim Overlap(HighProcess - 1, HighMech - 1) As Boolean
Dim Einv(HighProcess - 1) As Double
Dim Ainv(HighProcess - 1) As Double
Dim aAve(HighProcess - 1, HighMech - 1) As Double
Dim Tj As Integer
Dim Texp(HighProcess - 1, MaxSheets - 1) As Double
Dim TMin(HighProcess - 1, HighMech - 1) As Double
Dim TMax(HighProcess - 1, HighMech - 1) As Double
Dim TempComp(HighProcess - 1, MaxSheets - 1) As Integer
Dim TempComp1 As Integer
Dim TempComp2 As Integer
Dim Curvature(HighProcess - 1, HighMech - 1, MaxSheets - 1, MaxData - 1) As Double
Dim CurvatureMaximum(HighProcess - 1, HighMech - 1, MaxSheets - 1) As Double
Dim CurvatureMinimum(HighProcess - 1, HighMech - 1, MaxSheets - 1) As Double
Dim AlphaMechLow(HighProcess - 1, HighMech - 1, MaxSheets - 1) As Integer
Dim AlphaMechHigh(HighProcess - 1, HighMech - 1, MaxSheets - 1) As Integer
Dim NoSheets(HighProcess - 1, HighMech - 1) As Integer
Dim ShapeAlpha(HighProcess - 1, HighMech - 1, MaxSheets - 1) As Boolean
Dim Factor(HighProcess - 1, HighMech - 1, 2) As Double
Dim FactorA(HighProcess - 1, HighMech - 1) As Double
Dim E(HighProcess - 1, HighMech - 1) As Double
Dim A(HighProcess - 1, HighMech - 1) As Double
Dim Diverged As Boolean
Dim LoopCount As Integer
Dim Convergence(HighProcess - 1, HighMech - 1) As Boolean
Dim Fail(HighProcess - 1, HighMech - 1) As Boolean
Dim Multiple As Integer
Dim MaxCurv As Double
Dim MinCurv As Double
Dim AllFail As Boolean
Dim SheetCount(HighProcess - 1) As Integer
Dim NoneOverlapping As Boolean
Dim aAveBest(HighProcess - 1) As Double
Dim EFail(HighProcess - 1, HighMech - 1) As Double
Dim AFail(HighProcess - 1, HighMech - 1) As Double
Dim AStart(HighProcess - 1, HighMech - 1) As Double
Dim AEstimate As Double
Dim Weight As Double
Dim Weighting(HighProcess - 1, HighMech - 1, MaxSheets - 1, MaxData - 1) As Double
Dim ARatio As Double
Dim Pair(HighProcess - 1, HighMech - 1, 2) As Double
Dim Fmin(HighProcess - 1, HighMech - 1) As Double
Dim IntervalHalved(HighProcess - 1, HighMech - 1) As Boolean
Dim WeightingA(HighProcess - 1, HighMech - 1) As Double
Dim RefineA As Boolean
Dim PopUpString As String
Dim StringSection(HighProcess - 1) As String
Dim PopUp As Boolean
Dim FirstMech As Boolean
Dim FirstSheet As Boolean
Dim IKP As Integer
Dim Remove(HighProcess - 1) As Boolean
Dim Active(HighProcess - 1, HighMech - 1, MaxSheets - 1, 1) As Integer
Dim BondFraction(HighProcess - 1, MaxSheets - 1, MaxData - 1) As Double
Dim Resolved(HighProcess - 1, HighMech - 1, 2) As Boolean
Dim EError(HighProcess - 1, HighMech - 1) As Double
Dim AREs(HighProcess - 1, HighMech - 1) As Double
Dim Pnumerator As Double
Dim FDenominator As Double
Dim FStat(HighMech - 1, 1) As Double
Dim FStatBest(1) As Double
Dim FStatBestMech(1) As Integer
Dim F95 As Double
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```vba
Dim gAverage As Double
Dim RefineKP As Integer
Dim UserKP As Integer
Dim Mechanism(HighProcess - 1) As Integer
Dim Default(HighProcess - 1) As Integer
Dim NewSolution As Integer
Dim MechCode As String
Dim PriorMech(HighProcess - 1) As Integer
Dim Chart As String
Dim MaxRate As Double
Dim MinRate As Double
Dim Nature(HighProcess - 1, HighMech, MaxSheets - 1) As Integer
Dim Include(HighProcess - 1, MaxSheets - 1) As Boolean
Dim RateMinimum(HighProcess - 1, HighMech - 1, MaxSheets - 1) As Double
Dim RateMaximum(HighProcess - 1, HighMech - 1, MaxSheets - 1) As Double
Dim RateRange As Range
Dim CurvRange As Range
Application.ScreenUpdating = False
SampleT = ColOffset + 2 + 2 * HighMech + 2 + HighMech + 1
Graph = SampleT + 2
dalphadt = Graph + HighProcess + 1
Alpha = dalphadt + HighProcess + 1

' Collection of computational requirements and user requests for computations
' Previous results are moved to the right rather than deleted to facilitate comparison
' (Data must be manually moved if more than just the previous results are wished to be retained)

' If user is to input kinetic parameters, the compensation effect for the first sheet is used to suggest a reasonable pre-exponential factor for each activation energy

Sheets("Summary").Select
If StoredData = False Then
    CellHeight = ActiveSheet.Cells(1, 1).Height
    For Process = 1 To HighProcess
        If Cells(5 + N + Process, HighMech + 7).Value = "" Then
            IKPExist(Process - 1) = False
        Else
            IKPExist(Process - 1) = True
        End If
    Next
    For i = 1 To N
        SevereOverlap(i - 1) = True
    Next
    End If
    If Cells(8 + N + HighProcess + 1, HighMech + 7).Value = "" Then
    Cells(11 + N + HighProcess + HighProcess + HighMech + 2, HighMech + 7) = "= Most Probable Mechanism"
    Cells(11 + N + HighProcess + HighProcess + HighMech + 2, HighMech + 10) = "= Within 95% Confidence Interval"
    Else
    End If
    For Process = 1 To HighProcess
        If IKPExist(Process - 1) Then
            Einv(Process - 1) = Cells(5 + N + Process, HighMech + 7)
            Ainv(Process - 1) = Cells(5 + N + Process, HighMech + 9)
        End If
    Next
    IKP = MsgBox("Use invariant kinetic parameters to judge mechanism suitability?", vbYesNo + vbQuestion, "Invariant Kinetic Parameters")
    If IKP = vbNo Then
        UserKP = MsgBox("Enter in your own estimates for activation energy and pre-exponential factor?", vbYesNo + vbQuestion + vbDefaultButton2, "User-Defined Kinetic Parameters")
        If UserKP = vbYes Then
            For Process = 1 To HighProcess
            ' Code for further processing...
            End If
        End If
    End If
```
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\[ E_{\text{inv}}(\text{Process} - 1) = \text{InputBox("Activation Energy for Process " & Process & ") , "User-Defined Kinetic Parameters", Format(E_{\text{inv}}(\text{Process} - 1), 0))} \]
\[ A_{\text{E}} = \text{Exp(Cells(3, HighMech + 7 + 2 * (Process - 1)) * E_{\text{inv}}(\text{Process} - 1) + Cells(3, HighMech + 8 + 2 * (Process - 1)))} \]
\[ A_{\text{inv}}(\text{Process} - 1) = \text{InputBox("Pre-exponential Factor for Process " & Process & ", "User-Defined Kinetic Parameters", Format(A_{\text{E}}, "Scientific"))} \]

Next

Else

OK = MsgBox("Averaged apparent kinetic parameters will be used", vbOKOnly + vbInformation, "Apparent Kinetic Parameters")
End If
End If

RefineKP = MsgBox("Attempt to refine these kinetic parameters with model fitting?", vbYesNo + vbQuestion, "Model Fitting")
WholeRange = MsgBox("Use the entire conversion range for calculating statistics?", vbYesNo + vbQuestion, "Statistical Analysis")

' Labelling

Cells(7 + N + HighProcess, HighMech + 6).Select
With Selection
  .FormulaR1C1 = "Kinetic Parameters Associated with Most Probable Mechanism"
  .Font.Bold = True
End With
Cells(8 + N + HighProcess, HighMech + 7).Select
With Selection
  .FormulaR1C1 = "E_{j*} (J/mol)"
  .Font.Bold = True
  .HorizontalAlignment = xlCenter
End With
Cells(8 + N + HighProcess, HighMech + 8).Select
With Selection
  .FormulaR1C1 = "A_{j*} (min^{-1})"
  .Font.Bold = True
  .HorizontalAlignment = xlCenter
End With

ActiveCell.Characters(Start:=9, Length:=2).Font.Superscript = True
Cells(8 + N + HighProcess, HighMech + 9).Select
With Selection
  .FormulaR1C1 = "E_{j*} Resolution Limit (J/mol)"
  .Font.Bold = True
End With

With Selection
  .HorizontalAlignment = xlCenter
  .Font.Bold = True
  .MergeCells = True
  .ShrinkToFit = True
  .FormulaR1C1 = "Non-Linear Relative Prob"
End With

With Selection
  .HorizontalAlignment = xlCenter
  .Font.Bold = True
  .MergeCells = True
  .ShrinkToFit = True
End With

If IKP = vbYes Then
  Selection.FormulaR1C1 = "F-Statistic (IKP)"
Else
  If UserKP = vbYes Then
    Selection.FormulaR1C1 = "F-Statistic (User)"
  Else
    Selection.FormulaR1C1 = "F-Statistic (App)"
  End If
End If

End If

If RefineKP = vbYes Then
  With Selection
    .HorizontalAlignment = xlCenter
    .Font.Bold = True
    .MergeCells = True
    .ShrinkToFit = True
    .FormulaR1C1 = "F-Statistic (Ref)"
  End With
End If

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End With
For Process = 1 To HighProcess
  ActiveCell.FormulaR1C1 = "Fj" & Process
  With Selection
    .Font.Bold = True
    .HorizontalAlignment = xlCenter
  End With
Next
Cells(11 + N + HighProcess + HighProcess + HighProcess + HighMech + 3, HighMech + 6) = Chr(176) & "Unrefined E, Unrefined A; " & Chr(185) & "Unrefined E, Refined A; " & Chr(178) & "Refined E, Refined A"
With Selection
  .FormulaR1C1 = "E Within 95% Confidence Interval of Einv"
  .Font.Bold = True
End With
End If
For Process = 1 To HighProcess
  Cells(8 + N + HighProcess + Process, HighMech + 6).Select
  With Selection
    .FormulaR1C1 = "Process " & Process
    .Font.Bold = True
    .HorizontalAlignment = xlRight
  End With
Next
For Mech = 1 To HighMech
  With Selection
    .FormulaR1C1 = "Pj" & Process
    .Font.Bold = True
    .HorizontalAlignment = xlCenter
  End With
Next
For i = 1 To N
 Worksheets(i + 1).Select
  LastRow = Cells(RowOffset, Time).End(xlDown).Row
  For Process = 1 To HighProcess
    If StoredData = False Then
      If Cells(LastRow + 2, Alpha + Process).Value = "" Then
        InDataSet(Process - 1, i - 1) = -1
      Else
        LowerCompLimit(Process - 1) = Cells(LastRow + 2, Alpha + Process).Value
        UpperCompLimit(Process - 1) = Cells(LastRow + 3, Alpha + Process).Value
        If Cells(LastRow, Alpha + Process).Value < 1 Then
          InDataSet(Process - 1, i - 1) = 0
        Else
          InDataSet(Process - 1, i - 1) = 1
        End If
      End If
    End If
  Next
End If
End If
For i = 1 To N
 Worksheets(i + 1).Select
  LastRow = Cells(RowOffset, Time).End(xlDown).Row
  For Process = 1 To HighProcess
    If StoredData = False Then
      If Cells(LastRow + 2, Alpha + Process).Value = "" Then
        InDataSet(Process - 1, i - 1) = -1
      Else
        LowerCompLimit(Process - 1) = Cells(LastRow + 2, Alpha + Process).Value
        UpperCompLimit(Process - 1) = Cells(LastRow + 3, Alpha + Process).Value
        If Cells(LastRow, Alpha + Process).Value < 1 Then
          InDataSet(Process - 1, i - 1) = 0
        Else
          InDataSet(Process - 1, i - 1) = 1
        End If
      End If
    End If
  Next
End If
End If
If (InDataSet(Process - 1, i - 1) = -1) = False Then

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XFraction(Process - 1, i - 1) = Sheets("Summary").Cells(i + 3 * (i - 1) * 
HighProcess + 2 + 3 * (Process - 1), HighMech + 4) 
XStartRow(Process - 1, i - 1) = RowAssignment(Alpha + Process, LastRow, 
RowOffset, XPrecision, 0) 
XEndRow(Process - 1, i - 1) = RowAssignment(Alpha + Process, XStartRow(Process 
- 1, i - 1), LastRow, 1 - XPrecision, 0) 
XStartRow(Process - 1, i - 1), XEndRow(Process - 1, i - 1), Cells(LastRow + 2, Alpha + Process).Value, 1 
EndRow(Process - 1, i - 1) = RowAssignment(Alpha + Process, XStartRow(Process 
- 1, i - 1), Cells(LastRow + 3, Alpha + Process).Value, 
InDataSet(Process - 1, i - 1)) 
Call Derivative(Alpha + Process, Time, StartRow(Process - 1, i - 1), 
EndRow(Process - 1, i - 1), Alpha + HighProcess + Process) 
Call Derivative(Alpha + HighProcess + Process, Time, StartRow(Process - 1, i - 1), 
EndRow(Process - 1, i - 1), Alpha + HighProcess + HighProcess + Process) 
If StoredData = False Then 
Call MechAssignment(Process, StartRow(Process - 1, i - 1), EndRow(Process 
- 1, i - 1)) 
End If 
If EndRow(Process - 1, i - 1) - StartRow(Process - 1, i - 1) < 2 * (FilterN - 
1) Then 
If RefineKP Then 
OK = MsgBox("The computational range " & Format(LowerCompLimit(Process 
- 1), 0) & "-% is too small for refinement", vbOKOnly + vbWarning, "Process " & Process & "; Sheet " & Worksheets(i + 1).Name) 
InDataSet(Process - 1, i - 1) = -1 
End If 
End If 
End If 
Next 
Next 

' Collection and preparation of mechanism formulae from cells filled by Apparent() in the 
' first sheet for the last process 
' Exclude the random scission model with variable L as it has no analytical function fj 
' applicable for all conversions, and gj is printed as a number 
Worksheets(2).Select 
LastRow = Cells(RowOffset, Time).End(xlDown).Row 
Process = HighProcess 
Do 
If (InDataSet(Process - 1, 0) = -1) = False Then 
For Mech = 1 To HighMech 
If Mech = Scission Then 
Else 
Formula(Mech - 1) = Cells(StartRow(Process - 1, 0), ColOffset + 1 + 2 * 
Mech).FormulaR1C1 
ForCol = 1 To ColOffset + 1 
"RC" & ColOffset + 1) 
Formula(Mech - 1) = Right(Formula(Mech - 1), Len(Formula(Mech - 1)) - 1) 
Formula(Mech - 1) = Replace(Formula(Mech - 1), "RC" & Alpha + Process, 
"RC" & ColOffset + 1) 
Formula(Mech - 1) = Replace(Formula(Mech - 1), "RC" & Alpha + Process, 
"C[1]", Cells(RowOffset - 3, ColOffset + 1 + 2 * Mech + 1).Address(True, False)) 
Formula1(Mech - 1) = Cells(RowOffset - 3, ColOffset + 1 + 2 * Mech + 1)) 
Formula1(Mech - 1) = Replace(Formula1(Mech - 1), "RC" & Alpha + Process, 
"RC" & ColOffset + 1) 
Formula1(Mech - 1) = Replace(Formula1(Mech - 1), "RC" & Alpha + Process, 
"C", Cells(RowOffset - 3, ColOffset + 1 + 2 * Mech + 1).Address(True, False)) 
End If 
Next 
Else 
Process = Process - 1 
End If 
Loop While Formula(0) = ""

' Initialisations 
RefineA = True 
LoopCount = 0 
For Process = 1 To HighProcess 
Remove(Process - 1) = True 
For Mech = 1 To HighMech 
If Mech = Scission And Sheets("Summary").Cells(3, Mech + 1) = "" Then
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Shape(Process - 1, Mech - 1) = False
Else
    Shape(Process - 1, Mech - 1) = True
End If
Factor(Process - 1, Mech - 1, 1) = 1
Convergence(Process - 1, Mech - 1) = False
Fail(Process - 1, Mech - 1) = False
IntervalHalved(Process - 1, Mech - 1) = False
EError(Process - 1, Mech - 1) = 0
Fmin(Process - 1, Mech - 1) = 1
For i = 0 To 2
    Resolved(Process - 1, Mech - 1, i) = True
Next
' Allow computation with apparent kinetic parameters for sheets with useable data
' if invariant kinetic parameters could not be calculated but were requested
If (IKP = vbYes And IKPExist(Process - 1)) Or (IKP = vbNo And UserKP = vbYes) Then
    Remove(Process - 1) = False
    E(Process - 1, Mech - 1) = Einv(Process - 1)
    A(Process - 1, Mech - 1) = Ainv(Process - 1)
Else
    ' Average apparent kinetic parameters across all valid heating rates
    ' Omission of process if no sheets contain useable data or pre-exponential
    ' factor cannot be calculated for any mechanism
    E(Process - 1, Mech - 1) = 0
    A(Process - 1, Mech - 1) = 0
    Count = 0
    For i = 1 To N
        If InDataSet(Process - 1, i - 1) = -1 Then False Then
            If Sheets("Summary").Cells(i + 3 * (i - 1) * HighProcess + 1 + 3 * (Process - 1), Mech + 1) > 0 Then
                E(Process - 1, Mech - 1) = E(Process - 1, Mech - 1) +
                Sheets("Summary").Cells(i + 3 * (i - 1) * HighProcess + 1 + 3 * (Process - 1), Mech + 1)
                A(Process - 1, Mech - 1) = A(Process - 1, Mech - 1) +
                Sheets("Summary").Cells(i + 3 * (i - 1) * HighProcess + 2 + 3 * (Process - 1), Mech + 1)
                Count = Count + 1
            End If
        End If
    Next
    If Count = 0 Then
        Else
            If A(Process - 1, Mech - 1) / Count > 700 Then
                OK = MsgBox("Pre-exponential factor is too large for mechanism ", vbCritical, "Mechanism Failure")
                For i = 1 To N
                    InDataSet(Process - 1, i - 1) = -1
                Next
                Else
                    Remove(Process - 1) = False
                    E(Process - 1, Mech - 1) = E(Process - 1, Mech - 1) / Count
                    A(Process - 1, Mech - 1) = Exp(A(Process - 1, Mech - 1) / Count)
                End If
            End If
        End If
    End If
End If
' Initialise and store the fail defaults for the refinement process
EFail(Process - 1, Mech - 1) = E(Process - 1, Mech - 1)
AFail(Process - 1, Mech - 1) = A(Process - 1, Mech - 1)
ARes(Process - 1, Mech - 1) = A(Process - 1, Mech - 1)
AStart(Process - 1, Mech - 1) = A(Process - 1, Mech - 1)
Next
' Notify the user of a change to the requested computation method
If IKP = vbYes And IKPExist(Process - 1) = False And Remove(Process - 1) = False Then
    Cells(11 + N + HighProcess + HighProcess + HighMech + 4, HighMech + 6) = "^IKP unavailable; averaged apparent kinetic parameters used"
End If
If Remove(Process - 1) Then
    OK = MsgBox("Process " & Process & " & Process & " must be omitted from computation as no kinetic parameters are available", vbCritical, "Process " & Process & " & Process & " Failure")
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For i = 1 To N
    AlphaLimit(Process - 1, i - 1, 0) = LowerCompLimit(Process - 1)
    AlphaLimit(Process - 1, i - 1, 1) = UpperCompLimit(Process - 1)
    If (InDataSet(Process - 1, i - 1) = -1) = False Then
        Worksheets(i + 1).Select
        Zero(Process - 1, 0, i - 1) = False
        Set CurvRange = Range(Cells(StartRow(Process - 1, i - 1) + (FilterN - 1), Alpha + HighProcess + Process), Cells(EndRow(Process - 1, i - 1) - (FilterN - 1), Alpha + HighProcess + Process))
        Set RateRange = Range(Cells(StartRow(Process - 1, i - 1) + (FilterN - 1), Alpha + Process), Cells(EndRow(Process - 1, i - 1) - (FilterN - 1), Alpha + HighProcess + Process))
        MaxCurv = Application.WorksheetFunction.Max(CurvRange)
        MinCurv = Application.WorksheetFunction.Min(CurvRange)
        MaxRate = Application.WorksheetFunction.Max(RateRange)
        If Sgn(MaxCurv) = -Sgn(MinCurv) Then
            Nature(Process - 1, 0, i - 1) = 2
            Zero(Process - 1, 0, i - 1) = True
            TempComp(Process - 1, i - 1) = RowAssignment(Alpha + HighProcess + Process, StartRow(Process - 1, i - 1) + (FilterN - 1), EndRow(Process - 1, i - 1) - (FilterN - 1), MaxRate - Abs(MaxRate) * 10 ^ (-6), 0)
            Multiple = 0
            j = StartRow(Process - 1, i - 1) + (FilterN - 1)
            Do
                If (Cells(j, Alpha + HighProcess + Process) > 0 And Cells(j + 1, Alpha + HighProcess + Process) < 0) Or (Cells(j, Alpha + HighProcess + Process) < 0 And Cells(j + 1, Alpha + HighProcess + Process) > 0) Then
                    Multiple = Multiple + 1
                End If
                j = j + 1
            Loop While j < EndRow(Process - 1, i - 1) + (FilterN - 1)
        End If
        If Multiple > 1 Then
            Charts.Add
            ActiveChart.ChartType = xlLine
            ActiveChart.SetSourceData Source:=Union(RateRange, CurvRange), PlotBy:=xlColumns
            ActiveChart.Location Where:=xlLocationAsObject, Name:=Worksheets(i + 1).Name
            ActiveChart.SeriesCollection(1).Name = "Rate"
            ActiveChart.SeriesCollection(2).Name = "Curvature"
            With ActiveChart
                .HasTitle = True
                .ChartTitle.Characters.Text = "Rate and Curvature vs. Row"
                .Axes(xlCategory, xlPrimary).HasTitle = False
                .Axes(xlValue, xlPrimary).HasTitle = False
            End With
            With ActiveChart.Axes(xlCategory)
                .HasMajorGridlines = False
                .HasMinorGridlines = False
            End With
            With ActiveChart.Axes(xlValue)
                .HasMajorGridlines = False
                .HasMinorGridlines = False
            End With
            ActiveChart.SeriesCollection(2).Select
            With Selection
                .MarkerStyle = xlNone
                .AxisGroup = 2
            End With
            ActiveChart.ChartArea.Select
            Application.ScreenUpdating = True
        End If
    End If
End For

End If

' Specification of the nature of the curvature: 0 - positive; 1 - negative; 2 - mixed
' Identification of row(s) where the curvature is zero with respect to conversion
' (functional maximum rate) within computational range
' If multiple zeros exist, either the row of maximum rate is assigned, or the noise is
' accepted as excessive and the data is treated as if there were no zeros
' The curvature and rate signals are shown to assist the user with this decision
' If a zero is not identified within this range, the row equal to the average of the
' maximum and minimum rates is calculated and identified in its place
' A decreasing rate must be searched in the opposite sense for an intermediate point
' (i.e. an average value)
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0) & ".& Chr(13) & Chr(13) & "Use the average of the maximum and minimum rates instead of the row corresponding to maximum rate?", vbYesNo, "Potentially Excessive Noise")
Application.ScreenUpdating = False
ActiveWindow.Visible = False
'Selection.Delete
End If
If Multiple = vbYes Then
Zero(Process - 1, 0, i - 1) = False
End If
Else
If MinCurv > 0 Then
Nature(Process - 1, 0, i - 1) = 0
Else
Nature(Process - 1, 0, i - 1) = 1
End If
End If
If Zero(Process - 1, 0, i - 1) = False Then
MinRate = Application.WorksheetFunction.Min(RateRange)
If Cells(StartRow(Process - 1, i - 1) + (FilterN - 1), Alpha + HighProcess + Process) < Cells(EndRow(Process - 1, i - 1) - (FilterN - 1), Alpha + HighProcess + Process)
Then
TempComp1 = RowAssignment(Alpha + HighProcess + Process, StartRow(Process - 1, i - 1) + (FilterN - 1), EndRow(Process - 1, i - 1) - (FilterN - 1), (MaxRate + MinRate) / 2, 0)
TempComp2 = RowAssignment(Alpha + HighProcess + Process, TempComp1, StartRow(Process - 1, i - 1) + (FilterN - 1), (MaxRate + MinRate) / 2, 0)
End If
Else
TempComp1 = RowAssignment1(Alpha + HighProcess + Process, StartRow(Process - 1, i - 1) + (FilterN - 1), EndRow(Process - 1, i - 1) - (FilterN - 1), (MaxRate + MinRate) / 2, 0)
TempComp2 = RowAssignment1(Alpha + HighProcess + Process, TempComp1, StartRow(Process - 1, i - 1) + (FilterN - 1), (MaxRate + MinRate) / 2, 0)
End If
If Abs(Cells(TempComp1, Alpha + HighProcess + Process) - (MaxRate + MinRate) / 2) < Abs(Cells(TempComp2, Alpha + HighProcess + Process) - (MaxRate + MinRate) / 2)
Then
TempComp(Process - 1, i - 1) = TempComp1
Else
TempComp(Process - 1, i - 1) = TempComp2
End If
End If

' Collection of the rates and temperatures (if necessary) that correspond to these critical points
' The computational range is readjusted so a better comparison can be made to each model (Important for poorly resolved data or long filters)
aj0(Process - 1, i - 1) = Cells(TempComp(Process - 1, i - 1), Alpha + HighProcess + Process)
If RefineKP = vbYes Then
Temp(Process - 1, i - 1) = Cells(TempComp(Process - 1, i - 1), SampleT)
End If
If AlphaLimit(Process - 1, i - 1, 0) = Cells(StartRow(Process - 1, i - 1) + (FilterN - 1), Alpha + Process)
Else
If AlphaLimit(Process - 1, i - 1, 1) = Cells(EndRow(Process - 1, i - 1) - (FilterN - 1), Alpha + Process)
Else
' Setting Zero to false if the process was not identified in data set to avoid runtime errors in subsequent calculations
Zero(Process - 1, 0, i - 1) = False
End If
Next

' If a maximum is to be aligned for any sheet, all sheets that do not utilise a maximum are not used for optimization
Continue = False
For i = 1 To N
Include(Process - 1, i - 1) = True
If Zero(Process - 1, 0, i - 1) Then
Continue = True
End If
Next
If Continue Then
For i = 1 To N
If Zero(Process - 1, 0, i - 1) = False Then
Include(Process - 1, i - 1) = False
End If
Next
End If
Next

' Loop for calculation, shape assessment and refinement of predicted conversion, rate and ' curvature for each model
' Those mechanisms that pass the shape assessment are refined on subsequent passes until ' convergence (if refinement requested)
Do
PopUpString = ""
For i = 1 To N
Worksheets(i + 1).Select
LastRow = Cells(RowOffset, Time).End(xlDown).Row
For Process = 1 To HighProcess
If Remove(Process - 1) = False Then
If Shape(Process - 1, Scission - 1) And Convergence(Process - 1, Scission - 1) = False Then
For j = RowOffset To LastRow
BondFraction(Process - 1, i - 1, j) = 0
Next
End If
For Mech = 1 To HighMech
If Shape(Process - 1, Mech - 1) And Convergence(Process - 1, Mech - 1) = False Then
' Initialisation
For j = RowOffset To LastRow
AlphaMech(Process - 1, Mech - 1, i - 1, j) = 0
Rate(Process - 1, Mech - 1, i - 1, j) = ""
Curvature(Process - 1, Mech - 1, i - 1, j) = 0
Next
If Mech = ProutTompkins Then
AlphaMech(Process - 1, Mech - 1, i - 1, RowOffset) = Exp(-Cells(RowOffset - 3, ColOffset + 2 + 2 * Mech)) / (1 + Exp(-Cells(RowOffset - 3, ColOffset + 2 + 2 * Mech)))
Insignificant = False
Active(Process - 1, Mech - 1, i - 1, 0) = RowOffset
Else
Insignificant = True
End If
AlphaLessThan1 = True
Halve = False
Zero(Process - 1, Mech, i - 1) = False
CurvatureComp(Process - 1, Mech - 1, i - 1) = j - 2
AlphaMechLow(Process - 1, Mech - 1, i - 1) = j - 2
Alpha MechHigh(Process - 1, Mech - 1, i - 1) = j - 2
' Calculation of predicted kinetic curves using midpoint numerical ' integration
' For all but the P-T mechanism, conversion is assumed to be zero ' initially; a first guess for the second row is conversion = ' XPrecision ' If the model equation generates an error before solution ' convergence for the initialisation, conversion is set to zero ' and the process is repeated for the next row ' Conversion is never allowed to exceed one
' Random scission with variable L model is dependent on a first ' order reaction solution set ' If the kinetic parameters are the same for this and the first ' order reaction, conversion and rate can be calculated explicitly
j = RowOffset + 1
Do
If Mech = Scission Then
If A(Process - 1, Scission - 1) = A(Process - 1, FirstOrder - 1) Then
BondFraction(Process - 1, i - 1, j) =
Formulaf = "(" & ChainLength(Cells(j, SampleT)) & ")^" & BondFraction(Process - 1, i - 1, j) & ")^" & ChainLength(Cells(j, SampleT)) & "^"
Else
If Insignificant Then
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Formulaf = Replace(Formula(FirstOrder - 1), "RC" & ColOffset + 1, XPrecision / 2)
Else
Formulaf = Replace(Formula(FirstOrder - 1), "RC" & ColOffset + 1, BondFraction(Process - 1, i - 1, j - 1))
End If
Else
If Insignificant Then
Formulaf = Replace(Formula(Mech - 1), "RC" & ColOffset + 1, AlphaMech(Process - 1, i - 1, j - 1))
Else
Formulaf = Replace(Formula(Mech - 1), "RC" & ColOffset + 1, AlphaMech(Process - 1, Mech - 1, i - 1, j - 1))
End If
End If
If Mech = Scission And A(Process - 1, Scission - 1) = A(Process - 1, FirstOrder - 1) Then
Else
RateEquation = A(Process - 1, Mech - 1) & "*Exp(-" & E(Process - 1, Mech - 1) & "/" & R & ")" + Evaluate(RateEquation) * (Cells(j, Time) - Cells(j - 1, Time))
If IsError(Evaluate(RateEquation)) Then
AlphaKinetic = 1
Else
If Mech = Scission Then
AlphaKinetic = BondFraction(Process - 1, i - 1, j - 1) + Evaluate(RateEquation) * (Cells(j, Time) - Cells(j - 1, Time))
Else
AlphaKinetic = AlphaMech(Process - 1, Mech - 1, i - 1, j - 1) + Evaluate(RateEquation) * (Cells(j, Time) - Cells(j - 1, Time))
End If
End If
If AlphaKinetic > 1 Then
AlphaKinetic = 1
End If
End If
End If
If AlphaKinetic > 1 Then
AlphaKinetic = 1
End If
End If
If Mech = Scission Then
AlphaKinetic = BondFraction(Process - 1, i - 1, j - 1) + Evaluate(RateEquation) * (Cells(j, Time) - Cells(j - 1, Time))
Else
AlphaKinetic = AlphaMech(Process - 1, Mech - 1, i - 1, j - 1) + Evaluate(RateEquation) * (Cells(j, Time) - Cells(j - 1, Time))
End If
End If
End If
End If
End If
End If
End If

' Convergence is satisfied when the current and previous solutions are within 5 significant figures
' A notice is displayed if the initialization step does not converge on the first iteration, but processing is continued
' If the process is acceleratory, the average of the current and previous solutions is used for the next iteration
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If \[\text{Abs}(\text{AlphaKinetic1} - \text{AlphaKinetic}) \leq (\text{AlphaKinetic1} \times 10^{-5}) \text{ Or Count} > 100\] Then

\[\text{If Count} > 100 \text{ And Insignificant} \text{ And } \text{AlphaKinetic1} > 0 \text{ And LoopCount} = 0\] Then

\[\text{PopUpString} = \text{PopUpString} & \text{Worksheets(i + 1).Name} & ", \text{P"} & \text{Process} & ", \" & \text{Cells(RowOffset - 2, ColOffset + 1 + 2 * Mech)} & \" & \text{Format(}\text{Abs(AlphaKinetic1 - AlphaKinetic)}, \"\text{Scientific}\"\) & \" with a tolerance of \" & \text{Format(}\text{Abs(AlphaKinetic1 - AlphaKinetic)}, \"\text{Scientific}\") & \text{Chr(13)}\]

Else

\[\text{AlphaKinetic} = \text{AlphaKinetic1}\]

End If

Unconverged = False

Else

\[\text{If AlphaKinetic < AlphaKinetic1 Or Halve} \text{ Then}\]

\[\text{Halve} = \text{True}\]

\[\text{AlphaKinetic} = (\text{AlphaKinetic} + \text{AlphaKinetic1}) / 2\]

Else

\[\text{AlphaKinetic} = \text{AlphaKinetic1}\]

End If

End If

Count = Count + 1

Loop While Unconverged

If Mech = Scission Then

\[\text{BondFraction(Process - 1, i - 1, j) = AlphaKinetic}\]

\[\text{Formulaf} = \text{(\" & \text{ChainLength(Cells(j, SampleT))} & \" - 1) * (1 - \text{BondFraction(Process - 1, i - 1, j)}\]

\[\text{(ChainLength(Cells(j, SampleT)) - 1))}\]

End If

End If

If AlphaKinetic > 0 And AlphaKinetic < 1 Then

If Insignificant Then

\[\text{Active(Process - 1, Mech - 1, i - 1, 0) = j}\]

Else

\[\text{Formulaf} = \text{Replace(Formula(Mech - 1), \"RC\" & \text{ColOffset} + 1, \text{AlphaKinetic})}\]

\[\text{Rate(Process - 1, Mech - 1, i - 1, j) = A(Process - 1, Mech - 1) \times \text{Exp(-E(Process - 1, Mech - 1) / (R * (Cells(j, SampleT).Address(False, True) & \"273.16\") \times (\text{BondFraction(Process - 1, Mech - 1, i - 1, j) - AlphaLimit(Process - 1, i - 1, 0)) \times \text{Abs(AlphaMech(Process - 1, Mech - 1, i - 1, j) - AlphaLimit(Process - 1, i - 1, 0)) \times \text{Curvature(Process - 1, Mech - 1, i - 1, k) = Evaluate(Rate(Process - 1, Mech - 1, i - 1, j) \times E(Process - 1, Mech - 1) / (R * (Cells(k, SampleT) + 273.16) ^ 2) * Cells(k, ColOffset + 2) + A(Process - 1, Mech - 1) * Exp(-E(Process - 1, Mech - 1) / (R * (Cells(k, SampleT) + 273.16)) \times \text{fderivative(BondFraction(Process - 1, i - 1, k), Mech, 0, Cells(k, SampleT)))}}\]

Else

End If
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Curvature(Process - 1, Mech - 1, i - 1, k) = Evaluate(Rate(Process - 1, Mech - 1, i - 1, k)) * (E(Process - 1, Mech - 1) / (R * (Cells(k, SampleT) + 273.16)^2) * Cells(k, ColOffset + 2) + A(Process - 1, Mech - 1) * Exp(-E(Process - 1, Mech - 1) / (R * (Cells(k, SampleT) + 273.16)) * fderivative(AlphaMech(Process - 1, Mech - 1, i - 1, k), Mech, Cells(RowOffset - 3, ColOffset + 1 + 2 * Mech + 1), Cells(k, SampleT)))

CurvatureMaximum(Process - 1, Mech - 1, i - 1) = 
CurvatureMinimum(Process - 1, Mech - 1, i - 1) = 
Evaluate(Rate(Process - 1, Mech - 1, i - 1, k))
RateMaximum(Process - 1, Mech - 1, i - 1) = 
RateMinimum(Process - 1, Mech - 1, i - 1) = 

' Set curvature maximum, minimum and zero as necessary
' within the computational limits
' Set rate maximum and minimum within the
' computational limits

If AlphaMech(Process - 1, Mech - 1, i - 1, j) > AlphaLimit(Process - 1, i - 1, 0) And AlphaMech(Process - 1, Mech - 1, i - 1, j) < AlphaLimit(Process - 1, i - 1, 1) Then
    If Mech = Scission Then
        Curvature(Process - 1, Mech - 1, i - 1, j) = Evaluate(Rate(Process - 1, Mech - 1, i - 1, j)) * (E(Process - 1, Mech - 1) / (R * (Cells(j, SampleT) + 273.16)^2) * Cells(j, ColOffset + 2) + A(Process - 1, Mech - 1) * Exp(-E(Process - 1, Mech - 1) / (R * (Cells(j, SampleT) + 273.16)) * fderivative(BondFraction(Process - 1, i - 1, j), Mech, 0, Cells(j, SampleT)))
    Else
        Curvature(Process - 1, Mech - 1, i - 1, j) = Evaluate(Rate(Process - 1, Mech - 1, i - 1, j)) * (E(Process - 1, Mech - 1) / (R * (Cells(j, SampleT) + 273.16)^2) * Cells(j, ColOffset + 2) + A(Process - 1, Mech - 1) * Exp(-E(Process - 1, Mech - 1) / (R * (Cells(j, SampleT) + 273.16)) * fderivative(AlphaMech(Process - 1, Mech - 1, i - 1, j), Mech, Cells(RowOffset - 3, ColOffset + 1 + 2 * Mech + 1), Cells(j, SampleT)))
    End If
    If Curvature(Process - 1, Mech - 1, i - 1, j) > CurvatureMaximum(Process - 1, Mech - 1, i - 1) Then
        CurvatureMaximum(Process - 1, Mech - 1, i - 1) = Curvature(Process - 1, Mech - 1, i - 1, j)
    End If
    If Curvature(Process - 1, Mech - 1, i - 1, j) < CurvatureMinimum(Process - 1, Mech - 1, i - 1) Then
        CurvatureMinimum(Process - 1, Mech - 1, i - 1) = Curvature(Process - 1, Mech - 1, i - 1, j)
    End If
    If Evaluate(Rate(Process - 1, Mech - 1, i - 1, j)) > RateMaximum(Process - 1, Mech - 1, i - 1) Then
        RateMaximum(Process - 1, Mech - 1, i - 1) = Evaluate(Rate(Process - 1, Mech - 1, i - 1, j))
    End If
    If Evaluate(Rate(Process - 1, Mech - 1, i - 1, j)) < RateMinimum(Process - 1, Mech - 1, i - 1) Then
        RateMinimum(Process - 1, Mech - 1, i - 1) = Evaluate(Rate(Process - 1, Mech - 1, i - 1, j))
    End If
End If

And Curvature(Process - 1, Mech - 1, i - 1, j - 1) > 0 Then
    Zero(Process - 1, Mech, i - 1) = True
    If Abs(Curvature(Process - 1, Mech - 1, i - 1, j)) > Abs(Curvature(Process - 1, Mech - 1, i - 1, j)) Then
        CurvatureComp(Process - 1, Mech - 1, i - 1) = j
    Else
        CurvatureComp(Process - 1, Mech - 1, i - 1) = j - 1
    End If
Else
    End If
End If

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If AlphaMech(Process - 1, Mech - 1, i - 1, j) > AlphaLimit(Process - 1, Mech - 1, i - 1, j - 1) And AlphaMech(Process - 1, Mech - 1, i - 1, j) < AlphaLimit(Process - 1, Mech - 1, i - 1, 1) Then

If Mech = Scission Then
Curvature = Evaluate(Rate(Process - 1, Mech - 1, i - 1, j)) * (E(Process - 1, Mech - 1) / (R * (Cells(j, SampleT) + 273.16) ^ 2) * Cells(j, ColOffset + 2) + A(Process - 1, Mech - 1) * Exp(-E(Process - 1, Mech - 1) / (R * (Cells(j, SampleT) + 273.16)))) * fderivative(BondFraction(Process - 1, i - 1, j), Mech, 0, Cells(j, SampleT))
Else
Curvature = Evaluate(Rate(Process - 1, Mech - 1, i - 1, j - 1)) * (E(Process - 1, Mech - 1) / (R * (Cells(j, SampleT) + 273.16) ^ 2) * Cells(j, ColOffset + 2) + A(Process - 1, Mech - 1) * Exp(-E(Process - 1, Mech - 1) / (R * (Cells(j, SampleT) + 273.16)))) * fderivative(AlphaMech(Process - 1, Mech - 1, i - 1, j), Mech, Cells(RowOffset - 3, ColOffset + 2 * Mech + 1), Cells(j, SampleT))
End If

If AlphaMech(Process - 1, Mech - 1, i - 1, j) < UpperCompLimit(Process - 1) And Abs(AlphaMech(Process - 1, Mech - 1, i - 1, j) - AlphaLimit(Process - 1, i - 1, 1)) < Abs(AlphaMech(Process - 1, Mech - 1, i - 1, j - 1) - AlphaLimit(Process - 1, i - 1, 1)) Then

AlphaMechHigh(Process - 1, Mech - 1, i - 1, j) = j
If Curvature(Process - 1, Mech - 1, i - 1, j) > CurvatureMaximum(Process - 1, Mech - 1, i - 1, j) Then CurvatureMaximum(Process - 1, Mech - 1, i - 1, j) = Curvature(Process - 1, Mech - 1, i - 1, j)
End If
If Curvature(Process - 1, Mech - 1, i - 1, j) < CurvatureMinimum(Process - 1, Mech - 1, i - 1, j) Then CurvatureMinimum(Process - 1, Mech - 1, i - 1, j) = Curvature(Process - 1, Mech - 1, i - 1, j)
End If
If Evaluate(Rate(Process - 1, Mech - 1, i - 1, j)) > RateMaximum(Process - 1, Mech - 1, i - 1, j) Then RateMaximum(Process - 1, Mech - 1, i - 1, j) = Evaluate(Rate(Process - 1, Mech - 1, i - 1, j))
End If
If Evaluate(Rate(Process - 1, Mech - 1, i - 1, j)) < RateMinimum(Process - 1, Mech - 1, i - 1, j) Then RateMinimum(Process - 1, Mech - 1, i - 1, j) = Evaluate(Rate(Process - 1, Mech - 1, i - 1, j))
End If
Else
AlphaMechHigh(Process - 1, Mech - 1, i - 1, j) = j - 1
End If
End If
End If
End If
End If

' Exit loop when conversion reaches one or at end of data and note the row where this occurs
If AlphaKinetic = 1 Or j = LastRow Then
If Mech = Scission Then
Formulaf = Replace(Formula(Mech - 1), "RC" & ColOffset + 1, AlphaKinetic)
Rate(Process - 1, Mech - 1, i - 1, j) = A(Process - 1, Mech - 1) * Exp(-E(Process - 1, Mech - 1) & "/" & R & " " & Cells(j, SampleT).Address(False, True) & ", 273.16)")) * (" & Formulaf & ")"
AlphaMech(Process - 1, Mech - 1, i - 1, j) = AlphaKinetic
If IsError(Evaluate(Rate(Process - 1, Mech - 1, i - 1, j))) Then
Active(Process - 1, Mech - 1, i - 1, 1) = j - 1
Else
Active(Process - 1, Mech - 1, i - 1, 1) = j
End If
If AlphaLessThan1 = False Then
End If
j = j + 1
Loop While AlphaLessThan1
End If
'
' Fill in remaining rows
For k = j To LastRow

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\[\text{AlphaMech}(\text{Process} - 1, \text{Mech} - 1, i - 1, k) = 1\]

Next

' Characterisation of gross model shape over the computational range (as for 'experimental' data)

If \(\text{AlphaMechLow}(\text{Process} - 1, \text{Mech} - 1, i - 1) = \text{RowOffset} - 1\) Then

\[\text{Sgn}(\text{CurvatureMinimum}(\text{Process} - 1, \text{Mech} - 1, i - 1)) > 0\]

\[\text{Nature}(\text{Process} - 1, \text{Mech}, i - 1) = 0\]

Else

\[\text{Nature}(\text{Process} - 1, \text{Mech}, i - 1) = 1\]

End If

Else

\[\text{If } \text{CurvatureMinimum}(\text{Process} - 1, \text{Mech} - 1, i - 1) > 0 \text{ Then}\]

\[\text{Nature}(\text{Process} - 1, \text{Mech}, i - 1) = 1\]

End If

End If

' If there is no zero in the 'experimental' data nor the current data set, the row where the rate is midway between maximum and minimum is identified

If \(\text{Zero}(\text{Process} - 1, 0, i - 1) = \text{False}\) And \(\text{Zero}(\text{Process} - 1, \text{Mech}, i - 1) = \text{False}\) Then

\[j = \text{AlphaMechLow}(\text{Process} - 1, \text{Mech} - 1, i - 1)\]

\[\text{For } j = \text{AlphaMechLow}(\text{Process} - 1, \text{Mech} - 1, i - 1) \text{ To } \text{AlphaMechHigh}(\text{Process} - 1, \text{Mech} - 1, i - 1)\]

If \((\text{IsError}(\text{Evaluate}(\text{Rate}(\text{Process} - 1, \text{Mech} - 1, i - 1, j + 1))) = \text{False})\) And \((\text{IsError}(\text{Evaluate}(\text{Rate}(\text{Process} - 1, \text{Mech} - 1, i - 1, j))) = \text{False})\) Then

\[\text{If } (\text{Evaluate}(\text{Rate}(\text{Process} - 1, \text{Mech} - 1, i - 1, j + 1))) > \frac{\text{RateMaximum}(\text{Process} - 1, \text{Mech} - 1, i - 1) + \text{RateMinimum}(\text{Process} - 1, \text{Mech} - 1, i - 1)}{2} \text{ And } \text{Evaluate}(\text{Rate}(\text{Process} - 1, \text{Mech} - 1, i - 1, j)) < \frac{\text{RateMaximum}(\text{Process} - 1, \text{Mech} - 1, i - 1) + \text{RateMinimum}(\text{Process} - 1, \text{Mech} - 1, i - 1)}{2} \text{ Or } (\text{Evaluate}(\text{Rate}(\text{Process} - 1, \text{Mech} - 1, i - 1, j + 1))) < \frac{\text{RateMaximum}(\text{Process} - 1, \text{Mech} - 1, i - 1) + \text{RateMinimum}(\text{Process} - 1, \text{Mech} - 1, i - 1)}{2} \text{ And } \text{Evaluate}(\text{Rate}(\text{Process} - 1, \text{Mech} - 1, i - 1, j)) > \frac{\text{RateMaximum}(\text{Process} - 1, \text{Mech} - 1, i - 1) + \text{RateMinimum}(\text{Process} - 1, \text{Mech} - 1, i - 1)}{2}\]

\[\text{Multiple} = \text{Multiple} + 1\]

\[\text{If } \text{Abs}(\text{Evaluate}(\text{Rate}(\text{Process} - 1, \text{Mech} - 1, i - 1, j))) - \frac{\text{RateMaximum}(\text{Process} - 1, \text{Mech} - 1, i - 1) + \text{RateMinimum}(\text{Process} - 1, \text{Mech} - 1, i - 1)}{2} > \frac{\text{Abs}(\text{Evaluate}(\text{Rate}(\text{Process} - 1, \text{Mech} - 1, i - 1, j + 1))) - \frac{\text{RateMaximum}(\text{Process} - 1, \text{Mech} - 1, i - 1) + \text{RateMinimum}(\text{Process} - 1, \text{Mech} - 1, i - 1)}{2}}{2} \text{ Then}\]

\[\text{CurvatureComp}(\text{Process} - 1, \text{Mech} - 1, i - 1) = j + 1\]

Else

\[\text{CurvatureComp}(\text{Process} - 1, \text{Mech} - 1, i - 1) = j\]

End If

End If

End If

Next

Next

' The user is notified of all instances where convergence of the conversion starting point was not satisfied for the first pair of unrefined and refined kinetic parameters

If \(\text{PopUpString} = ""\) Then

\[\text{OK} = \text{MsgBox}(\text{PopUpString}, \text{vbExclamation}, "\text{Convergence failure}"")\]

End If

' Assessment of the agreement of model shape to that of each 'experimental' process

For \(\text{Process} = 1\) To \(\text{HighProcess}\)

' Initialisations. No need to initialise those models that will not be assessed

Next
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For Mech = 1 To HighMech
  If Shape(Process - 1, Mech - 1) And Convergence(Process - 1, Mech - 1) = False
    NoSheets(Process - 1, Mech - 1) = False Then
      NoSheets(Process - 1, Mech - 1) = 0
      aAve(Process - 1, Mech - 1) = 0
      FactorA(Process - 1, Mech - 1) = 0
    If RefineA Then
      WeightingA(Process - 1, Mech - 1) = 0
    Else
      WeightingA(Process - 1, Mech - 1) = 0
    End If
  End If
Next

' Verify that the entire computational range is included in the data set or the
' process reaches a functional maximum rate of conversion change.
' If this is the case, exclude any model that has curvature of opposite sign or
' does not agree with the existence or not of a maximum.
' Only assess those models that have previously been acceptable (all models on
' first pass) and haven't finished or failed the refinement process
'Bypass the refinement process if a maximum is not confirmed when it is for other
'data sheets.

For i = 1 To N
  Worksheets(i + 1).Select
  LastRow = Cells(RowOffset, Time).End(xlDown).Row
  If Include(Process - 1, i - 1) Then
    If (Cells(LastRow, Alpha + Process) >= UpperCompLimit(Process - 1) And
        InDataSet(Process - 1, i - 1) = -1) Or (Zero(Process - 1, 0, i - 1) And
        InDataSet(Process - 1, i - 1) = 1 Then
      For Mech = 1 To HighMech
        If Shape(Process - 1, Mech - 1) And Convergence(Process - 1, Mech - 1)
            = False And Fail(Process - 1, Mech - 1) = False And (AlphaMechLow(Process - 1, Mech - 1,
            i - 1) = RowOffset - 1) = False Then
          ShapeAlpha(Process - 1, Mech - 1, i - 1) = False
          If Zero(Process - 1, 0, i - 1) = Zero(Process - 1, Mech, i - 1) Then
            If Nature(Process - 1, 0, i - 1) = Nature(Process - 1,
                Mech, i - 1) Or (Nature(Process - 1, 0, i - 1) = 2 And Zero(Process - 1, 0, i - 1) = False) Then
              ' Use the selected point to assess model agreement and
              ' generate refined estimates for pre-exponential
              ' factor
              ' Exclude any model that passes the above shape
              ' assessment but has a conversion difference of more
              ' than 0.2 between the chosen model point and the
              ' corresponding point in the 'experimental' data
              If (Abs(Cells(TempComp(Process - 1, i - 1), Alpha +
                Process) - AlphaMech(Process - 1, Mech - 1, i - 1, CurvatureComp(Process - 1, Mech - 1, i - 1))) < 0.2) And
                aj0(Process - 1, i - 1) > 0 And (Rate(Process - 1, Mech - 1, i - 1, CurvatureComp(Process - 1, Mech - 1, i - 1))) = "") = False Then
                ShapeAlpha(Process - 1, Mech - 1, i - 1) = True
              End If
            End If
          End If
        End If
      End If
      ' Calculate the ratio between 'experimental' and model
      ' bypass rate at the corresponding points of curvature
      ' If refinement requested, use this ratio and the temperature
      ' and function (assuming correct model) ratios to calculate a
      ' factor for pre-exponential factor refinement
      ' The 'experimental' function of conversion for random
      ' scission with variable L model requires estimated bond
      ' fraction as input rather than conversion
      If ShapeAlpha(Process - 1, Mech - 1, i - 1) Then
        NoSheets(Process - 1, Mech - 1) = NoSheets(Process - 1,
            Mech - 1) + 1
        aj = aj0(Process - 1, i - 1) / Evaluate(Rate(Process - 1,
            Mech - 1, i - 1, CurvatureComp(Process - 1, Mech - 1, i - 1)))
        If RefineKF = vbYes Then
          If RefineA Then
            Tj = (Texp(Process - 1, i - 1) + 273.16) / (Cells(CurvatureComp(Process - 1, Mech - 1, i - 1), SampleT) + 273.16)
          End If
        End If
      End If
    End If
  End If
Next
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If \( T_j = 1 \) Then
\[
\text{Resolved}(\text{Process} - 1, \text{Mech} - 1, \text{Fmin}(\text{Process} - 1, \text{Mech} - 1)) = \text{False}
\]
End If

If Mech = Scission Then
\[
\text{ARatio} = \left(\frac{\text{ARatio}}{\left(\text{ARatio} \times \text{Eval}(\text{Replace}(\text{Formula(Mech - 1)}, \text{"RC"}, \text{ColOffset} + 1, \text{AlphaMech(\text{Process} - 1, \text{Mech} - 1, i - 1, \text{CurvatureComp(\text{Process} - 1, \text{Mech} - 1, i - 1, \text{SampleT}))}))} \right)} \right) ^ \left(\frac{\text{ARatio}}{\left(\text{ARatio} \times \text{Eval}(\text{Replace}(\text{Formula(Mech - 1)}, \text{"RC"}, \text{ColOffset} + 1, \text{Cells(\text{TempComp(\text{Process} - 1, i - 1, \text{SampleT})}))})} \right)} \right)
\]
Else
\[
\text{ARatio} = \text{ARatio} / \left(\text{ARatio} \times \text{Eval}(\text{Replace}(\text{Formula(Mech - 1)}, \text{"RC"}, \text{ColOffset} + 1, \text{Cells(\text{TempComp(\text{Process} - 1, i - 1, \text{SampleT})}))})} \right)
\]
End If

\[
\text{ARatio} = \text{aj} \times \exp\left(\frac{\text{E}(\text{Process} - 1, \text{Mech} - 1)}{R \times (\text{Cells(\text{CurvatureComp(\text{Process} - 1, \text{Mech} - 1, i - 1, \text{SampleT})}) + 273.16})} \times (\frac{1}{T_j} - 1)\right) \times \text{FactorA(\text{Process} - 1, \text{Mech} - 1)}
\]
End If

If RefineA And LoopCount = 0 Then
\[
\text{aAve(\text{Process} - 1, \text{Mech} - 1)} = \text{aAve(\text{Process} - 1, \text{Mech} - 1)} / \text{NoSheets(\text{Process} - 1, \text{Mech} - 1)}
\]
End If

FirstMech = True
\[
\text{aAveBest(\text{Process} - 1)} = 1
\]
For Mech = 1 To HighMech
If Shape(\text{Process} - 1, \text{Mech} - 1) And Convergence(\text{Process} - 1, \text{Mech} - 1) = False And Fail(\text{Process} - 1, \text{Mech} - 1) = False Then
If NoSheets(\text{Process} - 1, \text{Mech} - 1) > 0 Then
\[
\text{aAve(\text{Process} - 1, \text{Mech} - 1)} = \text{aAve(\text{Process} - 1, \text{Mech} - 1)} / \text{NoSheets(\text{Process} - 1, \text{Mech} - 1)}
\]
End If
End If
Next
Next

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If Abs(Application.WorksheetFunction.Ln(aAve(Process - 1, Mech - 1))) < Abs(Application.WorksheetFunction.Ln(aAveBest(Process - 1))) Or FirstMech Then
    aAveBest(Process - 1) = aAve(Process - 1, Mech - 1)
    Default(Process - 1) = Mech
    FirstMech = False
End If
End If

' Pre-exponential factor is refined (if requested) such that
' FactorA will average to unity on next pass
' Weighting for goodness of fit using unrefined pre-exponential
' factor is evaluated and stored
' If no refinement requested, the solution is specified as
' converged to break the loop
If RefineKP = vbYes Then
    FactorA(Process - 1, Mech - 1) = FactorA(Process - 1, Mech - 1) / NoSheets(Process - 1, Mech - 1)
    WeightingA(Process - 1, Mech - 1) = WeightingA(Process - 1, Mech - 1) / NoSheets(Process - 1, Mech - 1)
Else
    Convergence(Process - 1, Mech - 1) = True
End If
Else
    Weighting(Process - 1, Mech - 1) = Weighting(Process - 1, Mech - 1) / NoSheets(Process - 1, Mech - 1)
    If WeightingA(Process - 1, Mech - 1) <= Weighting(Process - 1, Mech - 1) And LoopCount < 3 Then
        Shape(Process - 1, Mech - 1) = False
    End If
Else
    Shape(Process - 1, Mech - 1) = False
End If
Else
    If Fail(Process - 1, Mech - 1) And Convergence(Process - 1, Mech - 1) = False Then
        Convergence(Process - 1, Mech - 1) = True
    End If
Next
Next

' Activation energy is altered for the next loop if pre-exponential factor has been
' refined and the refinement has not converged or failed
Diverged = False
If RefineA = False Then
    LoopCount = LoopCount + 1
    For Process = 1 To HighProcess
        For Mech = 1 To HighMech
            ' If the pre-exponential factor of the current pair is calculated when the
            ' temperature cannot be resolved to even one row, admit that the
            ' computation has reached its practical limit
            ' Set and recalculate for the middle pair of kinetic parameters before
            ' exiting the loop if they are not current
            ' Define absolute error in activation energy as the difference between the
            ' largest and middle values of activation energy
            ' A new value for activation energy is set after assessing the relative
            ' goodness of fit of three pairs of parameters
            ' Initially the three pairs are centred around the refined invariant or
            ' apparent kinetic parameters
            ' Activation energy is stepped in the direction of the best fitting pair
        Next
        Next
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' in order to keep a constant interval between the three activation energies
' If the middle pair is the best fitting, the step size is halved by ' setting a new activation energy halfway between the two best fitting ' values

If Shape(Process - 1, Mech - 1) And Convergence(Process - 1, Mech - 1) = False Then
  If Resolved(Process - 1, Mech - 1, 0) = False Or Resolved(Process - 1, Mech - 1, 2) = False Then
    If Fmin(Process - 1, Mech - 1) = 1 Then
      Convergence(Process - 1, Mech - 1) = True
    Else
      Fail(Process - 1, Mech - 1) = True
    End If
    EFail(Process - 1, Mech - 1) = Factor(Process - 1, Mech - 1, 1) * E(Process - 1, Mech - 1) - Factor(Process - 1, Mech - 1, 1)
    A(Process - 1, Mech - 1) = ARes(Process - 1, Mech - 1) * EFail(Process - 1, Mech - 1)
    Diverged = True
  End If
  EError(Process - 1, Mech - 1) = (Factor(Process - 1, Mech - 1, 2) - Factor(Process - 1, Mech - 1, 1)) * EFail(Process - 1, Mech - 1)
Else
  Select Case LoopCount
  Case 1
    ' Reset the fail default for pre-exponential factor to its first refined value
    AFail(Process - 1, Mech - 1) = A(Process - 1, Mech - 1)
    Factor(Process - 1, Mech - 1, 2) = 1 + EStep
    Pair(Process - 1, Mech - 1, 1) = Weighting(Process - 1, Mech - 1)
    Fmin(Process - 1, Mech - 1) = 2
  Case 2
    Factor(Process - 1, Mech - 1, 0) = 1 - EStep
    Pair(Process - 1, Mech - 1, 2) = Weighting(Process - 1, Mech - 1)
    Fmin(Process - 1, Mech - 1) = 0
  Case Else
    Pair(Process - 1, Mech - 1, Fmin(Process - 1, Mech - 1)) = Weighting(Process - 1, Mech - 1)
    If Pair(Process - 1, Mech - 1, 0) < Pair(Process - 1, Mech - 1, 1) And Pair(Process - 1, Mech - 1, 0) < Pair(Process - 1, Mech - 1, 2) Then
      Factor(Process - 1, Mech - 1, 2) = Factor(Process - 1, Mech - 1, 1)
      Factor(Process - 1, Mech - 1, 1) = Factor(Process - 1, Mech - 1, 0)
      Factor(Process - 1, Mech - 1, 0) = Factor(Process - 1, Mech - 1, 1) - (Factor(Process - 1, Mech - 1, 2) - Factor(Process - 1, Mech - 1, 1))
      Pair(Process - 1, Mech - 1, 2) = Pair(Process - 1, Mech - 1, 1)
      Pair(Process - 1, Mech - 1, 1) = Pair(Process - 1, Mech - 1, 0)
      Fmin(Process - 1, Mech - 1) = 0
    Else
      If Pair(Process - 1, Mech - 1, 2) < Pair(Process - 1, Mech - 1, 1) And Pair(Process - 1, Mech - 1, 2) < Pair(Process - 1, Mech - 1, 0) Then
        Factor(Process - 1, Mech - 1, 2) = Factor(Process - 1, Mech - 1, 1)
        Factor(Process - 1, Mech - 1, 1) = (Factor(Process - 1, Mech - 1, 0) + Factor(Process - 1, Mech - 1, 1)) / 2
        Pair(Process - 1, Mech - 1, 2) = Pair(Process - 1, Mech - 1, 1)
      End If
      Fmin(Process - 1, Mech - 1) = 2
    Else
      If Pair(Process - 1, Mech - 1, 0) < Pair(Process - 1, Mech - 1, 2) Then
        Factor(Process - 1, Mech - 1, 2) = Factor(Process - 1, Mech - 1, 1)
        Factor(Process - 1, Mech - 1, 1) = Factor(Process - 1, Mech - 1, 0)
        Pair(Process - 1, Mech - 1, 2) = Pair(Process - 1, Mech - 1, 1)
      Else
        If Pair(Process - 1, Mech - 1, 0) < Pair(Process - 1, Mech - 1, 1) Then
          Factor(Process - 1, Mech - 1, 2) = Factor(Process - 1, Mech - 1, 1)
          Factor(Process - 1, Mech - 1, 1) = Factor(Process - 1, Mech - 1, 0)
          Pair(Process - 1, Mech - 1, 2) = Pair(Process - 1, Mech - 1, 1)
        Else
          Factor(Process - 1, Mech - 1, 2) = Factor(Process - 1, Mech - 1, 1)
          Factor(Process - 1, Mech - 1, 1) = Factor(Process - 1, Mech - 1, 0)
          Pair(Process - 1, Mech - 1, 2) = Pair(Process - 1, Mech - 1, 1)
        End If
      End If
      Fmin(Process - 1, Mech - 1) = 1
    End If
  End Select
End If
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Factor(Process - 1, Mech - 1, 1) =
Factor(Process - 1, Mech - 1, 0) =
(Factor(Process - 1, Mech - 1, 2) + Factor(Process - 1, Mech - 1, 1)) / 2
Pair(Process - 1, Mech - 1, 1) = Pair(Process - 1, Mech - 1, 0)

End If
ARes(Process - 1, Mech - 1) = A(Process - 1, Mech - 1)
Pair(Process - 1, Mech - 1, 0) = Pair(Process - 1, Mech - 1, 1)
IntervalHalved(Process - 1, Mech - 1) = True

End If
End Select

When the multiple of the initial activation energy has converged
to better than 5 significant figures, convergence is achieved
New activation energy is calculated and assigned to the
appropriate pair (0, 1 or 2)
If too many iterations have been computed (with a stricter limit
if the stepping interval has not been at least halved), then the
model has failed and the kinetic parameters are reset to the
fail defaults

If Abs(Factor(Process - 1, Mech - 1, 0) - Factor(Process - 1, Mech
- 1, 2)) > Factor(Process - 1, Mech - 1, 1) * 10 ^ (-5) Then
If (IntervalHalved(Process - 1, Mech - 1) = False And
LoopCount > 10) Or LoopCount > 40 Then
Fail(Process - 1, Mech - 1) = True
E(Process - 1, Mech - 1) = EFail(Process - 1, Mech - 1)
A(Process - 1, Mech - 1) = AFail(Process - 1, Mech - 1)
Else
E(Process - 1, Mech - 1) = Factor(Process - 1, Mech - 1,
Fmin(Process - 1, Mech - 1)) * EFail(Process - 1, Mech - 1)
End If
Diverged = True
Else
EError(Process - 1, Mech - 1) = (Factor(Process - 1, Mech - 1,
2) - Factor(Process - 1, Mech - 1, 1)) * E(Process - 1, Mech - 1)
Convergence(Process - 1, Mech - 1) = True
End If
End If
Else
If Shape(Process - 1, Mech - 1) = False And (A(Process - 1, Mech - 1)
= AStart(Process - 1, Mech - 1)) = False Then
Shape(Process - 1, Mech - 1) = True
Fail(Process - 1, Mech - 1) = True
E(Process - 1, Mech - 1) = EFail(Process - 1, Mech - 1)
A(Process - 1, Mech - 1) = AFail(Process - 1, Mech - 1)
Diverged = True
End If
End If
Loop While Diverged

If all models fail the shape assessment, all models are considered (not including L(T)
if it is not computed)
For Process = 1 To HighProcess
AllFail = True
For Mech = 1 To HighMech
If Shape(Process - 1, Mech - 1) Then
AllFail = False
End If
Next
If AllFail Then
For Mech = 1 To HighMech
If Mech = Scission And Sheets("Summary").Cells(3, Mech + 1) = "" Then

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Else
    Convergence(Process - 1, Mech - 1) = True
End If
Next
End If
Next

' PopUpString is initialized in preparation for next possible message
PopUpString = "Index numbers of the sheets where each indicated model does not coincide with the computational range." & Chr(13) & "Only models that passed the shape assessment are tested." & Chr(13) & Chr(13)
PopUp = False

' Selection of model(s) that best correlate to overall experimental conversion
' Initialisations
For m = 0 To HighMech ^ HighProcess - 1
    Viable(m) = True
Next
For Process = 1 To HighProcess
    If Remove(Process - 1) = False Then
        FirstMech = True
        SheetCount(Process - 1) = 0
    For OtherProcess = 1 To HighProcess
        For Mech = 1 To HighMech
            Overlap(OtherProcess - 1, Mech - 1) = False
        Next
    Next

    ' Set range for model evaluation to either the limit of precision or the calculation limits specified for the process
    ' Range is contracted by one row at each end point if the former is selected to prevent any unnecessary calculation errors
    For i = 1 To N
        If (InDataSet(Process - 1, i - 1) = -1) = False Then
            SheetCount(Process - 1) = SheetCount(Process - 1) + 1
            Worksheets(i + 1).Select
        If WholeRange = vbYes Then
            CompStart(i - 1) = XStartRow(Process - 1, i - 1) + 1
            CompEnd(i - 1) = XEndRow(Process - 1, i - 1) - 1
        Else
            CompStart(i - 1) = StartRow(Process - 1, i - 1)
            CompEnd(i - 1) = EndRow(Process - 1, i - 1)
        End If
    Next

    ' Assess whether other process/mech combinations overlap with the computational range of any sheet to determine the significance of permutations
    For OtherProcess = 1 To HighProcess
        If OtherProcess < Process Or OtherProcess > Process Then
            For Mech = 1 To HighMech
                If Overlap(OtherProcess - 1, Mech - 1) = False Then
                    TotalNonActive = 0
                    For j = CompStart(i - 1) To CompEnd(i - 1)
                        If AlphaMech(OtherProcess - 1, Mech - 1, i - 1, j) < XPrecision Or AlphaMech(OtherProcess - 1, Mech - 1, i - 1, j) > 1 - XPrecision Then
                            TotalNonActive = TotalNonActive + 1
                        End If
                    Next
                    If TotalNonActive = CompEnd(i - 1) - CompStart(i - 1) + 1 Then
                        Else
                            Overlap(OtherProcess - 1, Mech - 1) = True
                        End If
                    Next
                Else
                    Overlap(OtherProcess - 1, Mech - 1) = True
                End If
            Next
        Else
            NoneOverlapping = True
        For Mech = 1 To HighMech
            If Convergence(Process - 1, Mech - 1) Then
                FirstSheet = True
            End If
            Else
            For i = 1 To N

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If (InDataSet(Process - 1, i - 1) = -1) = False Then
    Worksheets(i + 1).Select
    TotalNonActive = 0
    LastRow = Cells(RowOffset, Time).End(xlDown).Row
    For j = CompStart(i - 1) To CompEnd(i - 1)
        ' Track number of points that coincide with a zero rate for
        ' the model
        If IsError(Evaluate(Rate(Process - 1, Mech - 1, i - 1, j))) Then
            Rate(Process - 1, Mech - 1, i - 1, j) = "0"
            TotalNonActive = TotalNonActive + 1
        End If
    End If

    ' Initialise all required residuals to the overall
    ' experimental conversion minus the weighted subject process
    ' and mechanism
    ' Subtract the effects of all other viable processes/models
    ' for each permutation
    ' A permutation is deemed unsuitable for further consideration
    ' if any process/model combination fails the shape assessment
    ' Sum the squares of these residuals over all rows in the
    ' computational range
    For k = 1 To HighMech ^ (Process - 1)
        For m = L To L + HighMech ^ (HighProcess - Process) - 1
            If Viable(m) Then
                Remainder = m
                For OtherProcess = 1 To HighProcess
                    PermutMech(OtherProcess - 1) = Application.WorksheetFunction.RoundDown(Remainder / HighMech ^ (HighProcess - OtherProcess), 0) + 1
                    Remainder = Remainder - (PermutMech(OtherProcess - 1) - 1) * HighMech ^ (HighProcess - OtherProcess)
                Next
                Residual = Cells(j, ColOffset + 1) - XFraction(Process - 1, i - 1) * AlphaMech(Process - 1, Mech - 1, i - 1, j)
                For OtherProcess = 1 To HighProcess
                    If OtherProcess < Process Or OtherProcess > Process Then
                        If Remove(OtherProcess - 1) = 0 Then
                            If Convergence(OtherProcess - 1, PermutMech(OtherProcess - 1) - 1, i - 1, j) Then
                                Residual = Residual - XFraction(OtherProcess - 1, i - 1) * AlphaMech(OtherProcess - 1, i - 1, j)
                            Else
                                Viable(m) = False
                            End If
                        End If
                    End If
                Next
            End If
        Next
    Next

    ' Weighting conversion residuals with respect to
    ' the subject process and mechanism as recommended
    ' by Mamleev

    If Mech = Scission Then
        Forulaf = Replace(Formula(FirstOrder - 1), "RC" & ColOffset + 1, (BondFraction(Process - 1, i - 1, j) + ExpBondFraction(Process - 1, i - 1, j)) / 2)
        Forulag = Replace(Formula1(FirstOrder - 1), "RC" & ColOffset + 1, (Cells(j, Alpha + Process) + AlphaMech(Process - 1, Mech - 1, i - 1, j)) / 2)
    Else
        Forulaf = Replace(Formula(Mech - 1), "RC" & ColOffset + 1, (Cells(j, Alpha + Process) + AlphaMech(Process - 1, Mech - 1, i - 1, j)) / 2)
        Forulag = Replace(Formula1(Mech - 1), "RC" & ColOffset + 1, (Cells(j, Alpha + Process) + AlphaMech(Process - 1, Mech - 1, i - 1, j)) / 2)
    End If

    Residual = Residual / (Evaluate(Formulaf) * Evaluate(Formulag))

    Sum(Process - 1, i - 1, m) = Sum(Process - 1, i - 1, m) + Residual ^ 2
End If

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Next
Next
Next

' If the model does not coincide at all with the computational range, this is noted to display to the user

If TotalNonActive = CompEnd(i - 1) - CompStart(i - 1) + 1 Then
    If FirstMech Then
        PopUpString = PopUpString & "PROCESS " & Process & ": " & Chr(13)
        FirstMech = False
        PopUp = True
    End If
    If FirstSheet Then
        PopUpString = PopUpString & Cells(RowOffset - 2, ColOffset + 1 + 2 * Mech) & ": "
        FirstSheet = False
    End If
    PopUpString = PopUpString & i & ": "
Else
    NoneOverlapping = False
    Overlap(Process - 1, Mech - 1) = True
End If

' Normalise the variance to the computational range (account for DOF) and calculate an overall average

For k = 1 To HighMech ^ (Process - 1)
    For m = L To L + HighMech ^ (HighProcess - Process) - 1
        If Viable(m) Then
            Sj(Process - 1, i - 1, m) = Sum(Process - 1, i - 1, m) / (CompEnd(i - 1) - CompStart(i - 1))
            Sjave(Process - 1, m) = Sjave(Process - 1, m) + Sj(Process - 1, i - 1, m)
        End If
    Next
Next
End If

' Concatenation of two carriage returns to the pop-up string after each process that is associated with non-overlapping models

If FirstMech = False Then
    PopUpString = PopUpString & Chr(13) & Chr(13)
End If

' Definition of most probable permutation as corresponding to the model set with minimum variance
' If no models overlap with the computational range, use that selected based on the ratio of conversion rates if possible, otherwise default to a first order mechanism

FirstMech = True
If NoneOverlapping Then
    If Default(Process - 1) = 0 Then
        Default(Process - 1) = FirstOrder
        OK = MsgBox("No models pass the shape assessment nor overlap with the computational range", vbWarning, "Process " & Process & ": Failure")
    End If
    For k = 1 To HighMech ^ (Process - 1)
        L = k * (Default(Process - 1) - 1) * HighMech ^ (HighProcess - Process) + (k - 1) * (HighMech - Default(Process - 1) + 1) * HighMech ^ (HighProcess - Process)
        If Viable(m) Then
            Sjave(Process - 1, m) = Sjave(Process - 1, m) / SheetCount(Process - 1)
        End If
    Next
Next
End If

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For \( m = L \) To \( L + \text{HighMech} \wedge (\text{HighProcess} - \text{Process}) - 1 \)

If Viable(m) Then

If SJave(Process - 1, m) < Smin(Process - 1) Or FirstMech Then

\[ Smin(Process - 1) = SJave(Process - 1, m) \]

\[ \text{Permutation}(Process - 1) = m \]

FirstMech = False

End If

End If

Next

Next

Else

For Mech = 1 To HighMech

If Convergence(Process - 1, Mech - 1) Then

For \( k = 1 \) To \( \text{HighMech} \wedge (\text{Process} - 1) \)

\[ L = k \times (\text{Mech} - 1) \times \text{HighMech} \wedge (\text{HighProcess} - \text{Process}) + (k - 1) \times (\text{HighMech} - \text{Mech} + 1) \times \text{HighMech} \wedge (\text{HighProcess} - \text{Process}) - 1 \]

If Viable(m) Then

If SJave(Process - 1, m) < Smin(Process - 1) Or FirstMech Then

\[ Smin(Process - 1) = SJave(Process - 1, m) \]

\[ \text{Default}(Process - 1) = Mech \]

\[ \text{Permutation}(Process - 1) = m \]

FirstMech = False

End If

End If

Next

Next

End If

End If

End If

' Extracting Default identities for the other processes from the best fitting permutation
' If a process/model combination is selected that does not overlap with the computation range for any sheet, it is omitted from presentation

Remainder = Permutation(Process - 1)

For OtherProcess = 1 To HighProcess

PermutMech(OtherProcess - 1) = Application.WorksheetFunction.RoundDown(Remainder / HighMech \wedge (HighProcess - OtherProcess), 0) + 1

Remainder = Remainder - (PermutMech(OtherProcess - 1) - 1) \times \text{HighMech} \wedge (\text{HighProcess} - OtherProcess)

If Overlap(OtherProcess - 1, PermutMech(OtherProcess - 1) - 1) Then

Worksheet.Cells(RowOffset - 2, ColOffset + 1 + 2 * PermutMech(OtherProcess - 1)) & " - 

Else

StringSection(Process - 1) = StringSection(Process - 1) & " - "

End If

Next

' Calculation of probabilities based on fitting the ratio of the variances to an F-distribution and normalising to highest probability (nominally 0.5)
' F-Statistics smaller than that defining 95% of the tail area (i.e. 97.5% of the total area) are highlighted as significant
' Permutations are selected based on retaining the same mechanism association for the other processes as those for the best fitting permutation
' All probabilities will be identical if no models overlap for the subject process
' Inclusion of markers indicating the nature of the kinetic parameters and presentation on 'Summary' sheet

Sheets("Summary").Select

F95 = Application.WorksheetFunction.FInv(0.025, SheetCount(Process - 1) - 1, SheetCount(Process - 1) - 1)

For Mech = 1 To HighMech

If Convergence(Process - 1, Mech - 1) Then

\[ m = 0 \]

For OtherProcess = 1 To HighProcess

If OtherProcess = Process Then

\[ m = m + (\text{Mech} - 1) \times \text{HighMech} \wedge (\text{HighProcess} - \text{Process}) \]

Else

\[ m = m + (\text{PermutMech}(\text{OtherProcess} - 1) - 1) \times \text{HighMech} \wedge (\text{HighProcess} - \text{OtherProcess}) \]

End If

Next

Fj(Process - 1, Mech - 1) = SJave(Process - 1, m) / Smin(Process - 1)
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Pj(Process - 1, Mech - 1) = Application.WorksheetFunction.FDist(Fj(Process - 1, Mech - 1), SheetCount(Process - 1) - 1, SheetCount(Process - 1) - 1)
If Pj(Process - 1, Mech - 1) < F95 Then
End If
End If
Next
PjRaw = Pj(Process - 1, Default(Process - 1) - 1)
For Mech = 1 To HighMech
  If Convergence(Process - 1, Mech - 1) Then
    Pj(Process - 1, Mech - 1) = Pj(Process - 1, Mech - 1) / PjRaw
  End If
Next
If RefineKP = vbYes Then
  For Mech = 1 To HighMech
    If Convergence(Process - 1, Mech - 1) Then
      If A(Process - 1, Mech - 1) = AStart(Process - 1, Mech - 1) Then
        ActiveCell.FormulaR1C1 = ActiveCell.FormulaR1C1 & Chr(176)
      Else
        If E(Process - 1, Mech - 1) = EFail(Process - 1, Mech - 1) Then
          ActiveCell.FormulaR1C1 = ActiveCell.FormulaR1C1 & Chr(185)
        Else
          ActiveCell.FormulaR1C1 = ActiveCell.FormulaR1C1 & Chr(178)
        End If
      End If
    End If
  Next
End If
Cells(8 + N + HighProcess + Process, HighMech + 7).Select
With Selection
  .NumberFormat = "0"
  .FormulaR1C1 = E(Process - 1, Default(Process - 1) - 1)
End With
Cells(8 + N + HighProcess + Process, HighMech + 8).Select
With Selection
  .NumberFormat = "0.00E+00"
  .FormulaR1C1 = A(Process - 1, Default(Process - 1) - 1)
End With
If EError(Process - 1, Default(Process - 1) - 1) > 0 Then
  Cells(8 + N + HighProcess + Process, HighMech + 9).Select
  With Selection
    .NumberFormat = "0"
    .FormulaR1C1 = EError(Process - 1, Default(Process - 1) - 1)
  End With
Else
  Cells(8 + N + HighProcess + Process, HighMech + 9) = "Untested"
End If

' Calculation and presentation of absolute F-statistics from 'experimental' data using raw and refined kinetic parameters if they exist
' Linearised solution is necessarily recalculated for each activation energy
' Computational range is set as for the IKP calculation

If RefineKP = vbYes Then
  L = 1
Else
  L = 0
End If
For k = 0 To L
  For Mech = 1 To HighMech
    FStat(Mech - 1, k) = 0
    If k = 0 Then
      EStat(Mech - 1, k) = EFail(Process - 1, Mech - 1)
      AStat(Mech - 1, k) = AStart(Process - 1, Mech - 1)
    Else
      EStat(Mech - 1, k) = E(Process - 1, Mech - 1)
      AStat(Mech - 1, k) = A(Process - 1, Mech - 1)
    End If
  Next
  FStatBest(k) = 0
  For Mech = 1 To HighMech
    If Mech = Scission And Sheets("Summary").Cells(3, Mech + 1) = "" Then
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Else
  If EStat(Mech - 1, k) > 0 Then
    If A(Process - 1, Mech - 1) = AStart(Process - 1, Mech - 1) And k = 1 Then
      FStat(Mech - 1, 1) = FStat(Mech - 1, 0)
    Else
      For i = 1 To N
        If (InDataSet(Process - 1, i - 1) = -1) = False Then
          Worksheets(i + 1).Select
          If Mech = Scission Then
            For j = StartRow(Process - 1, i - 1) To EndRow(Process - 1, i - 1)
              Formulag = Replace(Formula1(FirstOrder - 1),
                "RC" & ColOffset + 1, ExpBondFraction(Process - 1, i - 1, j))
              Cells(j, ColOffset + 2 + 2 * Mech).FormulaLocal = "=\" & Formulag
            Next
          Else
            Formulag = Replace(Formula1(Mech - 1), "RC" & ColOffset + 1, Cells(StartRow(Process - 1, i - 1), Alpha + Process).Address(False, True))
          End If
          Range(Cells(StartRow(Process - 1, i - 1), ColOffset + 2 + 2 * Mech), Cells(EndRow(Process - 1, i - 1), ColOffset + 2 + 2 * Mech)).FormulaLocal = "=\" & Formulag
        Next
      End If
    End If
  End If
Else
  Formulag = Replace(Formula1(Mech - 1), "RC" & ColOffset + 1, Cells(StartRow(Process - 1, i - 1), Alpha + Process).Address(False, True))
  Range(Cells(StartRow(Process - 1, i - 1), ColOffset + 2 + 2 * Mech), Cells(EndRow(Process - 1, i - 1), ColOffset + 2 + 2 * Mech)).FormulaLocal = "=\" & Formulag
End If

For j = StartRow(Process - 1, i - 1) To EndRow(Process - 1, i - 1)
  If IsError(Cells(j, ColOffset + 2 + 2 * HighMech + Mech)) Then
    Cells(j, ColOffset + 2 + 2 * HighMech + Mech) = ""
  End If
Next
FNumerator = 0
FDenominator(k) = 0
For j = StartRow(Process - 1, i - 1) To EndRow(Process - 1, i - 1)
  FNumerator = FNumerator + (Cells(j, ColOffset + 2 + 2 * HighMech + Mech) - Application.WorksheetFunction.Average(Range(Cells(StartRow(Process - 1, i - 1), ColOffset + 2 + 2 * HighMech + Mech), Cells(EndRow(Process - 1, i - 1), ColOffset + 2 + 2 * HighMech + Mech)))) * (Cells(j, ColOffset + 2 + 2 * HighMech + 1) - Application.WorksheetFunction.Average(Range(Cells(StartRow(Process - 1, i - 1), ColOffset + 2 + 2 * HighMech + 1), Cells(EndRow(Process - 1, i - 1), ColOffset + 2 + 2 * HighMech + 1))))
End If
If AStat(Mech - 1, k) = 1 Then
  FDenominator(k) = FDenominator(k) + (Cells(j, ColOffset + 2 + 2 * HighMech + 2 + Mech) + EStat(Mech - 1, k) / R * Cells(j, ColOffset + 2 + 2 * HighMech + 1)) ^ 2
Else
  FDenominator(k) = FDenominator(k) + (Cells(j, ColOffset + 2 + 2 * HighMech + 2 + Mech) - (-EStat(Mech - 1, k) / R * Cells(j, ColOffset + 2 + 2 * HighMech + 1) + Application.WorksheetFunction.Ln(AStat(Mech - 1, k) * R / (Cells(UserInputRow, UserInputCol + 1) * EStat(Mech - 1, k)))) ^ 2
End If
Next
FStat(Mech - 1, k) = FStat(Mech - 1, k) + Abs(EStat(Mech - 1, k) / R * (EndRow(Process - 1, i - 1) - StartRow(Process - 1, i - 1) - 1) * FNumerator / FDenominator(k))
End If
Next
FStat(Mech - 1, k) = FStat(Mech - 1, k) / SheetCount(Process - 1)
End If
If FStat(Mech - 1, k) > FStatBest(k) Then
  FStatBest(k) = FStat(Mech - 1, k)
End If
Sheets("Summary").Select
With Selection
  .FormulaR1C1 = FStat(Mech - 1, k)
  .Font.Bold = False
End If
If IKPEExist(Process - 1) Then
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    .Font.Bold = True
End If
End If
End If
End If
Next
Next
End If

' Display of complete pop-up string if it has been filled
If PopUp Then
    OK = MsgBox(PopUpString, vbInformation, "No Overlap")
End If

' Notification of solution consistency or display of the inconsistent permutation selections for each process
PopUp = False
For Process = 2 To HighProcess
    If Remove(Process - 1) = False Then
        If Permutation(Process - 1) = Permutation(0) Then
            Else
                PopUp = True
        End If
    End If
Next
If PopUp Then
    PopUpString = "The permutations selected as the best fit are:" & Chr(13) & Chr(13)
    For Process = 1 To HighProcess
        PopUpString = PopUpString & "PROCESS " & Process & ":" & Chr(9) & StringSection(Process - 1) & Chr(13) & Chr(13)
    Next
    OK = MsgBox(PopUpString, vbExclamation, "Inconsistent Permutation Selection")
End If

' Creation of graph to show the probability distribution(s)
Charts.Add
ActiveChart.ChartType = xl3DColumn
    :=xlColumns
For Process = 1 To HighProcess
    ActiveChart.SeriesCollection(Process).Name = "Process " & Process
Next
ActiveChart.Location Where:=xlLocationAsObject, Name:="Summary"
With ActiveChart
    .HasTitle = True
    .ChartTitle.Characters.Text = "Model Probabilities Relative to the Most Probable"
    .Axes(xlCategory).HasTitle = True
    .Axes(xlSeries).Delete
    .Axes(xlValue).HasTitle = True
    .Axes(xlCategory).CategoryType = xlAutomatic
End With
ActiveChart.Axes(xlValue).AxisTitle.Select
With Selection
    .HorizontalAlignment = xlCenter
    .VerticalAlignment = xlCenter
    .Orientation = xlUpward
End With
If (HighProcess = 1) = 0 Then
    ActiveChart.HasLegend = True
    ActiveChart.Legend.Select
    With Selection
        .Position = xlTop
        .Border.LineStyle = xlNone
    End With
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Else
    ActiveChart.HasLegend = False
End If
Chart = Replace(ActiveChart.Name, "Summary ", "")
With ActiveSheet.Shapes(Chart)
    If Repeat = vbYes Then
        .Left = ActiveSheet.Shapes(Chart).Width * HighProcess
    Else
        .Left = ActiveSheet.Shapes(Chart).Width * (HighProcess + 1)
    End If
End With
ActiveWindow.Visible = False
' Initialise the kinetic solution and set the default to the most probable model(s)
For Process = 1 To HighProcess
    If Remove(Process - 1) = False Then
        Mechanism(Process - 1) = Default(Process - 1)
    End If
Next
Continue = True
Do
    ' Query whether to select different model(s) for at least a visual assessment
    ' Allow the user to see the current statistical output before requesting a permutation
    ' to present
    NewSolution = MsgBox("Select different model(s) for the predicted kinetics and graphical comparison? & Chr(13) & ">(Click 'Cancel' to finalise the analysis with the most probable model(s))", vbYesNoCancel + vbQuestion, "Predicted Kinetic Solution")
    If NewSolution = vbYes Then
        Sheets("Summary").Select
        ActiveWindow.ScrollRow = 1
        If RefineKP = vbYes Then
        Else
        End If
        Application.ScreenUpdating = True
        For Process = 1 To HighProcess
            If Remove(Process - 1) = False Then
                MechCode = InputBox("Input model code for process " & Process & Chr(13) & "(case sensitive)", "Select Model", Sheets(2).Cells(RowOffset - 2, ColOffset + 1 + 2 * Default(Process - 1)).Value)
                If MechCode = "D1*" Then
                    MechCode = "D1"
                Else
                    If Right(MechCode, 1) = "*" Then
                        MechCode = Replace(MechCode, ",,", " -*"")
                    End If
                End If
            End If
        Next
    Else
        If NewSolution = vbCancel Then
            For Process = 1 To HighProcess
                If Remove(Process - 1) = False Then
                    Mechanism(Process - 1) = Default(Process - 1)
                End If
            Next
        End If
    End If
End If
Application.ScreenUpdating = False
' Place conversion and rate solutions to the selected model(s) in the appropriate columns if this has not been already done for the current kinetic solution
' No need to recalculate for an individual process that has been assigned the same model as for the preceding iteration
If NewSolution = vbNo And (Sheets(2).Cells(RowOffset, Alpha).Value = "") = False Then
    Else
        For i = 1 To N
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Worksheets(i + 1).Select
LastRow = Cells(RowOffset, Time).End(xlDown).Row
For Process = 1 To HighProcess
    If Remove(Process - 1) = False And (PriorMech(Process - 1) =
        Mechanism(Process - 1)) = False Then
        If Mech = ProutTompkins Then
            Else
                Range.Cells(RowOffset, Graph + Process), Cells(Active(Process - 1,
                    Mechanism(Process - 1) - 1, i - 1, 0) - 1, dalphadt + Process)) = "0"
        End If
        For j = Active(Process - 1, Mechanism(Process - 1) - 1, i - 1, 0) To
            Active(Process - 1, Mechanism(Process - 1) - 1, i - 1, 1)
            If Rate(Process - 1, Mechanism(Process - 1) - 1, i - 1, j) = "" Or
                IsError(Evaluate(Rate(Process - 1, Mechanism(Process - 1) - 1, i - 1, j))) Then
                    Rate(Process - 1, Mechanism(Process - 1) - 1, i - 1, j) = "0"
            End If
            Cells(j, Graph + Process) = "=" & Rate(Process - 1,
                Mechanism(Process - 1) - 1, i - 1, j)
        Next
        If Active(Process - 1, Mechanism(Process - 1) - 1, i - 1, 1) < LastRow
            Then
                Range.Cells(Active(Process - 1, Mechanism(Process - 1) - 1, i - 1, 1) + 1, Graph + Process), Cells(LastRow, Graph + Process)) = ""
                Range.Cells(Active(Process - 1, Mechanism(Process - 1) - 1, i - 1, 1) + 1, dalphadt + Process), Cells(LastRow, dalphadt + Process)) = "1"
            End If
        End If
    Next
    ' Uses the bisection method to optimise the distribution of weight lost via
    ' each process (XFraction)
    ' The basis of minimum variance between predicted and experimental conversion
    ' is chosen, accounting for interfering processes
    ' XFraction defaults to that previously estimated if the overall solution does
    ' not appear to converge
    ' Reinitialise the weight fraction distribution prior to finding each new
    ' solution
    For Process = 1 To HighProcess
        If Remove(Process - 1) = False Then
            XFraction(Process - 1, i - 1) = Sheets("Summary").Cells(i + 3 * (i -
        End If
    Next
    Count = 0
    Do
        Unconverged1 = False
        For Process = 1 To HighProcess
            If Remove(Process - 1) = False And (InDataSet(Process - 1, i - 1) = -
                1) = False Then
                XPrevious(Process - 1) = XFraction(Process - 1, i - 1)
                For m = 0 To 2
                    Variance(m) = 0
                    Xf(m) = 0.5 * m
                Next
                Do
                    Unconverged = True
                    For m = 0 To 2
                        If Variance(m) = 0 Then
                            If = XStartRow(Process - 1, i - 1) To
                                XEndRow(Process - 1, i - 1)
                                Experimental(m) = Cells(j, Co10ffset + 1)
                                For k = 1 To HighProcess
                                    If k = Process Then
                                        Else
                                            If XFraction(k - 1, i - 1) > 0 Then
                                                Experimental(m) = Experimental(m) - XFraction(k - 1, i - 1) * Cells(j, dalphadt + k)
                                            End If
                                        End If
                                    End If
                                Next
                                OverallNoise / XFraction(k - 1, i - 1) Then
                                    Experimental(m) = Experimental(m)
                                End If
                                End If
                                End If
                        End If
                    Next
        Next
    Do
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\[ \text{Variance}(m) = \text{Variance}(m) + \left( \text{Experimental}(m) - Xf(m) \times \text{Cells}(j, \text{dalphadt} + \text{Process}) \right)^2 \]

Next

End If

Next

If Variance(0) < Variance(1) And Variance(0) < Variance(2)

Then

\[ Xf(2) = Xf(1) \]
\[ Xf(1) = \left( Xf(0) + Xf(1) \right) / 2 \]
\[ \text{Variance}(2) = \text{Variance}(1) \]
\[ \text{Variance}(1) = 0 \]
\[ \text{Xmin} = 0 \]

Else

If Variance(2) < Variance(0) And Variance(2) < Variance(1)

Then

\[ Xf(0) = Xf(1) \]
\[ Xf(1) = \left( Xf(1) + Xf(2) \right) / 2 \]
\[ \text{Variance}(0) = \text{Variance}(1) \]
\[ \text{Variance}(1) = 0 \]
\[ \text{Xmin} = 2 \]

Else

\[ Xf(0) = \left( Xf(0) + Xf(1) \right) / 2 \]
\[ Xf(2) = \left( Xf(1) + Xf(2) \right) / 2 \]
\[ \text{Variance}(0) = 0 \]
\[ \text{Variance}(2) = 0 \]
\[ \text{Xmin} = 1 \]

End If

End If

If Abs(Xf(0) - Xf(1)) < XPrecision Then

\[ \text{XFraction}(\text{Process} - 1, i - 1) = Xf(\text{Xmin}) \]

End If

End If

Next

For Process = 1 To HighProcess

If Remove(\text{Process} - 1) = False Then

If Abs(XFraction(\text{Process} - 1, i - 1) - XPrevious(\text{Process} - 1)) > 0.0001 Then

If Count > 100 Then

\[ \text{XFraction(\text{Process} - 1, i - 1)} = \text{Sheets("Summary")}.Cells(i + 3 \times (i - 1) \times \text{HighProcess} + 2 + 3 \times (\text{Process} - 1), \text{HighMech} + 4).Value \]

OK = MsgBox("The fraction converted via process " & Process & " in sheet " & i & " does not converge and is set to " & Format(XFraction(\text{Process} - 1, i - 1), "0.00"), vbCritical, "Warning")

Else

Unconverged1 = True

End If

End If

End If

Next

Count = Count + 1

Loop While Unconverged1

' Printing of XFraction in appropriate position in spreadsheet

For Process = 1 To HighProcess

If Remove(\text{Process} - 1) = False Then

\[ \text{Cells(LastRow + 4, Alpha + \text{Process}).Value} = \text{XFraction(\text{Process} - 1, i - 1)} \]

End If

Next

' Weighted summations of individual conversions and rates for a theoretical prediction of overall conversion using updated XFraction

For Process = 1 To HighProcess

If Remove(\text{Process} - 1) = False Then

If Process = 1 Then

\[ \text{dalphadtOverall} = \text{XFraction(\text{Process} - 1, i - 1)} \times \text{RC} & \text{Graph} + 1 \]
\[ \text{AlphaOverall} = \text{XFraction(\text{Process} - 1, i - 1)} \times \text{RC} & \text{dalphadt} + 1 \]

Else

\[ \text{dalphadtOverall} = \text{dalphadtOverall} + \text{RC} & \text{Graph} + \text{Process} \]

End If

End If

Next
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\[
\text{AlphaOverall} = \text{AlphaOverall} + \text{XFraction(Process - 1, i - 1)} \times \text{RC} + \text{dalphadt} + \text{Process}
\]

End If
End If
Next

Range(Cells(RowOffset, dalphadt), Cells(LastRow, dalphadt)) = "=" & dalphadtOverall
Range(Cells(RowOffset, Alpha), Cells(LastRow, Alpha)) = "=" & AlphaOverall
Next

' Store current model associations

For Process = 1 To HighProcess
If Remove(Process - 1) = False Then
PriorMech(Process - 1) = Mechanism(Process - 1)
End If
Next
End If

' Generate graphs to aid in the interpretation of the goodness of fit of the prediction

Call SolutionGraph

' Determine whether to retain the current solution or compute a new one, referencing activation energy
' Indicate a finalised model that is not the most probable with a green highlight

If NewSolution = vbCancel Then
Continue = False
Else
Application.ScreenUpdating = True
PopUpString = 
For Process = 1 To HighProcess
PopUpString = PopUpString & Chr(13) & "E(\text{Process}) = \text{Format(E(Process - 1, Mechanism(Process - 1) - 1), 0)} \text{ J/mol}"
Next
NewSolution = MsgBox("End program with the current solution?\n\text{PopUpString, vbYesNo + vbQuestion, "Finalisation"}
If NewSolution = vbYes Then
Continue = False
For Process = 1 To HighProcess
If Remove(Process - 1) = False Then
If (Mechanism(Process - 1) = Default(Process - 1)) = False Then
If RefineKP = vbYes Then
Else
End If
End If
End If
Next
End If
Loop While Continue
Application.ScreenUpdating = True
End Sub

Sub SolutionGraph()
' Shortcut: Ctrl + j
' Produces graphs for conversion and conversion rates for the current predicted solution and the experimental data

Dim SheetName As String
Dim LastRow As Integer
Dim X As Range
Dim Y As Range
Dim V As Range
Dim W As Range
Dim Process As Integer

Application.ScreenUpdating = False
SampleT = ColOffset + 2 + 2 * HighMech + 2 + HighMech + 1
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Graph = SampleT + 2
\[ \text{dalphadt} = \text{Graph} + \text{HighProcess} + 1 \]
\[ \text{Alpha} = \text{dalphadt} + \text{HighProcess} + 1 \]

' Sheet selection

If N = 0 Then
    Sheets("Summary").Select
End If

SheetName = InputBox("Enter the name of a data sheet to display a comparison between predicted and experimental conversion and conversion rates", "Pick a Worksheet", Sheets(2).Name)

Sheets(SheetName).Select
i = Worksheets(SheetName).Index - 1
LastRow = Cells(RowOffset, Time).End(xlDown).Row

'Setting axes for plots of conversion and rate

Set X = Range(Cells(RowOffset, Temp), Cells(LastRow, Temp))
Set Y = Range(Cells(RowOffset, Graph), Cells(LastRow, dalphadt))
Set W = Union(Range(Cells(RowOffset, ColOffset + 1), Cells(LastRow, ColOffset + 1)), Range(Cells(RowOffset, dalphadt + 1), Cells(LastRow, Alpha)))

'Delete sheets of the same name as those about to be created if they already exist

If WorksheetExists("DTG_" & SheetName) = True Then
    Application.DisplayAlerts = False
    Sheets("DTG_" & SheetName).Delete
    Application.DisplayAlerts = True
End If

If WorksheetExists("TG_" & SheetName) = True Then
    Application.DisplayAlerts = False
    Sheets("TG_" & SheetName).Delete
    Application.DisplayAlerts = True
End If

'Creation of graph for comparison of conversion rates

Charts.Add
ActiveChart.ChartType = xlXYScatterSmoothNoMarkers
ActiveChart.SetSourceData Source:=Union(X, Y), PlotBy:=xlColumns
ActiveChart.SeriesCollection(1).Name = "Experimental"
For Process = 1 To HighProcess
    If Sheets(SheetName).Cells(RowOffset, Graph + Process).End(xlDown).Row = 65536 Then
        Else
            ActiveChart.SeriesCollection(Process + 1).Name = "Process " & Process & " Prediction"
    End If
Next
ActiveChart.SeriesCollection(HighProcess + 2).Name = "Overall Prediction"
ActiveChart.Location Where:=xlLocationAsNewSheet, Name:="DTG_" & SheetName
With ActiveChart
    .HasTitle = False
    .Axes(xlCategory, xlPrimary).HasTitle = True
    .Axes(xlValue, xlPrimary).HasTitle = True
    .Axes(xlValue, xlPrimary).AxisTitle.Characters.Text = "d alpha/dt (min-1)"
End With
With ActiveChart.Axes(xlCategory)
    .HasMajorGridlines = False
    .HasMinorGridlines = False
End With
With ActiveChart.Axes(xlValue)
    .HasMajorGridlines = False
    .HasMinorGridlines = False
End With
If WorksheetExists("Summary(0)") Then
    Sheets("DTG_" & SheetName).Move After:=Sheets("Summary(0)")
Else
    Sheets("DTG_" & SheetName).Move After:=Sheets(N + 2)
End If

'Creation of graph for comparison of conversion

Charts.Add
ActiveChart.ChartType = xlXYScatterSmoothNoMarkers
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ActiveChart.SetSourceData Source:=Union(V, W), PlotBy:=xlColumns
ActiveChart.SeriesCollection(1).Name = "Experimental"

For Process = 1 To HighProcess
If Sheets(SheetName).Cells(RowOffset, Graph + Process).End(xlDown).Row = 65536 Then
Else
    ActiveChart.SeriesCollection(Process + 1).Name = "Process " & Process & " Prediction"
End If
Next
ActiveChart.SeriesCollection(HighProcess + 2).Name = "Overall Prediction"
ActiveChart.Location Where:=xlLocationAsNewSheet, Name:="TG_" & SheetName
With ActiveChart
    .HasTitle = False
    .Axes(xlCategory, xlPrimary).HasTitle = True
    .Axes(xlValue, xlPrimary).HasTitle = True
End With
With ActiveChart.Axes(xlCategory)
    .HasMajorGridlines = False
    .HasMinorGridlines = False
End With
With ActiveChart.Axes(xlValue)
    .HasMajorGridlines = False
    .HasMinorGridlines = False
    .MinimumScale = 0
    .MaximumScale = 1
End With
If WorksheetExists("Summary(0)") Then
    Sheets("TG_" & SheetName).Move After:=Sheets("Summary(0)")
Else
    Sheets("TG_" & SheetName).Move After:=Sheets(N + 2)
End If
Sheets("DTG_" & SheetName).Select
Application.ScreenUpdating = True
End Sub

Function fderivative(Conversion As Double, Mech As Integer, Order As Double, Temp As Double) As Double
    ' Function to evaluate derivatives of mechanism formulae (fj). Must correspond to mechanisms defined in MechAssignment()
    Select Case Mech
        Case 1 To 4
            fderivative = (Order - 1) * Conversion ^ (-1 / Order)
        Case 5 To 9
        Case 10
            fderivative = 1 - 2 * Conversion
        Case 11 To 13
            fderivative = (1 - Order) * (1 - Conversion) ^ (-1 / Order)
        Case 14 To 15
            fderivative = -Order * (1 - Conversion) ^ (Order - 1)
        Case 16
            fderivative = Conversion ^ (-1 / 2) - 2
        Case 17
            fderivative = 1 / Conversion + ChainLength(Temp)
        Case 18
            fderivative = -1 / Conversion ^ 2
        Case 19
            fderivative = -1 / ((2 * (-Application.WorksheetFunction.Ln(1 - Conversion) ^ (1 / 2))) ^ 2 * (1 - Conversion))
        Case 20
            fderivative = -1 / ((2 * (Application.WorksheetFunction.Ln(1 + Conversion) ^ (1 / 2))) ^ 2 * (1 + Conversion))
        Case 21
            fderivative = -1 / 3 * ((1 - Conversion) ^ (-1 / 3) - 1) ^ (-2) * (1 - Conversion) ^ (-4 / 3)
        Case 22
            fderivative = -1 / 3 * (1 - (1 + Conversion) ^ (-1 / 3)) ^ (-2) * (1 + Conversion) ^ (-4 / 3)
    End Select
End Function
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Sub Reduce()
' Shortcut: Ctrl + r
' Reduces the data set by a specified factor to reduce the processing time for kinetic
' analysis to a feasible length
    Dim R As Integer
    Dim LastRow As Integer
    Dim i As Integer
    Application.ScreenUpdating = False
    R = InputBox("By what factor would you like to reduce the size of the data set?", "Data
Set Reduction", 5) - 2
    LastRow = Cells(RowOffset, Time).End(xlDown).Row
    For i = 1 To (LastRow - RowOffset - 1) / (R + 2)
        Rows(RowOffset + i & : & RowOffset + i + R).Delete Shift:=xlUp
    Next
    Application.ScreenUpdating = True
End Sub

Sub CompRequirements()
' Sets certain array elements to the corresponding values specified in global declarations
' CompRequirements() must be called from each procedure that uses Reaction, LowerCompLimit or
' UpperCompLimit
    Reaction(0) = Reaction1
    LowerCompLimit(0) = LowerCompLimit1
    UpperCompLimit(0) = UpperCompLimit1
    Reaction(1) = Reaction2
    LowerCompLimit(1) = LowerCompLimit2
    UpperCompLimit(1) = UpperCompLimit2
    Reaction(2) = Reaction3
    LowerCompLimit(2) = LowerCompLimit3
    UpperCompLimit(2) = UpperCompLimit3
End Sub

Function WorksheetExists(WSName As String) As Boolean
' Negates the runtime error caused by referring to a sheet that does not exist
    On Error Resume Next
    WorksheetExists = Len(Sheets(WSName).Name) > 0
    End Function

Function RowAssignment(Range As Integer, BeginRow As Integer, QuitRow As Integer, Limit As
Double, BackStep As Integer) As Integer
' Returns the row corresponding to a given value within a specified, generally ascending range
' If search is unsuccessful within range, the last row of the range is returned (minus or plus
' BackStep)
    Dim Switch As Boolean
    Dim RowNumber As Integer
    RowNumber = BeginRow
    If QuitRow > BeginRow Then
        Do
            Switch = True
            If Cells(RowNumber, Range) > Limit Or RowNumber = QuitRow Then
                RowAssignment = RowNumber - BackStep
                Switch = False
            Else
                RowNumber = RowNumber + 1
            End If
        Loop While Switch
    Else
        Do
            Switch = True
            If Cells(RowNumber, Range) < Limit Or RowNumber = QuitRow Then
                RowAssignment = RowNumber + BackStep
                Switch = False
            Else
                RowNumber = RowNumber - 1
            End If
        Loop While Switch
    End If
End Function
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Loop While Switch
End If
End Function

Function RowAssignment1(Range As Integer, BeginRow As Integer, QuitRow As Integer, Limit As Double, BackStep As Integer) As Integer
' Returns the row corresponding to a given value within a specified, generally descending range
' If search is unsuccessful within range, the last row of the range is returned (minus or plus BackStep)
Dim Switch As Boolean
Dim RowNumber As Integer
RowNumber = BeginRow
If QuitRow > BeginRow Then
    Do
        Switch = True
        If Cells(RowNumber, Range) < Limit Or RowNumber = QuitRow Then
            RowAssignment1 = RowNumber - BackStep
            Switch = False
        Else
            RowNumber = RowNumber + 1
        End If
    Loop While Switch
Else
    Do
        Switch = True
        If Cells(RowNumber, Range) > Limit Or RowNumber = QuitRow Then
            RowAssignment1 = RowNumber + BackStep
            Switch = False
        Else
            RowNumber = RowNumber - 1
        End If
    Loop While Switch
End If
End Function

Sub Derivative(YCoord As Integer, XCoord As Integer, BeginRow As Integer, FinishRow As Integer, Placement As Integer)
' Calculates numerical derivative using the Savitzky-Golay algorithm for a quadratic fit to FilterN data points
Dim k As Integer
Dim Coefficient As String
Dim Summation As String
Coefficient = 6 / (((FilterN - 1) / 2) * ((FilterN - 1) / 2 + 1) * (2 * (FilterN - 1) / 2 + 1))
For k = 2 To (FilterN - 1) / 2
    Summation = Summation & k ^ 2 & "*(R[" & k & "]C" & YCoord & "& XCoord & "-R[" & k & "]C" & XCoord & ")."
Next
Range(Cells(BeginRow + (FilterN - 1) / 2, Placement), Cells(FinishRow - (FilterN - 1) / 2, Placement)) = "=" & Coefficient & "*" & Summation & ""
End Sub

Sub MechAssignment(Stage As Integer, Beginning As Integer, Completion As Integer)
' Mechanism formulae. Must be edited here. Computes the values of fj and gj for all mechanisms
Dim Conversion As Integer
Dim LastRow As Integer
LastRow = Cells(RowOffset, Time).End(xlDown).Row
SampleT = ColOffset + 2 + 2 * HighMech + 2 + HighMech + 1
Graph = SampleT + 2
dalphadt = Graph + HighProcess + 1
Alpha = dalphadt + HighProcess + 1
Conversion = Alpha + Stage
' Mechanisms 1-4 (Power Law)
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Cells(Beginning, ColOffset + 3) = "=R" & RowOffset - 3 & "C[1]*RC" & Conversion & "^(1-1/R" & RowOffset - 3 & "C[1])"
Cells(Beginning, ColOffset + 4) = "=RC" & Conversion & "^(1/R" & RowOffset - 3 & "C[1])"
Range(Cells(Beginning, ColOffset + 3), Cells(Beginning, ColOffset + 4)).AutoFill
Destination:=Range(Cells(Beginning, ColOffset + 3), Cells(Beginning, ColOffset + 10)),
Type:=xlFillDefault

' Mechanisms 5-9 (Avrami-Erofe'ev (doubling with F1 (n = 1)))
Cells(Beginning, ColOffset + 11) = "=R" & RowOffset - 3 & "C[1]*(1-RC" & Conversion & ")*(-LN(1-RC" & Conversion & "))^(1-1/R" & RowOffset - 3 & "C[1])"
Cells(Beginning, ColOffset + 12) = "=(-LN(1-RC" & Conversion & ")^(1/R" & RowOffset - 3 & "C)"
Range(Cells(Beginning, ColOffset + 11), Cells(Beginning, ColOffset + 12)).AutoFill
Destination:=Range(Cells(Beginning, ColOffset + 11), Cells(Beginning, ColOffset + 20)),
Type:=xlFillDefault

' Mechanism 10 (Frout-Tsompkins)
Cells(Beginning, ColOffset + 21) = "=RC" & Conversion & "*(1-RC" & Conversion & ")"
Cells(Beginning, ColOffset + 22) = "=LN(RC" & Conversion & "/(1-RC" & Conversion & "))+R" & RowOffset - 3 & "C"

' Mechanisms 11-13 (Contracting Volume (doubling with P1 and F0 (n = 1)))
Cells(Beginning, ColOffset + 23) = "=R" & RowOffset - 3 & "C[1]*(1-RC" & Conversion & ")^(1-1/R" & RowOffset - 3 & "C[1])"
Cells(Beginning, ColOffset + 24) = "=1-(1-RC" & Conversion & ")^(1/R" & RowOffset - 3 & "C)"
Range(Cells(Beginning, ColOffset + 23), Cells(Beginning, ColOffset + 24)).AutoFill
Destination:=Range(Cells(Beginning, ColOffset + 23), Cells(Beginning, ColOffset + 28)),
Type:=xlFillDefault

' Mechanisms 14-15 (Reaction Order)
Cells(Beginning, ColOffset + 29) = "=(1-RC" & Conversion & ")^R" & RowOffset - 3 & "C[1]"
Cells(Beginning, ColOffset + 30) = "=1/(1-R" & RowOffset - 3 & "C)*((1-(1-RC" & Conversion & ")^(1-R" & RowOffset - 3 & "C)"
Range(Cells(Beginning, ColOffset + 29), Cells(Beginning, ColOffset + 30)).AutoFill
Destination:=Range(Cells(Beginning, ColOffset + 29), Cells(Beginning, ColOffset + 32))

' Mechanism 16 (Random Scission: L = 2)
Cells(Beginning, ColOffset + 33) = "=2*(sqrt(RC" & Conversion & ")-RC" & Conversion & ")"
Cells(Beginning, ColOffset + 34) = "=LN(1/(1-sqrt(RC" & Conversion & "))"

' Mechanism 17 (Random Scission: L = L(t))
Set f and g to reference a column (initialised to zero) that will be goal-seeked using

the adjacent column to experimental estimates of unbroken bond fraction

Both columns will be subsequently overwritten once the unbroken bond fraction estimates

have been stored and f and g have been copied as values

'Store the facility to exclude this model given its computational intensity
If Scission = 0 Then
If Stage = 1 Then
Range(Cells(RowOffset, ColOffset + 35), Cells(LastRow, ColOffset + 36)) = ""
End If
Else
Range(Cells(Beginning, ColOffset + 37), Cells(Completion, ColOffset + 37)) = 0
For j = Beginning To Completion
Cells(j, ColOffset + 35) = "=" & ChainLength(Cells(j, SampleT)) & "*1-RC[2])^(" & ChainLength(Cells(j, SampleT)) & "*(-1)*RC[2])" & ChainLength(Cells(j, SampleT)) & "=" & LN(1-RC[1])
Cells(j, ColOffset + 36) = "=" & --LN(1-RC[1])
Cells(j, ColOffset + 38) = "=" & 10000*(RC" & Conversion & "+(-1)*ChainLength(Cells(j, SampleT)) & "*(-1)*RC[-1])" & ChainLength(Cells(j, SampleT)) & "*(-1))") Cells(j, ColOffset + 38).GoalSeek Goal:=0, ChangingCell:=Cells(j, ColOffset + 37)
ExpBondFraction(Stage - 1, ActiveSheet.Index - 2, j) = Cells(j, ColOffset + 37)
Next
Range(Cells(Beginning, ColOffset + 35), Cells(Completion, ColOffset + 36)).Select
Selection.Copy
Selection.PasteSpecial Paste:=xlPasteValues
End If

' Mechanism 18 (1D Diffusion and Anti-Diffusion)
Cells(Beginning, ColOffset + 37) = "=1/R" & Conversion
Cells(Beginning, ColOffset + 38) = "=1/2*R" & Conversion & "+2"
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' Mechanism 19 (2D Diffusion)
Cells(Beginning, ColOffset + 39) = "=1/LN((1-RC & Conversion & ")^((1/2))"
Cells(Beginning, ColOffset + 40) = "=1/(2*(1-RC & Conversion & ")*LN(1-RC & Conversion & ")+RC & Conversion & ")"

' Mechanism 20 (2D Anti-Diffusion)
Cells(Beginning, ColOffset + 41) = "=1/LN((1+RC & Conversion & ")^((1/2))"
Cells(Beginning, ColOffset + 42) = "=1/2*(1+RC & Conversion & ")*LN(1+RC & Conversion & ")-RC & Conversion & ")"

' Mechanism 21 (3D Diffusion)
Cells(Beginning, ColOffset + 43) = "=1/((1-RC & Conversion & ")^-1/3-1"
Cells(Beginning, ColOffset + 44) = "=3/2*(1-2/3*RC & Conversion & ")-(1-RC & Conversion & ")^2/3)"

' Mechanism 22 (3D Anti-Diffusion)
Cells(Beginning, ColOffset + 45) = "=1/(1-(1-RC & Conversion & ")^-1/3"
Cells(Beginning, ColOffset + 46) = "=3/2*(1+2/3*RC & Conversion & ")-(1+RC & Conversion & ")^2/3)"

' Filling down all mechanism functions to last row of computation
' If the random scission with variable L model is the last listed model, the inverse
' temperatures must be recopied
' Must not fill down for random scission with variable L model

Range(Cells(Beginning, ColOffset + 3), Cells(Beginning, ColOffset + 2 + 2 * (Scission - 1))).AutoFill Destination:=Range(Cells(Beginning, ColOffset + 3), Cells(Completion, ColOffset + 2 + 2 * (Scission - 1))), Type:=xlFillDefault
If Scission = HighMech Then
  Range(Cells(Beginning, ColOffset + 2 + 2 * HighMech + 2), Cells(Completion, ColOffset + 2 + 2 * HighMech + 2)) = "=1/(RC & Temp + 273.16)"
  Range(Cells(Beginning, ColOffset + 2 + 2 * HighMech + 1), Cells(Completion, ColOffset + 2 + 2 * HighMech + 1)) = "=1/(RC & SampleT & ") + 273.16)"
Else
  Range(Cells(Beginning, ColOffset + 2 + 2 * Scission + 1), Cells(Beginning, ColOffset + 2 + 2 * Scission + 1), Cells(Completion, ColOffset + 2 + 2 * Scission + 1), Cells(Completion, ColOffset + 2 + 2 * HighMech)), Type:=xlFillDefault
End If
End Sub

Function ChainLength(Temp As Double) As Integer
' Returns the floor of the function for a chain length one unit longer than that which boils

ChainLength = Int(2.7 * Exp(0.0035 * (Temp + 273)) - 2)
End Function

Function TempIntegralApprox(u As String) As String
' Selected approximation for the temperature integral that arises in constant heating rate
' experiments

TempIntegralApprox = "(0.9999936** & u & "^4+7.5739391** & u & "^3+12.4648922** & u & 
"^2+3.6907232** & u & ")/( & u & "^4+9.5733223** & u & "^3+25.6329561** & u & 
"^2+21.0996531" & u & "+3.9584969)"
End Function

Sub ApparentGraph()
' Shortcut: Ctrl + g
' The graphical relationship used to obtain the apparent kinetic parameters for a selected
' process and mechanism is displayed
' Sheet with experimental data of choice must be selected
' Must only be run once data have been filled by Apparent()

Const R As Double = 8.314
Dim LastRow As Integer
Dim XStartRow As Integer
Dim XEndRow As Integer
Dim StartRow As Integer

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```
Dim EndRow As Integer
Dim Mech As Integer
Dim Xaxis As Integer
Dim Yaxis As Integer
Dim Process As Integer
Dim InvPT(HighProcess - 1, 1) As Double
Dim SheetName As String
Dim X As Range
Dim Y As Range
Dim Slope As Double
Dim Intercept As Double
Dim B As Double
Dim MechCode As String

' Assigning necessary parameters
Application.ScreenUpdating = False
SampleT = ColOffset + 2 + 2 * HighMech + 2 + HighMech + 1
Graph = SampleT + 2
dalphadt = Graph + HighProcess + 1
Alpha = dalphadt + HighProcess + 1
B = Cells(UserInputRow, UserInputCol + 1)
LastRow = Cells(RowOffset, Time).End(xlDown).Row
If (HighProcess = 1) = 0 Then
    Process = InputBox("Enter the process of interest (1-" & HighProcess & ")", "Select Process", 1)
Else
    Process = 1
End If
MechCode = InputBox("Enter the mechanism code" & Chr(13) & "(case sensitive)", "Select Mechanism", "F1")
If MechCode = "D1*" Then
    MechCode = "D1"
Else
    If Right(MechCode, 1) = "*" Then
        MechCode = Replace(MechCode, "*", "~*)
    End If
End If
Mech = Application.WorksheetFunction.Match("*" & MechCode & "*", Range(Cells(AETableRow, AETableCol), Cells(AETableRow, AETableCol + HighMech - 1)), 0)
If MechCode = "D1(*)" Then
    MechCode = "D1(*)
Else
    If Right(MechCode, 1) = "*" Then
        MechCode = Replace(MechCode, "~*", "*-")
    End If
End If
Xaxis = ColOffset + 2 + 2 * HighMech + 1
Yaxis = ColOffset + 2 + 2 * HighMech + 2 + Mech
LowerCompLimit(Process - 1) = Cells(LastRow + 2, Alpha + Process).Value
UpperCompLimit(Process - 1) = Cells(LastRow + 3, Alpha + Process).Value
StartRow = RowAssignment(Alpha + Process, RowOffset, LastRow, LowerCompLimit(Process - 1), 0)
EndRow = RowAssignment(Alpha + Process, LastRow, RowOffset, UpperCompLimit(Process - 1), 0)

' Recalculating gj if any processes overlap severely (data may have been overwritten)
SheetName = ActiveSheet.Name
If SevereOverlap(Worksheets(SheetName).Index - 2) = True Then
    Call MechAssignment(Process, StartRow, EndRow)
End If
Set X = Range(Cells(StartRow, Xaxis), Cells(EndRow, Xaxis))
Set Y = Range(Cells(StartRow, Yaxis), Cells(EndRow, Yaxis))

' Creation of graph
Charts.Add
ActiveChart.ChartType = xlXYScatter
ActiveChart.SetSourceData Source:=Union(X, Y), PlotBy:=xlColumns
ActiveChart.Location Where:=xlLocationAsObject, Name:=SheetName
With ActiveChart
    .HasTitle = True
    .Axes(xlCategory, xlPrimary).HasTitle = True
    .Axes(xlValue, xlPrimary).AxisTitle.Characters.Text = "1/Tv (1/K)"
    .Axes(xlValue, xlPrimary).HasTitle = True
```

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Sub CEGraph()
' Shortcut: Ctrl + h
' Displays a plot of the 'false' compensation effect for a specific process and heating rate
' as requested by the user

    Dim B As Double
    Dim X As Range
    Dim Y As Range
    Dim Process As Integer

    ' Assigning necessary parameters
    i = InputBox("Enter the number of the data sheet of interest (1-" & N & ") NB: A 'Summary'
    sheet does not count as a data sheet", "Select Data Sheet", 1)
    Sheets(i + 1).Select
    B = Cells(UserInputRow, UserInputCol + 1)
    If (HighProcess = 1) = 0 Then
        Process = InputBox("Enter the process of interest (1-" & HighProcess & ")", "Select
        Process", 1)
    Else
        Process = 1
    End If

    ' Creation of graph
    Sheets("Summary").Select
    Set X = Range(Cells(i + 3 * (i - 1) * (Process - 1) + 1 + 3 * (Process - 1), 2), Cells(i + 3
    * (i - 1) * HighProcess + 1 + 3 * (Process - 1), 2), Cells(i + 3
    * (i - 1) * HighProcess + 1 + 3 * (Process - 1), HighMech + 1))
    Set Y = Range(Cells(i + 3 * (i - 1) * HighProcess + 2 + 3 * (Process - 1), 2), Cells(i + 3
    * (i - 1) * HighProcess + 2 + 3 * (Process - 1), HighMech + 1))
    Charts.Add
    ActiveChart.ChartType = xlXYScatter
    ActiveChart.SetSourceData Source:=Union(X, Y), PlotBy:=xlRows
    ActiveChart.Location Where:=xlLocationAsObject, Name:="Summary"
    With ActiveChart
        .HasTitle = True
        .ChartTitle.Text = "CE for process " & Process & " and a heating rate of " & B & Chr(186) & "C/min"
        .Axes(xlCategory, xlPrimary).HasTitle = True
        .Axes(xlCategory, xlPrimary).AxisTitle.Text = "Ejv (J/mol)"
        .Axes(xlValue, xlPrimary).HasTitle = True
        .Axes(xlValue, xlPrimary).AxisTitle.Text = "ln Ajv"
    End With
    End Sub
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Sub SecondDerivative(YCoord As Integer, XCoord As Integer, BeginRow As Integer, FinishRow As Integer, Placement As Integer)
' Calculates numerical second derivative using Holoborodko's noise robust differentiator
Dim k As Integer
Dim Coefficient As String
Dim Summation As String
Dim s((FilterN - 1) / 2 + 1) As Double
Coefficient = 2 ^ (5 - FilterN)
s((FilterN - 1) / 2 + 1) = 0
s((FilterN - 1) / 2) = 1
Summation = ((FilterN - 1) / 2) ^ 2 & "/(R[" & (FilterN - 1) / 2 & "]C" & XCoord & "-R[-" & (FilterN - 1) / 2 & "]C" & XCoord & "]" & 2 * (FilterN - 1) / 2 & "]C" & YCoord & "+R[-" & (FilterN - 1) / 2 & "]C" & YCoord & "]" & 2 * RC & YCoord & "]")
k = (FilterN - 1) / 2 - 1
Do
If k > 0 Then
s(k) = ((2 * FilterN - 10) * s(k + 1) - (FilterN + 2 * k + 3) * s(k + 2)) / (FilterN - 2 * k - 1)
Summation = Summation & "+" & k ^ 2 & "*" & s(k) & "/(R[" & k & "]C" & XCoord & "]" & 2 * (FilterN - 1) / 2 & "]C" & YCoord & "+R[-" & k & "]C" & YCoord & "]") & 2 * RC & YCoord & "]")
k = k - 1
End If
Loop While k > 0
Range(Cells(BeginRow + (FilterN - 1) / 2, Placement), Cells(FinishRow - (FilterN - 1) / 2, Placement)) = "+" & Coefficient & "+" & Summation & "]"
End Sub
References


Labsys TG- Commissioning/ Utilisations (C/LABTG-1A), Caluire, France: Setaram Instrumentation, 2004.


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