

Theory of solid-state thermal decomposition reactions

Scientific stagnation or chemical catastrophe? An alternative approach appraised and advocated

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Abstract A case is presented to recommend strongly that scientists interested in thermal chemistry should make comprehensive, conscientious, clinical and critical analyses of the strengths and weaknesses of *The L'vov Thermochemical Theory* (L'vov, Thermal decomposition of solids and melts—new thermochemical approach to the mechanism, kinetics and methodology, Springer, Berlin, 2007), used to interpret the kinetics and mechanisms of reactions that occur on heating. The shortcomings underlying the theory (some originally developed for solid decompositions) currently uncritically accepted in this field are reviewed, and these deficiencies are contrasted with the successes of L'vov's approach. To promote the use of this alternative theory, features that may have discouraged researchers unfamiliar with its assumptions, methodology and applications are discussed here. A new scientific theory cannot be ignored or discounted without adequate consideration and testing, particularly in a stagnant area of chemistry that lacks guiding principles and unifying concepts. Novel ideas in the literature (L'vov 2007) deserve recognition, critical appraisal and, if possible, exploitation to maintain the progress of scientific research.

Keywords CDV mechanism · Solid state kinetics · Solid state mechanisms · Thermal analysis · Thermochemical kinetics

Introduction

It should, by now, be obvious to researchers interested in *Thermal Decompositions of Solids* that the theoretical foundations of this subject are (at best) of doubtful validity or (at worst) nonexistent. The metamorphosis of this speciality field into *Thermal Analysis* (after 1970) further distanced mechanistic investigations of these reactions from mainstream chemical sciences. A feature of this development was the retention of solid-state kinetic models in thermal analysis theory, which justifies publication in this Journal. This article confronts the problem that a majority of recent thermal analysis publications cannot be regarded as advancing science because they neither systematically extend ordered knowledge nor develop adequate foundations for the prediction of untested behaviour from systematic information already available. (Dictionary definitions of *science* identify its ability to systematically order knowledge/observations and its capacity to generalize from the particular (induction). Science may also enable observations/behaviour to be represented/expressed through models: mathematical, physical, chemical, etc.)

During 1950s, kinetic studies were enthusiastically used for investigating the behaviour observed on heating (selected) solids. Unfortunately, subsequent research has neither advanced our understanding of the rate controls of these reactions nor provided mechanistic insights. The limitations of this approach are now apparent in the stagnation that has beset the subject. Moreover, while researchers specializing in solid state decompositions have 'borrowed' theoretical models from homogeneous kineticists, this class of reaction has never been integrated into the wider, general theories of rate processes successfully applied to homogeneous reactions in gas or liquid phases. It is, surely, time to recognize and accept the limitations,

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shortcomings, failures of these attempts to use kinetic theories applicable to *homogeneous* reaction to interpret controls and mechanisms of *heterogeneous* reactions.

Possibly because the serious limitations of solid-state kinetic theory, as applied in thermal analysis, are now becoming apparent, the publication rate is declining, though slow growth of this huge literature continues. These articles rarely, if ever, question ‘accepted theory’ or explore replacement or novel perspectives. This is inexplicable when an alternative general theory of thermal reactions is available: L’vov’s ‘Thermochemical Approach’ [1]. This theory has successfully [1–4] characterized the mechanisms and rate controls for many of these reactions. Despite the publication of this novel approach and its demonstrated achievements, its advent has been almost totally ignored by researchers (apparently) preferring to retain theoretical concepts that, in recent decades, have failed either to introduce order or to advance their subject.

The advent of a new hypothesis offers exciting opportunities, the challenges of exploiting its potential to resolve recalcitrant difficulties and obtain new insights into familiar phenomena. Improved theoretical models may represent observed behaviour more accurately, apply more widely, show improved or extended predictive capacities, identify unsuspected links between the hitherto unrelated phenomena, etc. However, before new ideas achieve the status of *theory*, it is important to appraise most carefully their relevance and applicability, by stringent, clinical comparisons of their strengths and weaknesses against the ‘older ideas’. All the aspects of the value and reliability of the (would-be) incoming theory must be critically and rigorously tested, questioned, and compared. Careful evaluation of CDV theory, with its potential to replace inadequate current theory, could increase our understanding of the controls and mechanisms of thermal reactions in solids and melts [1].

It would be expected, therefore, that the publication of an innovative concept would be greeted by researchers with pleasurable anticipation. It is astonishing, therefore, that thermal chemists have apparently decided neither to embrace nor test to destruction, the L’vov’s model [1–4]. However, science is not a democratic activity: a majority of chemists ignoring a theory is not a *proof* that it is ‘wrong’. Rejection can only follow adverse *scientific* appraisal, a procedure absent from this unusual, indeed unacceptable, situation. The novel ideas proposed by L’vov should stimulate concerned scientists to re-examine the accepted assumptions that underlie their current theories, test their validity, ranges of applicability and reliability in predicting untested behaviour. A period of reappraisal can be expected to stimulate fruitful progress, resulting from the comprehensive re-examination of all relevant theories and

thereby benefit the subject. Deciding between the merits of rival theories can, and should, be a ‘festival of fruitful ferment’, lasting until the alternative scientific explanations are resolved by one becoming dominant and the other disappearing.

This idealized portrayal of ‘Progress of Theory in Science’ does not always apply. One variation occurs when exponents of a niche topic maintain a comfortable existence as a group publishing extensively, but exclusively, within their cosy coterie. However, the policy of ignoring dissent must ultimately lead to stagnation within the isolated subject area which inevitably becomes impotent. In this way, rate studies and theories of thermal reactions have become detached from mainstream chemical kinetics. In contrast, the CDV model is founded on the van’t Hoff equation [1–4], based on theory applicable to thermal reactions on fundamental principles accepted throughout physical chemistry. Indeed, the CDV model repeats the Volmer’s two-step model and was discovered 60 years later, absolutely independently, by L’vov [2, 3]. This foundation has, however, never been ‘noticed’ or cited in the literature of thermal reactions. The policy of ‘ignoring the dissenting voice’ is unacceptable and particularly inexplicable in a field so badly served by its current, and scientifically inadequate, theoretical foundations.

The present review surveys the unsustainable and unscientific situation now accepted by researchers interested in *Thermal Decompositions of Solids* [5–7], latterly transformed into *Thermal Analysis* [8–12]. This history, told below, is a ‘Cautionary Tale’ from which lessons should be learned. Theory advances, separated by long time intervals [2, 3], can be portrayed as a few discontinuous, random (quantum- or frog-like) leaps, described below.

This author was trained in 1950s in the older tradition [5–7], which is now regarded by him as demonstrably inadequate. Here, I argue that theories still conventionally used throughout our subject urgently require fundamental review. I also discuss my problems when confronting and accepting the new concepts required to replace them [1–4]. I hope the present optimistic recommendation that the subject can now move forward will encourage other open-minded researchers to similarly (re-)examine the CDV mechanism [1] and recognize its potential to reinvigorate the *science* of thermal reactions. My dissatisfactions with current attitudes pervading reports of kinetic studies in thermal chemistry include (i) the absence of efforts to identify links between kinetic parameters and reaction chemistry/reactant constituents, (ii) no attempts being made to systematize (to order) the countless kinetic parameters reported in the literature, (iii) uncritical acceptance of the errors and shortcomings inherent in many computer programs used in kinetic analyses, (iv) the absence of comparative literature reviews and (v) other

reservations given in [8–12]. Many researchers seem to have forgotten the objectives of science, ignored a new theory and failed to apply their critical faculty.

This article was written because (i) The shortcomings of the (restricted and restricting) theory routinely applied to analyse thermokinetic data [8–12] is overdue for comprehensive and critical reappraisal. (ii) The existence of the CDV mechanism [1–4] must be admitted and its applicability considered and adequately tested. The thermoanalytical community is inescapably obliged to identify the strengths and weaknesses this theory or, alternatively, to demonstrate its inapplicability rigorously. Continuing to ignore it is not a scientific option. Background to these recommendations is given below, by summarizing the torturous history of this subject—revealing its indirect route to its present unsatisfactory state of stagnation. This ‘Cautionary Tale’ is told from my personal viewpoint to encourage others to appreciate fully the problems inherent in current attitudes and be stimulated ‘to advance our subject’ through open-ended and open-minded scientific curiosity.

Thermal decomposition reactions of solids: a retrospective

The different theoretical models that have been used in kinetic and mechanistic studies of *Thermal Decompositions of Solids* over the past few decades have recently been reviewed by L’vov [2, 3]. This fully referenced history does not require repetition here. The present article presents my personal appraisal of the strengths and weaknesses of L’vov’s thermochemical approach [1–4] in explaining the chemical changes observed when solids are heated. My survey is influenced by my research training, starting in 1955, a time of great optimism in this field. Garner’s highly influential study [5] had just appeared, and theoretical understanding of reactions of solids appeared to be advancing rapidly. This was not maintained. Progress subsequently slowed and the topic metamorphosed into *Thermal Analysis*. These changes in emphasis were the background to my career but now, following recent promising developments, I present a strong case for renewed optimism that this subject is, at last, poised for future advance.

Early theory (before 1938)

L’vov has recently reviewed early (pre 1938) publications [2, 3] on the heterogeneous catalytic and autocatalytic reactions which relate directly to solid decompositions. Two features of these rate processes are still of particular interest, by providing significant insights into this first era of

solid-state kinetic theory development. First, Volmer [13] identified two stages in silver oxide decomposition. The first step is reactant dissociation into silver atoms and oxygen molecules which, at reaction temperature, represents supersaturation by a factor of about 10^4 . After nucleation, this is relieved by condensation of silver atoms to form the metal product. *This is exactly the same rate-determining process as that proposed by L’vov in the CDV mechanism, some six decades later [1–4].* Second, the essential role of the contact interface between solid reactant/solid product in salt breakdown was emphasized by Ostwald [14] for the hydrate/anhydrite phases during gypsum dehydration. Similarly, Langmuir [15] referred to the phase rule in identifying the necessity for carbonate and oxide solid phase contact interfaces in calcite decomposition.

References [13–15] confirm that the earliest investigators of this type of chemical change identified ‘reactant dissociation equilibrium’ as the initial step in solid decompositions. However, it appears [3] that this model was replaced at a 1938 Conference [16], to which the principal advocates of the early theory did not contribute. Subsequently, effectively unanimously, research workers adopted the kinetic approach based on the Arrhenius reaction model to represent the activation process, where the rate-limiting step is the breakdown of an unstable, transitory complex. This kinetic theory was adopted because it was (and still is) successful in elucidating mechanisms and identifying kinetic controls for *homogeneous* reactions in gases, liquids and solutions. Its extension to decompositions of solids remains without adequately demonstrated theoretical foundations.

‘Classical’ studies of solid-state reactions (after 1938)

Post-1938 literature concerned with the theory and kinetic interpretation of rate data for solid-state decompositions is extensive. Particularly influential was the book, *Chemistry of the Solid State* [5], giving detailed accounts of important aspects of the subject, most authored by researchers dominant in their field. Later reviews include [6, 7]. The theory of this subject is well-known. The present critical appraisal concerns the less-widely recognized, or discussed, limitations and unjustified assumptions inherent in this approach to kinetic and mechanistic analyses of rate data for thermal reactions of solids.

In accounting for the displacement of CDV-type models for solid state reactions from its formerly pre-eminent position, L’vov [3] points to the role of the 1938 Bristol Conference [16]. Here, crystal disorder, involving movements of ions and electrons, became accepted as dominant participants in controlling (most) reactions of solids, concepts based on proposals by Wagner [17]. (It now appears that, while diffusion, defect and imperfection movements are

important in various solid-state rate processes, their roles in thermal decompositions are less clear.) However, after 1938, it became accepted that the rate-determining step in solid decompositions is activated complex breakdown, a behaviour represented by the Arrhenius equation. This approach, ‘borrowed’ by solid-state kinetics, expresses rate data for solid decompositions using (originally homogeneous) Arrhenius parameters: activation energy, E ; and frequency factor, A . Similarities with the transition state theory, widely used and highly influential throughout homogeneous reaction kinetics, were emphasized. However, this (homogeneous) success depends on the ability to portray the activated complex, the essential intermediate, reliably and accurately. In gas reactions, the controlling process is represented as an energetic collision between stable reactant molecules of known structures and dimensions, but without contacts with other species. In liquids, solvent interactions may be considered. Comparable information about identities, dimensions and structures of reaction precursors in solid decompositions is not available.

Mechanistic interpretations of kinetic data for solid decompositions (often) base identification of a transient activated complex, at the reactant/product contact interface, on unstated assumptions. However, we have no *independent* knowledge of the chemical identity, structure or any other feature of the transition ‘molecule’ assumed for any solid/solid interface reaction. Moreover, any ‘interphase/interface activated complex’ is composed of an unknown number of unidentified precursors, perhaps ions. Such interactions involving one/two ions might be treated as analogous to a mono/bimolecular reaction but, within a distorted intercrystalline (condensed) reaction zone, analogues of higher molecularity reactions (unlikely in homogeneous reactions) cannot be excluded. Without independent information about the identity of (assumed) activated species, the following fundamental uncertainties (with others [8–12]) arise when it is assumed that Arrhenius parameters measured for the overall reaction represent the rate of activated complex breakdown within a solid(?) intercrystalline contact zone of chemical change:

1. The identities/structures/numbers/concentrations/mobilities of reactant precursors to the rate-limiting step are unknown.
2. Reaction precursor concentrations may vary with temperature, influencing E [18].
3. The bond rupture step that controls the overall reaction rate is unknown.
4. The energy distribution function within the disordered contact interface is unknown.

Despite the absence of the demonstrated fundamental theory, numerous kinetic studies for diverse solid decompositions have reported measured Arrhenius parameters,

and interpreted these magnitudes by assuming parallels with homogeneous kinetic theory. E values are often identified with the activation that precedes a controlling bond rupture step, though without independent verification. A values are compared with vibration frequencies within the reactant solid, and entropy values are calculated for the formation of an assumed (but otherwise unknown) activated intermediate. Conclusions identifying such magnitudes as those consistent with a proposed intermediate complex are (implicitly) regarded as supporting/justifying/confirming the (homogeneous theory) model used in the analysis.

Appraisal of the huge volume of the literature [8–12] reveals (at least) two shortcomings within this science. First, no correlation has yet been identified that links reported E values with any chemical feature of the reactants: systematic order is absent from these data. Second, no trend has been found within the wide range of Arrhenius parameters available, that enables E values to be predicted for the hitherto untested reactions. Thus, two *scientific* expectations, demonstrating and extending order, remain unmet. Indeed, agreement between (A and E) magnitudes measured for the same solid by different authors has often been poor, or very poor. While the theory of homogeneous reaction kinetics has been enthusiastically embraced, and used, by solid-state chemists, more general chemical texts tend to regard thermal reactions of solids as a ‘speciality subject’. Perhaps this is a hint from the wider scientific community that the subject requires a more substantial theory.

After the optimism of the 1950s for kinetic/mechanistic studies of solid decompositions, an appreciable decline in interest is apparent during the subsequent decades. Perhaps this was due to the absence of progress in elucidating mechanisms and controls of interfacial reactions. Whatever the reason, it is undeniable that researchers redirected their efforts towards the subject that (later) became known as *Thermal Analysis*. Interestingly, the lack of scientific order in the kinetics of reactions already studied was replaced by an urge to develop machines that could measure reaction rates ever more rapidly and so flood the literature with A , E values for the decompositions of diverse old, new, novel, obscure, etc., reactants. Interest in reaction chemistry was replaced by the urge to make more and more data available and more and more rapidly: we had entered the new *Age of the Machine*. However, no systematic order has emerged from the observations reported.

Thermal analysis (after about 1970)

Although fewer reports of ‘classical’ studies of solid decompositions appeared after about 1970, rapid progress was made in developing various types of equipment (TG,

DTA, DSC etc.) capable of measuring (both isothermal and non-isothermal) rate data for thermal reactions together with computer programs designed to extract kinetic parameters. Such apparatus became highly efficient at rapidly completing each kinetic investigation with minimum input (and, some might argue, output), particularly using non-isothermal techniques, which became the preferred method. Significantly, these studies tended to avoid clearly stating that the reactions occurred in the solid state by making no reference to, or direct detection of, melting. However, by basing kinetic analyses on the well-known set of rate equations characteristic of solids [5–7], there is the clear (if unstated) implication that the chemical changes occurred in that state. After the decline of ‘classical’ isothermal investigations, and the proliferation of TG, DTA and DSC studies (perhaps with fewer recently), it appeared that by about 1980, *Thermal Analysis* had effectively replaced the older subject [5–7].

The early *Thermal Analysis* literature reported instrumentation advances, including computer programs to calculate kinetic parameters. These, largely automated, methods enabled the rapid and efficient determination, for any selected thermal reaction, of the ‘kinetic triad’: both Arrhenius parameters, A and E , together with whichever rate equation, $f(x) = kt$, (usually solid state [5–7]) provided the ‘best fit’ to data measured (Confusingly, the rate equation, $f(x) = kt$, is sometimes referred to as the ‘reaction mechanism’). The results from these numerous kinetic studies (often devalued by unrecognized mathematical shortcomings in their computer programs) form a huge literature [8–12]. However, few of these articles discuss chemical mechanisms or identify reaction rate controls. There have been surprisingly few reviews of this literature, and individual reports do not correlate kinetic parameters with reactant compositions or any other variable. No examples of systematic order or of data trends capable of predicting behaviour in hitherto untested systems have been described. This situation is reminiscent of ‘classic’ solid decomposition studies, where recent declining interest is also attributable to the absence of the reliable scientific foundations needed to stimulate organic growth of a coherent subject.

Attempts have been made [8–12] to draw attention to fundamental limitations inherent in the theory, assumptions and methodology widely accepted and used in non-isothermal kinetic studies of solid(?)–state reactions. Such inadequate foundations reduce the reliability of all chemical and mechanistic interpretations reached. For example, a proposal redefining the important concept, *activation energy*, as a *variable* is regarded as unacceptable [8] when this term, already ‘borrowed’ from homogeneous kinetic theory, has no adequate theoretical justification in this field. These adverse comments [8–12] have attracted little, or no,

literature attention, presumably on the assumption that ‘If ignored, perhaps they will disappear’. (An identical boycott has ignored L’vov’s CDV theory.)

Science does not advance by *ignoring* problems: indeed the recognition of inconsistencies is more realistically regarded as a *starting point* for future progress. However, the opportunities offered by current stagnation remain unrecognized by the Thermal Analysis Community. The scientific problem is the absence of theoretical principles capable of bringing systematic order and coherence into the large, disorganized collection of kinetic data published for thermal reactions of innumerable, initially solid, reactants. This stagnation, declining interest, isolation from mainstream kinetic theory, etc., is only likely to be reversed by the introduction of stimulating ideas, novel concepts and fresh thinking to develop suitable scientific principles. The efforts since 1938 have failed to provide insights into the mechanisms, controls and chemistry of these interesting reactions.

Many researchers in this field are financed by public money and, therefore, have a clear obligation to contribute positively towards advancing science. Indeed, the present declining activity in this field may be due to a disinclination, by financial controllers, to invest in research that appears to be so unpromising. To fulfil their social contract, and also to continue to attract funding, researchers interested in investigating thermal reactions of solids might (profitably) reappraise the scientific foundations of their subject, including unfamiliar theories that they have hitherto chosen to ignore (evidently selectively). One such theory excluded from serious appraisal is the L’vov Thermochemical Approach [1–4].¹

Congruent dissociative vaporization mechanism

It appears that progress in understanding the thermal *chemistry* of solids has effectively ceased. Theories widely applied lack adequate scientific foundations, are incapable of finding order within the copious published data or of identifying trends within related systems. This situation is inexplicable and unacceptable because a comprehensive theory is already available: the L’vov CDV mechanism of thermal reactions [1–4]. However, despite dozens of articles by L’vov, presenting, refining, extending and applying

¹ Readers interested in the ethics of science publication and current problems in the communication of research to both specialist and lay audiences will find a stimulating and thought-provoking general review of shortcomings in the present situation in p. 375–383 of [19]. This particular analysis is specifically concerned with the debate on ‘Global Warming’ but is critical of diverse limitations in the refereeing system and the reliability of the contents of some recent articles appearing in physical science journals. It is mentioned here because it suggests that researchers funded by public money have an obligation to ensure that the science they publish is demonstrably reliable.

this mechanism [1], it remains unconsidered, uncited and uncriticized. This demonstrably successful approach is ignored and rejected for unexplained reasons [1–3], while authors persist in using the older sterile theories, which have failed to stimulate progress.

Why do Thermal Analysts voluntarily accept this unscientific situation? No answer. However, comprehensive critical examination and rigorous testing of CDV mechanism is now overdue and essential to establish its value. The author's comments below are offered to encourage Thermal Analysts to appraise, with open mind, the potential validity and relevance of CDV theory [1] to their research. If such appraisal identifies models or criteria capable of recognizing [1] trends within the abundant data available, then this is a reason to celebrate, enabling the subject to move on from stagnation (at last!). Alternatively, if the theory is shown to be unsatisfactory, for positively identified *scientific* reasons, then it can be legitimately dismissed as unacceptable and discounted. However, any meaningful examination of theory in this area of chemistry is expected to be profitable and revealing.

Initially, I found great difficulty in understanding, visualizing and accepting CDV theory. The factors controlling overall reaction rates are quite distinct from the mechanisms of thermal reactions accepted throughout the recent literature. The latter were familiar from my training, further reinforced during subsequent decades of active research. Reappraisal of deeply rooted beliefs always requires effort ('high E !'): I had to re-examine my assumptions to confront the reasons why one view (or prejudice) is to be preferred to alternatives. The accounts below trace how I personally resolved some of the considerable problems encountered in appraising the merits of CDV theory. Later, gradually, I came to regard it as superior to theories I had previously accepted, without critically questioning their validity. This history is not intended to be patronizing but my approach to overcoming my difficulties may find resonance with Thermal Analysts concerned about unacceptable uncertainties inherent in the theories currently used.

Taste

My starting point in appraising CDV mechanism was the shortcomings in theory conventionally accepted in kinetic studies of thermal reactions. (The subject of a PhD thesis and subsequent research career.) I never was a Thermal Analyst because I adjudged the methodology to be inadequate for the elucidation of reaction *chemistry*, see [8–12]. Later, I reached similar conclusions for the 'classic' theory of solid decompositions. Specifically, I came to regard the 'transition complex' as an unreliable import into the subject, and this dissatisfaction with available theory made me a sceptic, receptive to new ideas.

Test

Initially, I welcomed L'vov's early articles [2, 4] because they emphasized the importance of *general* physico-chemical concepts and methods. The temperature coefficient of reaction rate (expressed as E) is identified with the molar enthalpy of the overall decomposition. This interpretation has a recognizable physical significance (through the van't Hoff equation) rather than the assumed (but never justified) participation of an activated intermediate (as in the Arrhenius model). However, my first problem was to confront the most formidable difficulty of all, the (initially seemingly unlikely) possibility of reactant *volatilization*. Solid-state chemists do not often admit that their reactants might *melt*: during my long experience of the subject, the idea of *sublimation* had rarely, if ever, been contemplated (ammonium salts, e.g. NH_4ClO_4 [20], being regarded as exceptional).

Thoughts

After long deliberation, I recognized that my initial prejudice against CDV theory was unacceptable for two reasons. First, many crystalline substances volatilize on heating and, therefore, solids have *some* vapour pressure. Consequently, my initial instinctive assumption that such pressures were effectively zero was without evidential support. After consideration, I accepted that, at reaction temperatures, all solids *must* exert a vapour pressure, though some are extremely low. Also, according to the CDV model, interfacial chemical changes are envisaged as being completed very rapidly, before a volatile entity could move further than the length of 'a few atoms'. Second, Prof. L'vov had already established a considerable scientific reputation from his studies of atomization processes for solid reactants, analytical samples in electrothermal atomic absorption (ET AAS) [2, 21, 22]. He applied this directly relevant expertise to model the chemistry of the important initial volatilization step, after which subsequent interface processes completed the overall breakdown reaction. This study was the foundation of the Thermochemical Kinetic Theory [1]. As a scientist, I had to dismiss my unfounded opinions and accept this previously unfamiliar, but already established (in ET AAS), theory. Science benefits from exchanges between its different branches: this is an outstanding example of the cross-fertilization of ideas. Now, aware of the successes of Thermochemical Kinetic Theory in accounting for the thermal behaviour of many and diverse solids [1], I accepted that the models established in ET AAS were more valuable and scientifically reliable than concepts 'borrowed', without theoretical support, from the kinetics of homogeneous reactions.

Trust

After careful appraisal of the CDV mechanism, and face-to-face discussions with Prof. L'vov [2], I decided that this approach offered the best, indeed only available, route towards data ordering and to obtaining mechanistic insights into the chemistry of thermal reactions. I commend it here as the preferred theory, meriting provisional acceptance, pending its intensive appraisal. I have watched its development, through successful applications to ever-widening ranges of reactions, with my appreciation of its value progressively rising. Comments made below, to specific aspects and applications of the theory, are given as page references in [1], where all aspects of CDV theory and its uses are clearly explained (excepting the more recent recognition of its earlier existence [2, 3]).

Top trend

I regard the (almost) constant magnitude of T_{in}/E (defined temperature of reaction onset (K)/activation energy (kJ mol^{-1})), Table 5.3, p. 70–71 in [1], for decompositions of 50 compounds yielding both gaseous and solid products, as strong, indeed conclusive, evidence of a common, *simple* initial reactant vaporization step. If decompositions of these diverse compounds (carbonates, carboxylates, hydrates, etc.) involved *different* activation steps, i.e. *different* transition complexes, then it is *extremely* unlikely that these several chemical mechanisms would exhibit this single trend. Simple surface species sublimation explains the common behaviour pattern for all the diverse reactants in Tables 5.1, 5.2 and 5.3, pp. 67–71 [1]. This pattern, therefore, resembles Trouton's Rule (p. 66 [1]) for liquid evaporation: no activated intermediate is envisaged, the energetic entity simply volatilizes. 'No activated complex/transition state' is an essential feature of the CDV theory [1].

Transfer parameter τ

Initial vaporization of the reactant is immediately followed by its decomposition and the energy released by condensation of the low-volatility component is shared between reactant and product solids in the ratio given by the τ coefficient. This fraction of the released condensation energy transferred to the reactant at the interface (τ), increases the rate of the first step in reaction (volatilization). Analysis of τ values for 15 compounds (pp. 111–114 [1]) showed these to be related to supersaturation (S) of the low-volatility component at the instant of decomposition by [23] (correlation coefficient 0.96):

$$\tau = 0.351 \log \log S + 0.017$$

This unusual (doubly logarithmic) relationship between τ and S may become a key point in understanding the

mechanism of energy transfer in condensation. This correlation has not yet been interpreted by a physical model, a limitation that requires further consideration.

Third-law method

The novel third-law method for determining the Arrhenius activation energy, E , is introduced, explained and recommended as giving a more precise magnitude than the conventional graphical method, p. 53 [1]. The consistency of values determined for sublimations of metals and simple substances are shown in Table 5.1, for decompositions to gaseous products only in Table 5.2, and for decompositions to gaseous and solid products in Table 5.3, pp. 67–70 in [1]. A *quantitative* trend in measured kinetic data has never previously been reported for thermal decompositions of groups of solids and this important achievement in identifying a significant behaviour pattern is to be most highly commended.

Two modes

The equimolar and isobaric modes (regimes) of decomposition reactions, p. 39 [1], are described for the first time. *Equimolar* reactions proceed in the absence, or in low pressures, of products and *isobaric* reactions take place in product pressures greater than equilibrium values. CDV theory, based on reactant dissociative volatilization, quantitatively accounts for the kinetic effects of the pressure of product gas present within the reaction zone in changing the magnitude of the measured value of E , pp. 40–41, 78–84 [1]. This important kinetic feature is not considered in the Arrhenius model, though reversibility in reactions of solids has long been viewed as a 'complication' in rate studies [5–7].

Topley–Smith effect

The kinetic consequences of *Reactant Self-Cooling* in endothermic reactions are considered quantitatively in pp. 87–98 [1]. Recent researchers have forgotten this significant kinetic influence, though its importance was recognized in earlier studies [5–7]. Its role in explaining the *Topley–Smith Effect* is discussed pp. 99–109 [1] and as one of several reasons for *Compensation Effects* pp. 139–141 [1] (see also [18]). Many Thermal Analysts treat compensation behaviour as a positive, even interesting, kinetic result, whereas its appearance is usually evidence of errors in data analysis and/or interpretation [8–12, 18].

The future: where do we go from here?

The immediate, indeed overdue, necessity is that all the scientists interested in *Thermal Decompositions of Solids*,

and its successor, *Thermal Analysis*, should make an impartial, objective and critical appraisal of the value of comprehensively replacing the inadequate theory, currently accepted, with the CDV mechanism and Thermochemical Kinetic Theory [1]. This considered opinion was reached after a lifetime research in this field and only after my, initially sceptical, evaluation of ideas [1] that conflicted with long-held views. However, aware of the serious limitations in the theories now in use, I was persuaded that a comparative reassessment of all assumptions underlying all available theories offered the only realistic prospect for progress. This led me to L'vov's studies [1–4]. I now recommend that all the scientists, who are interested, contribute to meaningful reappraisal of all the scientific and theoretical foundations used to interpret the kinetics and mechanisms of thermal reactions. Selected research areas, offering promising prospects for profitable progress, are suggested below.

Everyone using CDV theory [1] must be made aware of a potential ambiguity in the symbolism used. E , *activation energy*, 'borrowed' from homogeneous kinetics, identifies with the energy required to form the 'activated' transition complex in an assumed 'rate-determining step'. This usage is maintained because E is conventionally accepted as a measure of the temperature coefficient of reaction rate. However, in CDV theory, E represents the total reaction enthalpy; see pp. 43–47, Fig. 3.3 of [1] and Appendix below.

Confirming published conclusions

Reliability of experimental data is an essential foundation in all scientific research. (As I was taught when starting research, though the importance of reproducibility is stressed less often in recent reports.) Accordingly, based on best scientific practice [19], L'vov identifies, for scrutiny, all relevant aspects of his formulation, development and testing of CDV theory [1–4]: literature sources, relevant theory, methodology, experimental data, calculations, interpretations and conclusions. Further, careful re-examinations of published data for selected rate processes would either confirm and strengthen the theory as presented [1] or identify inconsistencies, thereby opening a debate, which could lead to new understanding and insights into the reactions concerned. Such tests of this potentially influential theory are required to confirm its reliability before its application, development and acceptance.

Directions for future development

L'vov's recommended use of the third-law method for E determination (p. 53ff [1]) is of particular interest by increasing the accuracy of E measurements. Using this

experimental approach to extend the ranges of substances studied, beyond those already listed in Tables 5.1, 5.2 and 5.3 (pp. 67–72 [1]), would be of considerable interest and value. Moreover, re-examination of those compounds listed in these Tables, which show greatest deviations from the mean, could increase reliability overall and confirm the conclusions reached. Systematic quantitative measurement of the kinetic consequences of variations of product pressure present during selected isobaric reactions would be of value in ordering a field characterized by the diversity of behaviour reported [24].

Reactant volatility is the essential, and novel, feature of CDV theory (and, as I found initially, a concept unfamiliar to a solid state chemist). Research into evaporation processes established the foundation from which L'vov originally developed his thermal reaction model [1, 2, 21, 22]. There is, therefore, value in further experimental investigations of the entities evolved on heating selected reactants, which may include 'complex and diverse' volatile species (pp. 28–30 [1]). This presents itself as an open field of considerable potential interest.

CDV theory is applicable to the interface advance reaction, describing the overall rate process after nucleation [5–7], pp. 18–28, 43–44 of [1]. Nucleation chemistry and the subsequent early growth of nuclei have been considered through the same CDV model, (see e.g. [23], pp. 19–20) and could benefit from further investigations.

Recommendation

I strongly recommend that the CDV theory [1] is subjected to stringent testing, with a view to promoting its adoption for application in the interpretation of kinetic data for thermal reactions. This approach has revealed (hitherto unsuspected) scientific order within data published (mainly) in the older literature [1] (but with significantly less input from shorter, often superficial, thermoanalytical studies). The potential for such analyses to predict behaviour in the hitherto untested systems remains to be fully explored, offering opportunities to researchers eager to advance a subject that has not advanced appreciably in recent years. The challenge is either to confirm the promise of CDV theory and exploit its novel features or to demonstrate the scientific superiority of other/older theories. My preference is for the positive and optimistic former rather than the languishing and lagging latter.

By reverting to the earlier theory of thermal reactions, we can back out of the 'thermal analysis cul-de-sac', so essential, before forward progress is attempted to obtain insights into the interesting, if misunderstood, controls of thermal decomposition reactions.

Appendix: Notes on the CDV mechanism

All the features of the CDV mechanism are comprehensively, rigorously and logically presented in [1], with support from citations of many thermochemical articles, dating back to 1997 [2] (some deriving from earlier ET AAS research). The virtual ‘invisibility’ of this interesting, careful and detailed science in the recent literature is inexplicable. To facilitate wider appreciation of the value of this theory in its applications to thermal reactions, selected mechanistic features are expanded below. These points arose in discussions with Prof. L’vov (personal communication), after my request for a ‘more chemical’ portrayal of the theory. Some aspects could benefit from further detailed theoretical and experimental research.

The τ parameter

An essential difference between the CDV mechanism and the Arrhenius activation mechanism is that, during interface reactions, a proportion of the energy released on condensation of a non-volatile product is transferred to the reactant solid, reducing the energy barrier to further reactant volatilization. Thus, ‘recycled’ energy is responsible for the autocatalytic behaviour, justifying the following important generalizations:

- (i) Models identifying the preferred occurrence of chemical change at reactant/product contact interfaces with (uncharacterized, qualitative) ‘strain’, ‘catalysis by product’, etc. [5–8] can now be discarded as providing no insights into reaction controls and mechanisms.
- (ii) Autocatalytic behaviour, resulting from redistribution of product condensation energy, occurs when decomposition proceeds within a reactant/product contact interface. Reactions yielding no condensed (non-volatile) product transfer no energy, so that $\tau = 0$.
- (iii) Because energy transfer is responsible for autocatalysis, the variations in τ , found for a range of diverse substances [23], are identified with supersaturation of the non-volatile component rather than the chemical properties of the different original reactants.

The simplest expectation for energy redistribution at an interface is that the condensation energy will be shared equally between reactant and product solids, expressed as $\tau = 0.5$, pp. 111–114 [1]. Deviations, where ΔH_{cond} (see below) is distributed unequally between solid reactant and product phases in the ratio $\tau/(1 - \tau)$, are ascribed to the degree of supersaturation of the

non-volatile vapour. In accordance with (ii) above, kinetic studies for (the deceleratory) sublimations of many reactants give values that agree well with theory and $\tau = 0$ (Ch. 16 [1]): As and Sb; oxides, sulphides and selenides of Cd and Zn; together with the nitrides of Mg, B, Al, Ga, In and Si. The influence of the τ term is relatively small for decompositions of some azides and oxalates (for mercury oxalate, $\tau = 0$) but is significantly larger for several divalent hydroxides [1]. A range of τ values, found for decompositions of diverse reactants, exhibit a single common trend [23]: (iii) above and Chs. 8 and 16 of [1], confirming the role of energy transfer in autocatalytic behaviour, rather than through the chemical properties of reactants and products.

The magnitude of τ depends only on the degree of vapour supersaturation (S) of the low-volatility product [1, 23]. Under isothermal conditions, τ remains constant, when excess energy from the condensing product is transferred to both reactant and product solids by collisions within the narrow contact interface. While details of this transfer process require more detailed investigation, we note that atoms are very readily condensed on ‘their own lattice’ [25]. It is suggested (L’vov, personal communication) (qualitatively) that at low S (product) condensation occurs preferentially on the solid product: τ values are <0.5 . At high S values, preferential condensation on the reactant may be expected, because this is relatively cooler due to the energy withdrawn by the initial volatilization step. Consequently, τ values are >0.5 . This explanation requires both theoretical and experimental confirmation. Nevertheless, the theory, providing insights into the specific chemical processes that participate in different thermal decompositions (Ch. 16 of [1]) and τ values that conform quantitatively to a single overall pattern (Chs. 8, 16 [1]), is infinitely more valuable (and scientific!) than a collection of innumerable individual A and E values that exhibit no demonstrated trends or significance!

Comparison of energy changes in the CDV mechanism with the Arrhenius model

The Arrhenius model is often represented by the familiar graph of energy variations as reaction progresses by ‘Advance along the Reaction Coordinate’. This shows an initial rise to a maximum value, to form the ‘transition complex’, followed by a decline thereafter.

Corresponding features for the CDV mechanism, exemplified by the (endothermic) decomposition of calcite, are represented diagrammatically, Fig. 1, as follows:

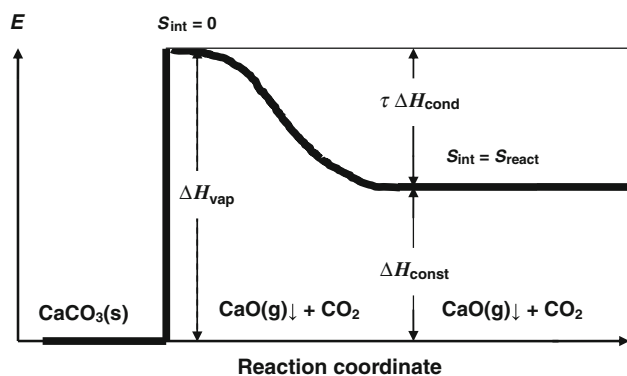


Fig. 1 Schematic energy curve for isothermal calcite decomposition: the CDV mechanism. Initial congruent volatilization of a reactant ‘CaCO₃ molecule’ (Step 1) yields gaseous intermediates, one of which, here CaO, is metastable. In the subsequent, and distinct, Step 2, the non-volatile product is immediately condensed, releasing energy, ΔH_{cond} . The significant feature, contrasting with the Arrhenius model, is the absence of a ‘transition state’. The overall reaction involves two separate processes, between which the energy curve is (very briefly) constant. S_{react} is the reactant surface area, and S_{int} is the active interfacial area (which undergoes geometric changes as decomposition advances). Within the active interface, transferred energy promotes reaction, and τ is constant

Notes: (i) The E parameter is the vaporization enthalpy, ΔH_{vap} pp. 44–45 [1]. (ii) Primary gaseous products are neutral molecules or atoms: Tables 2.2, 4.1, 6.1, etc. in [1]. (iii) When the gaseous product (here CO₂) is present in excess concentration, the (reversible) volatilization step may be inhibited, accounting for the difference between isobaric and equimolar kinetic behaviours. (iv) The (isothermal) sigmoid (fractional reaction) α -time curve, typical of many solid-state decompositions [5–7], is identified as resulting from energy transfer, a characteristic feature of the active reactant–product interface. During the induction period, S_{int} is zero (no energy transfer, $\tau = 0$), nucleation of the product phase takes place (not discussed here) and areas of active reaction interface are established. Thereafter, the growth of nuclei increases the area of active reaction interfaces across reactant surfaces during the subsequent acceleratory phase of reaction (promoted by transferred energy: τ is constant). When all the reactant surfaces have been covered by product, ‘contracting envelope’ behaviour is maintained during the deceleratory completion of reaction, the (constant) proportion, $\tau\Delta H_{\text{cond}}$, of condensation energy being transferred to reactant. This explains the sigmoid shaped yield–time curves characteristic of many isothermal solid-state decomposition [5–8].

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