

Review

DECOMPOSITION REACTIONS OF SOLIDS (AN EXPERIMENT IN REVIEWING)

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1. FOREWORD

The literature search and analysis methods used in this survey were partly conventional and partly novel and experimental. Following the conventional approach, as widely practiced in the writing of chemical reviews, we have identified and discussed the most notable contributions to our selected topic. In addition, and unusually, we have complemented this progress report with what we consider to be a profitable semi-quantitative comparative examination of the subject contents of all articles identified within our defined field. This method of literature analysis was considered to be of interest because scientific progress results not only from individual articles of outstanding merit, but also through the continual accumulation of knowledge contained in the larger number of more modest publications. The outstanding articles are already well served by the present review system. For the others the totality of output is often perceived qualitatively or simply as an impression. We, therefore, describe here a method whereby the general progress within a subject may be characterized more reliably and positively from a quantitative consideration of the total contents of all the information contained in the literature. This approach has yielded new insights into current trends of interests and achievements in our own speciality subject, decompositions of solids: these are described below. More generally, however, we recommend the approach as being equally applicable and useful for the assessment of progress in diverse branches of science.

As is evident from the literature output described below, a considerable research effort is currently concerned with decomposition reactions of solids. This topic has, however, been the subject of relatively few critical reviews, an omission that may well have adversely influenced the rate and directions of subject development. Thus we consider the time to be opportune for a comprehensive, comparative and critical appraisal of the aims, methods and achievements of recent work in the field, together with some discussion about its possible future evolution.

2. REVIEW PROCEDURES

From the various dictionary definitions for "review" we regard the following as providing the most satisfactory description of our present aims and objectives. A review assesses or reconsiders published material contained within a selected topic, possibly including comparative appraisals and critical comment. Such material constitutes an invaluable component of the chemical literature by summarizing important developments, charting progress, providing critical insights and often giving selected lists of literature sources. These systematic treatments of a subject sometimes reveal gaps in our knowledge, inconsistencies or disagreements between observations by different workers and can indicate directions of potentially profitable future research.

Chemical reviews often emphasize those individual papers that have been identified by the reviewer as representing the most significant contributions towards scientific progress in the field. Papers adjudged to be of lesser importance may not be mentioned, even though their content was considered and their omission resulted from a conscientious decision on the part of the reviewer. We are, however, aware of little discussion of methods used by review authors to locate relevant papers and criteria used to assess the worth of individual articles. Most surveys probably represent the accumulated experience of workers long active in the field both in the research laboratory and in the library. It is important that this knowledge is disseminated to others interested and this is currently effectively achieved through the well-known review journals.

The present article reports the results of a complementary and novel alternative review procedure. We have employed several different literature search methods to find as many as possible of the articles concerned with our selected topic: decompositions of solids. From these we have then sought to characterize the trends and achievements within the subject by semi-quantitative statistical methods. These methods also enable objective comparisons to be made between the research and interpretive techniques employed by different workers. If it can be accepted that all papers published in reputable journals exert some influence on our common scientific heritage, then it follows that a quantitative examination of these papers enables us to identify those advances that result from the cumulative acquisition of information and ideas in the whole literature. Such an analysis must include contributions from the many useful articles that individually report modest advances but together constitute the greater part of research output. This accumulated knowledge, information and theory constitutes the foundation from which future advances develop.

We believe that an assessment of the possible value of alternative methods of literature review is now opportune. The development of computer techniques for data processing can be expected to offer new possibilities in this,

as in so many other fields of science.

The present article is the result of our own fundamental reconsideration of the useful objectives and desirable aims of a literature review, exploited within the field of our specialist interest.

3. REVIEW CONTENT

We define the object of this review as a quantitative investigation of the contents of those articles published in 1981 which were concerned with investigating the stoichiometries, the kinetics and the mechanisms of decomposition reactions of single solids. We have attempted to classify the contents of as many articles as we could find with greater precision than is usually the practice. Details of our search methods, classification criteria and conclusions are given below. In summary the pattern of literature content that emerged was as follows.

A total of 368 relevant papers were found in the (three) literature searches and these constituted our *source set* that was used for the subsequent content analyses. Every article accepted as being of interest here gave some information concerning decompositions of solids, though not all were exclusively or even primarily concerned with this topic. The range of reactants for which studies were reported was exceedingly diverse and included virtually every type of solid. Just over half the articles (196) report stoichiometric conclusions but do not include kinetic observations. Some of the balanced stoichiometric equations given are not, however, fully characterized by the observations reported and the possibility of more complicated behaviour is not always discussed.

Data from the 65 isothermal kinetic studies found were interpreted using that relatively small group of rate expressions which have already been accorded wide acceptance by providing satisfactory descriptions of behaviour for solid state decompositions. Mechanistic conclusions concerning interface development in these studies were, however, not usually supported by the positive confirmation that can sometimes be provided by microscopic observations.

In the more difficult field of non-isothermal rate measurements (59 papers) many approximate methods were used in the interpretation of data. However, no clear consensus of opinion has yet identified a preferred approach capable of overcoming the considerable problems inherent in this method of kinetic investigation.

These, and other conclusions discussed below, result from the quantitative examination of our source set. They are, therefore, more reliable than the trends perceived as qualitative impressions during background reading undertaken during preparation of the recently published comprehensive review of the kinetics of decompositions of solids [1]. Indeed it was the insubstantial

foundation of some of these generalizations that prompted us to undertake the present more detailed content survey.

(a) Interface phenomena

When considering the interpretation of kinetic measurements for solid-state decompositions below, it is convenient to regard interface phenomena from two different but complementary points of view [2]. Firstly, it is usually assumed that a reaction occurs at a reactant/product contact interface and systematic changes in the overall reaction rate, as decomposition progresses, result from progressive changes in the area of this active contact zone. Information concerning the geometry of interface development may, therefore, be deduced from isothermal rate measurements together with a demonstration of the obedience of these to an appropriate rate expression [1]. Alternatively, direct observation (microscopy) can be used and conclusions from both complementary methods should, of course, agree. While the kinetic analysis method bears some apparent resemblance to the determination of the order of a homogeneous rate process, it must be remembered that the observed obedience for a heterogeneous reaction gives no evidence concerning the molecularity of a rate-limiting step. Secondly, it may be difficult to characterize the chemistry of bond redistribution steps at the reaction interface, which is often inaccessible to direct investigation, restricted in extent and thickness and usually located between two solid substances.

Thus reaction geometry and interface chemistry are distinguished below as representing different, but closely connected and complementary, aspects of the decomposition of a solid. A more extensive account of this topic has already appeared [2].

4. LITERATURE SEARCHES

We have attempted to list in our source set as many as possible of the articles published in 1981 which contain information concerning the stoichiometry, the kinetics and/or the mechanisms of decomposition of one or more solids. Publications dated 1981 were the most recent set accessible and abstracted at the time of writing (1983). The time period selected for this experimental examination was restricted to a single year. This represents a compromise between obtaining a sufficiently large sample to be representative and meaningful and limiting the amount of material for consideration within realistic boundaries to enable it to be processed within a reasonable time.

For the large majority of articles considered by us, the decision as to whether each should be incorporated into the source set or omitted was easily and unambiguously reached. However, no absolute criteria for this distinction exist. Consistent classification of borderline material was occasionally difficult and ultimately required the exercise of some subjective choice. We believe that by maximizing the objectivity of our approach and by being consistent, the effects of "boundary blur" are no greater than those inherent in all literature surveys. Both authors have conducted independent searches of most of the source material and we have synthesized our conclusions with positive agreement. Thus we consider that this possible source of uncertainty has exerted little influence on the trends which we have discerned in this complicated and diverse field.

The review process generally can, in one sense, be regarded as a subjective assessment and a subjective comment/criticism of the topic under discussion. While we exercised some choice in the initial selection of material, our subsequent analysis here is probably less influenced by personal value-judgements than is usual in literature surveys.

(a) Source set range

We have adopted a wide interpretation of the term "decomposition of a solid" to include all rate processes involving bond redistribution steps at a coherent interface involving a single immobilized reactant phase. Reactions such as phase transformations, recrystallizations, devitrifications or polymerizations of a glass, a polymer or a polymorph are no different in many essential respects from the decomposition of a crystalline solid. These have, therefore, been accepted into our source set but only where the investigation satisfied our other criteria by reporting the stoichiometry, the kinetics and/or the mechanism of a chemical change (i.e., bond redistribution) for a single solid reactant.

(b) Literature sources

We have based our search of the literature on sources available to every chemist having access to a well-stocked library, with positive support from a knowledgeable and helpful staff. We believe that we have achieved acceptably comprehensive coverage for articles appearing in the major primary journals, those having world-wide coverage and using generally understood languages. Most of these are published by learned societies, often a chemical society of those nations most active in the scientific field, or by the major international publishing houses. Inevitably, however, our survey of the less generally distributed periodicals is less than comprehensive and any survey of these is

limited by availability or accessibility of journals, language barriers and time. Many articles in this group of publications are listed in Chemical Abstracts, which we also searched, and once an entry had been identified as being of interest, the full text could usually be obtained by the library.

For our present purposes it was not practicable for us to obtain translated copies of every article of potential interest where these appeared in journals of limited distribution and/or in languages of restricted usage. When such articles could not be obtained readily or rapidly, our coverage here was provided by the summaries appearing in Chemical Abstracts. While such summaries constituted only a small proportion of our source set and incorporated much of the information we required, it must be conceded that these sources were incomplete. It is difficult to assess the significance of these less readily available publications on the work of the international scientific community.

References in Chemical Abstracts recorded as "Title only translated" or from restricted sources were discounted from consideration as not having achieved general publication.

(c) Literature searches

Our source set, intended to include the maximum number of relevant reports, was compiled through three complementary searches of (a) journals, (b) Chemical Abstracts (manual), and (c) Chemical Abstracts (computer). These searches will be discussed in greater detail in the following Section (5). The parallel application of these alternative methods provides a direct test of the effectiveness of the computer search method as employed in this field. (We may note in passing that a detailed specification of the literature search upon which any review is based is not invariably provided.)

Analysis of these source data shows the distribution of subject reports in the literature. It is found that a high proportion of the articles in our source set appear in a relatively few journals.

(d) Quantitative reporting

Throughout this article we report (*italicised*) the total number of papers classified under any particular heading or exhibiting a specified feature. These are always readily related to the total number of articles in the source set (368), or the appropriate sub-set, and thus there is no ambiguity as to the basis of a percentage comparison. This method of reporting is preferred here, particularly in the subsets where the total numbers are small, as providing a more realistic basis for the comparisons.

(e) Library staff

The positive co-operation of the staff in the Library of The Queen's University of Belfast is gratefully acknowledged. Their assistance was most

appreciated in locating and obtaining copies of journals not available locally and in the construction and execution of the computerized literature search which supplemented our own searches of primary journals, their indexes and Chemical Abstracts.

(f) Conference proceedings

A single collection of papers, constituting the proceedings of a major international conference, was published in 1981 (D. Dollimore (Ed.), 2nd European Symposium on Thermal Analysis [3]). A partial content analysis of this volume is given below. To avoid duplication, however, these relatively short papers were not included in the source set, since the contents of many appeared later as or in journal articles.

An investigation of the role and significance of published conference proceedings in the dissemination of scientific knowledge would be a most useful addition to the literature. This is not, however, an objective of the present review.

5. SEARCH SOURCES AND METHODS

(a) Journals

Thorough searches were made of the indexes of 40 primary journals. These were selected to include those periodicals known, from our parallel searches of Chemical Abstracts, to publish articles in our field of interest. They were either immediately available, or quickly borrowed, and included the most prestigious international periodicals concerned with our selected topic.

As anticipated, and rapidly confirmed during the early stage of our search, article titles do not always state, or even imply, that a decomposition reaction reported proceeded in the solid state. This problem of identification of the relevant material was the most general and the most difficult that we encountered during our source set selection. The only apparent solution is the use of more precise titles by authors publishing in this field.

Many of the articles accepted into our source set followed our recognition, or inference, that a particular substance did not melt before or during breakdown. The decision as to whether or not a paper was relevant was often made only after reading the abstract or even some or all of the text. Very occasionally, when the reactant was unfamiliar and the author made no clear statement that the reaction proceeded in the solid state, our classification had to be based on comparisons with related compounds.

Kinetic, stoichiometric and/or mechanistic information for solid-state reactions sometimes appears as minor contributions to studies primarily directed towards other objectives (e.g., reactivity in inorganic chemistry,

preparative chemistry, crystallography, etc.). When such observations are not mentioned in the article title or abstract, they can only be found by reading the text. Some relevant information of this type was located during our journal search and these articles were accepted into the source set. This problem of identification makes the achievement of a comprehensive survey for this subject particularly difficult. Literature searches intended to be comprehensive must, therefore, be extended to consider relevant related topics also.

Analysis of the frequency with which the various journals searched were represented in the source set showed that a limited number of different periodicals published a high proportion of the constituent articles. The contents of these have been classified below for those journals which contained 20 or more articles. (Content analysis was considered to be of little value when fewer contributions appeared in the subset.) Numbers of articles accepted into the source set from different journals were as follows.

Russian Journal of Inorganic Chemistry, 26 (1981)	79	} 92
Russian Journal of Physical Chemistry, 55 (1981)	13	
Thermochimica Acta, 43-51 (1981)	71	
Journal of Thermal Analysis, 20-22 (1981)	36	
Journal of Inorganic and Nuclear Chemistry, 43 (1981)	32	
Indian Journal of Chemistry, 20A (1981)	21	

A short account of the contents of articles appearing in each of these publications is given in section 11 below.

To minimize the number of divisions and retain uniformity of classification, the two closely related Russian journals (both published by the Academy of Sciences of the U.S.S.R.) were considered together.

From searches of 34 of the most prestigious English, French and German language journals a further 42 articles were accepted into the source set. (These will be referred to as the "Combined Search of Journal Indexes".) Each of these journals contained fewer relevant reports than those cited above: Inorganic Chemistry and Bulletin of the Chemical Society of Japan yielded 7 each. Seven journals contained only a single article each and seventeen included none.

(b) Chemical Abstracts (manual search)

This search covered Chemical Abstracts volumes 94-97 (i.e., 1981 and 1982), to find as many articles dated 1981 as possible while completing the acquisition of source material in a reasonable time. Interest was concentrated on Sections 65, 66, 67 and 78 and the greater proportion of acceptable citations appeared towards the end of Sections 67 and 78.

This search yielded an additional 48 references, accepted into our source set: these were in journals not immediately available. Reprints of 37 of these

were readily obtained but the content analysis of the remaining 11 had to be based on the abstract alone due to delay in obtaining a copy or as a result of a translation difficulty. During this search no attempt was made to duplicate the coverage of the 40 journals already individually examined during the journal indexes search, referred to in the previous section.

(c) *Chemical Abstracts (computer search)*

A computer search of Chemical Abstracts was made using the DIALOG

TABLE 1

Comparison of numbers of articles accepted into the source set^a from manual and from computer searches (further explanation in text)

Literature sources searched	Manual search (numbers of articles accepted into source set)	Computer search of Chemical Abstracts	
		Numbers of articles in source set which also appear in computer listing	Numbers of articles listed for these sources but which were not accepted into source set
Russian Journals of Inorganic Chemistry	79	7	5
Physical Chemistry	13 } 92	3 } 10	19 } 24
Thermochimica Acta	71	9	8
Journal of Thermal Analysis	36	4	8
Journal of Inorganic and Nuclear Chemistry	32	2	5
Indian Journal of Chemistry	21	2	2
Combined search of journal indexes	42	12	163
Chemical Abstracts: manual search of Sections 65, 66, 67 and 78	48	16	—
Chemical Abstracts: computer search	(26) ^b	26	1319
Total	368	81	1264
2nd European Symposium on Thermal Analysis [3]	38	3	12

^a See p. 363.

^b Computer search.

Information Retrieval Service. The following search statement was entered:
Papers published in 1981

and

SOLID? or CRYSTAL?

and

DECOMPOSITION or THERMAL (W) ANALYSIS or PYROLYSIS or KINETIC or MECHANISM? or THERMOLYSIS or STOICHIOMETRIC or THERMOGRAVIMET? but excluding MATHEMAT? or MODEL? or THEOR? and limited to NON-PATENT RECORDS.

This search was dated 16 December 1982.

The print-out was composed of 1345 entries of which only 26 constituted additions to our source set and only 55 had already been found in our journal (40 indexes) and Chemical Abstracts (manual) searches (which together yielded 342 source set entries). This comparison of the effectiveness of the different search methods is shown in Table 1.

The first column of Table 1 lists the sources searched and the second records the total number of entries found from each which were accepted into our source set. The last two columns compare these findings with the computer listings. Column 3 shows the number of source set citations recorded by the computer which had already been found in the manual search (except for the "computer search" row). Column 4 shows the number of entries listed by the computer for each source which we regard as not being acceptable into our source set.

This computer search, therefore, located only 81 articles, which we accept as being of interest, out of the 1345 recorded. We regard this dilution factor, of 1 source set article in ~16.6 listed, as being unacceptably high. More seriously, the identification of only 81 entries from our 368 source set (22%) is surprisingly low. Reasons for this unsatisfactory performance of the computer search are discussed in the following section.

6. THE COMPUTER SEARCH

Preliminary attempts to use the computer for information retrieval showed that considerable difficulties attend the selection of key or index words that precisely specified our requirements. While the term "decomposition of a solid" is, to the chemist interested in the field, a meaningful description of a recognizable group of processes, both the words *decomposition* and *solid* have much more general usage. There is no specific designatory term applicable to this group of reactions; such a term could provide a valuable index reference. (One possibility is the word *crystolysis* which implies breakdown or re-arrangement, as in hydrolysis, electrolysis, pyrolysis, etc., but avoids the prefix "sol", which may imply solution phenomena.)

Our preliminary index searches demonstrated that single words tended to

be too general, for example, "decomposition" yielded some thousands of citations (7315). In contrast, combinations of words tended to be too restrictive yielding only some tens of citations. At the time that we were making these initial computer searches we knew from our manual searches that the source set would contain > 300 entries. Accordingly, the search statement ultimately used, given in Section 5(c) above, represented a compromise between unacceptably large and unrealistically small coverage of the topic. The result obtained, however, cannot be regarded as having satisfactorily achieved the objectives intended.

Other reasons for the obvious shortcomings of our computer search are evident and some are easier to state than to rectify. Firstly, authors frequently do not mention in the title of their article, or even in their abstract, that the reaction proceeds in the solid state. Accordingly, that article is not classified or indexed under this heading. Secondly, it is not practicable to define meaningful limits to the subject, though our computer survey has included many references to papers well outside our intended topic.

While it is inappropriate to examine in detail the contents of the 1264 papers we discarded from the computer retrieval, it is, nevertheless, worth mentioning some main reasons for their rejection. Our decision was not always based on title alone but often included, in cases of doubt, consideration of the abstract or sometimes of the full text of the article. We have not accepted reports of rate processes involving a second reactant, so discussions of reactions of a solid with a gas, a liquid or another solid have been rejected. Similarly, melting, electrode processes, purely diffusion studies and topics described by exceptionally generalized titles, such as "waste disposal" have been treated as being outside our range of current interests. Photochemical and radiation induced decompositions were also omitted, except where accounts directly related to the reaction in the absence of radiation. In many papers the words "solid" and "decomposition" applied to separate and distinct phenomena. This appeared, for example, in the many studies involving the characterization of a solid substance (precipitated from solution, deposited as a film, etc.) prepared through the homogeneous decomposition of a dissolved precursor or from the gas phase. Other listed, but not accepted, papers were concerned with mechanisms of heterogeneous catalytic reactions involving the breakdown of an adsorbed intermediate. For a very few retrieved articles it was not apparent to us why these had been recorded in response to our request.

(a) Comment

It seems probable that our literature search methods are not very different from those employed by others in this, and related, fields. Accordingly, we present the unsatisfactory features of the comparisons embodied in Table 1 as a constructive comment and illustration of the problems inherent in indexing articles concerned with this subject. We hope that by presenting

this quantitative demonstration of the existing situation we may stimulate interest which can lead to an improvement. We were disappointed by the results we obtained, since we had originally applied the method with optimism. Our alternative searches yielded no improvement and we identify the central problem as the omission of the word "solid" (etc.) from article titles. While current practice may be acceptable and understood by the interested reader, it is certainly not effective in presently available retrieval systems.

7. CLASSIFICATION OF THE CONTENTS OF ARTICLES IN THE SOURCE SET

Our primary classification of the 368 multifarious component articles of our source set was the separation into those including quantitative kinetic data (124) from those concerned with stoichiometry (196) while the remainder (48) are grouped as miscellaneous. This somewhat hierarchical approach regards rate studies as, in general, intended to investigate reaction mechanisms. Thus such work is considered to be more fundamental than stoichiometric investigations. Kinetic measurements, moreover, usually require or presuppose the identity of the chemical change occurring and examine its properties in greater detail. Evidence of both types can be considered in the formulation of a reaction mechanism.

We further subdivided both larger categories on the basis of the reliability or comprehensiveness of the experimental evidence provided. Papers which included isothermal kinetic measurements (65) were adjudged [1,2] to be usually more reliable than rising temperature rate measurements: this point is discussed below. Similarly, stoichiometric studies providing comprehensive evidence concerning the identities and amounts of all products (106) have been separated from reports in which the experimental evidence for the chemical change occurring was less complete (90). This division is certainly not sharp and required some subjective judgement. The miscellaneous category included mechanistic investigations in which kinetic measurements were not described but reaction models were deduced from observations by microscopy, X-ray diffraction, etc.

The source set classification on the above criteria is recorded in Table 2. Articles of the five types distinguished occur distributed throughout the range of publications examined. The six journals identified as being most active in the field incorporated broadly similar distributions of relevant contents. While the classification in Table 2 cannot be regarded as absolute, we believe that the general pattern revealed is meaningful and is based on significant samples.

The subsections that follow consider the chemical information contained in the papers of each category (the columns in Table 2). Subsequent sections below discuss: (a) the types and numbers of reactants investigated and the techniques employed in the individual studies; (b) the chemical information

TABLE 2
Content classification of source set articles

Literature source	Isothermal kinetics	Non-isothermal kinetics	Stoichiometry (complete)	Stoichiometry (incomplete)	Miscellaneous	Total
Russian Journal of Inorganic Chemistry	2 } 8	9 } 10	46 } 48	20 } 23	2 } 3	79 } 92
Physical Chemistry	6 } 8	1 } 10	2 } 48	3 } 23	1 } 3	13 } 92
Thermochimica Acta	16	24	12	10	9	71
Journal of Thermal Analysis	3	7	10	11	5	36
Journal of Inorganic and Nuclear Chemistry	3	4	10	11	4	32
Indian Journal of Chemistry	5	2	4	9	1	21
Combined search of journal indexes	11	1	9	14	7	42
Chemical Abstracts (manual search)	19	5	5	7	12	48
Chemical Abstracts (computer search)	0	6	8	5	7	26
Total	65	59	106	90	48	368
Chemical Abstracts (total listings from computer search)	21	12	17	17	14	81
2nd European Symposium on Thermal Analysis	5	16	9	6	2	38

obtainable from the various journals and sources constituting the rows in Table 2; and (c) the chemical conclusions reached from the study as a whole.

(a) *Isothermal kinetic studies*

(i) *Reactants, methods and objectives*

Most of the isothermal studies were concerned with a single reactant (50), and smaller numbers were concerned with two (5), three (4), or more (6) substances. Altogether a highly diverse group of chemical compounds was investigated. The most widely employed experimental method of measuring reaction rates was thermogravimetry (45), though DSC (10) and DTA (11) were also used. Rate studies were often supplemented by further observations including X-ray diffraction (20), microscopy (14), spectra (9) and chemical analysis (7): other techniques were less frequently applied.

Eight articles represent continuing interest in already extensively studied compounds, silver oxalate [4,5], ammonium perchlorate [6–8], calcium carbonate [9], strontium and barium azides [10,11]. These studies extend previous work to elucidate reaction characteristics in greater detail and to determine the influences of mechanical pretreatment, additives or irradiation on kinetic behaviour. Three further papers were concerned with rate measurements, including the deuterium isotope effect on dehydrations previously studied: boric acid [12], copper sulphate pentahydrate [13] and calcium oxalate monohydrate [14]. Dehydration rates were also used to investigate site preferences of H_2O/D_2O in copper sulphate pentahydrate [15].

Three papers reported isothermal kinetic studies of reactions in polymers [16–18] and discussed behaviour in terms of homogeneous kinetics (usually as a first-order reaction). Microscopic investigations were not mentioned for these.

(ii) *Kinetic analysis*

The equations used for the kinetic analysis of measured rate data throughout this group of 65 articles were almost exclusively those listed previously [19]. The following frequency distribution records the numbers of individual articles in which each particular rate expression was used at least once. (Each equation applied quantitatively in a particular paper was scored, but multiple use of the same equation in any paper was counted once only.)

Avrami–Erofeev equation	}	13
$n = 2$ (12), $n = 3$ (5), $n = 4$ (1)		
Contracting cube equation		
Contracting area equation		6
Prout–Tompkins equation		6
Diffusion control		4
Zero-order equation (constant rate)		11
First-order equation		19
Second-order equation		1

We noted that occasionally rate processes for which there was evidence of some initial acceleratory character were described as obeying rate expressions which were deceleratory throughout. Such kinetic analyses must be regarded with strong reservation.

Fifty-four of these 65 papers reported obedience of kinetic data to a rate expression but only 14 papers described microscopic observations. This is positive confirmation that at present it is not usual to confirm geometric deductions based on the interpretation of kinetic results [2] by direct observation of interface development during product phase nucleation and growth.

Magnitudes of activation energies (E) were reported in 50 articles and pre-exponential factors (A) in about half this number. Comparisons between E values calculated from constant temperature rate measurements with those for the same salt using rising temperature data were given in 9 papers. In three instances [20–22] there was acceptable agreement but in the remaining six [13,14,23–26] the disagreement was significant. This disagreement was variously ascribed to differences in the methods [27] of kinetic analysis or in the conditions prevailing within the reaction vessel. Collectively the discussions appearing in the latter group of reports [13,14,23–26] again strongly emphasize the well-known difficulties inherent in the use of non-isothermal methods to measure kinetic characteristics.

(iii) Reaction mechanisms

The space devoted to the theoretical consideration of reaction mechanisms varied considerably between the articles. Our content analysis considered two main types of information [2]: reaction geometry and interface chemistry. *Twenty-two* articles included some discussion of both aspects of reaction, 14 considered interface chemistry but not reaction geometry and 7 were concerned with reaction geometry but did not discuss interface chemistry. A further 6 papers discussed behaviour in terms applicable to homogeneous chemical reactions.

(b) Non-isothermal kinetic studies

Content analysis in this section is based on 68 articles, since it is appropriate to include the 9 that also report isothermal kinetic data (Section 7(a,ii) above). *Eight* were available in abstract form only and some of these provided little detail concerning the aims and experimental methods of the work.

(i) Reactants, methods and objectives

Thirty-five papers were concerned with the decomposition of a single substance and a further 10 with two substances. The groups encountered most frequently in the reactants were oxalates (6) (including a group of oxalates [28]) and various sulphates [13,15,29–31] (5). However, 4 articles,

containing only non-isothermal kinetic measurements, each dealt with more than 20 substances and these included studies of 73 polynitro compounds [32] and of 44 diverse reactants [33].

Together the reactants considered covered a wide and varied range of substances. A surprising feature of this group of articles was that only just over half specified the stoichiometry of decomposition, though some others provided evidence concerning the origin of the parameters used to measure the reaction rate. Thermogravimetry was the most widely used experimental technique (61).

In 22 papers the authors stated no reason for undertaking the study, except that it represented a continuation from a previous contribution in the field. In a further 23 articles the work also continued an earlier study but additional reasons justifying the work were provided. Such reasons here included a mention of the absence of previous studies (11), commercial interests (10), the characterization of the thermal properties of compounds hitherto not studied (5) or new compounds (5). Ten papers stated no aims of the authors or indication of their previous activities in the subject area.

(ii) Kinetic analysis

Calculation of kinetic parameters [$f(\alpha) = kt$, the isothermal variation of fractional reaction (α) with time (t), also A and E] requires a quantitative combination of this rate expression [$f(\alpha) = kt$] with the Arrhenius equation [$k = A \exp(-E/RT)$]. There have been numerous discussions as to the most suitable methods of analysis of the resulting intractable equations. Many approximate solutions have appeared in the literature, which are intended to permit the determination of [$f(\alpha) = kt$] and the magnitudes of A and E from a single set of measurements.

Our examination revealed that a total of 29 apparently different calculation methods had been used to determine kinetic parameters in this group of papers (68). More than a single method was used in 20 articles, the greatest number of alternatives used being six and the overall average was 1.5 methods/paper. Each identification of an alternative calculation method is based on the supporting authority cited and some of these are closely related or represent minor variations of older techniques. Interestingly, authors seldom, if ever, gave a justification of their reasons for adopting a particular approach in preference to all others. The most popular method was undoubtedly that due to Coats and Redfern [34] (24), followed by that of Freeman and Carroll [35] (11). Other methods cited most frequently were those of Nirsha et al. [36] (7), Piloyan et al. [37] (6), Horowitz and Metzger [38] (5), Satava [39] (4) and Zsako [40] (4).

Magnitudes of E were reported in all but six papers (62) and A values in 32. Comparisons of E values obtained for the same reaction using alternative methods of non-isothermal calculation resulted in good agreement in only 8 out of 20 instances. (Compare 3 out of 9 satisfactory comparisons between

isothermal and non-isothermal measurements reported in the previous section.) Compensation effects [41] were reported in 4 studies [24,42–44].

(iii) Reaction mechanisms

Only about half of the papers gave any discussion of reaction mechanisms, very few of which could be regarded as comprehensive. These discussions were equally divided between consideration of the reaction geometry and of the bond-breaking step (interface chemistry). Geometric deductions were based on an observed obedience to a rate expression, but the provision of microscopic evidence in support of such conclusions was rare (4, two of which also included isothermal data). We found no correlation between the method of kinetic analysis and the mechanistic interpretations reported, though studies using the calculation methods given by Zsako et al. [40] (4) and by Thomas and Clarke [45] (3) all contained some discussion of reaction models.

(iv) Comment

We believe that the pattern of subject development described in the foregoing paragraphs reveals a state of considerable disorder. Various approaches to the kinetic analysis of non-isothermal data are being applied with apparently little or no reference to each other and providing no realistic appraisal of their advantages or weaknesses. We suggest that a comprehensive and critical review of this topic is overdue: this should include an examination of the factors which control accuracy of interpretation and the distinguishability [46] of the kinetic parameters, A , E and $f(\alpha) = kt$.

Reasons for embarking on particular studies were not always evident and there was sufficient uncertainty expressed by the authors themselves about the reliability of their kinetic conclusions to cast considerable doubt upon the value of many rising temperature kinetic measurements. Consequently, it is surprising to us that microscopy is so rarely used in support of kinetic interpretations. Indeed, we suspect that in favourable systems observational methods provide a more rapid and reliable method of obtaining information about reaction geometry than non-isothermal kinetic measurements. In systems unfavourable for microscopy it may be argued that isothermal methods are the more satisfactory.

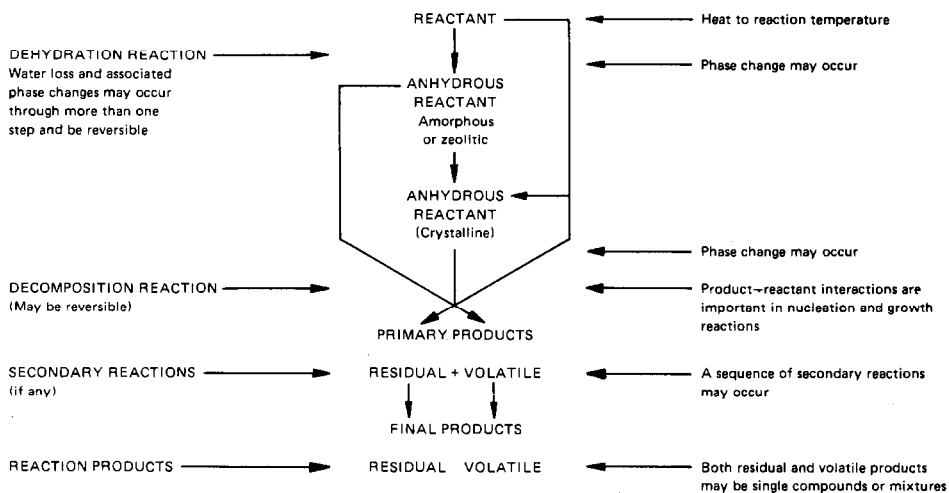
(c) Stoichiometric studies

Just over half of the source set articles were concerned with the characterization of reaction stoichiometries (196), though these did not always report the quantitative determination of every product. Many papers were concerned with either one (73) or two (35) reactants, though the overall average was 3.58 compounds/paper. Reactants investigated were extremely diverse; this point is discussed further below. These investigations of stoichiometry

tended to use several complementary experimental techniques (mean ~ 3.8 different experimental methods/paper) of which the most frequently applied were thermogravimetry (158), spectra (134), DTA (127), X-ray diffraction (122) and chemical analysis (104).

Many reactions have been identified as being simple, yielding stable and well-defined products by a single, irreversible step. Such processes are particularly suitable for kinetic investigations. However, other diverse chemical changes of solids are more complicated and characterization of their stoichiometry is not as straightforward as is sometimes assumed. Some of the possible types of behaviour are presented diagrammatically in Scheme 1

SCHEME 1. Diagrammatic representation of the steps that may participate in the decomposition of a solid.



where water (or other ligand) removal is followed by decomposition. Each reaction may, of course, occur in more than one step, involving concurrent or consecutive rate processes that are differently dependent on temperature, the rate of volatile product removal, the nature and pressure of gases or catalysts present, light, etc. The possibility that behaviour may be complex must be remembered when interpreting stoichiometric observations: some examples to illustrate this point are given below (not all from our source set).

Reliable identification of the chemical change(s) occurring is a necessary prerequisite for a kinetic study and is an essential foundation for mechanistic proposals.

(i) Dehydration of hydrated salts

These reactions are of interest since studies of such reactants contributed to the early development of the kinetic foundations of the subject.

Removal of the water of hydration (or other ligand) can influence a subsequent solid-state decomposition in two ways. Firstly, extensive textural

reorganization may accompany or follow dehydration and this can profoundly influence the generation and development of the interface in any later chemical change of the solid. Microscopic observations have shown [47] that removal of water from alums is accompanied by a marked particle size reduction and changes in shapes and orientations of crystals. Secondly, dehydrations may result in redistribution of the bonding within the solid, also described for alums [47]. Dehydration of crystalline nickel malonate dihydrate yields [48] an amorphous reactant for subsequent decomposition.

Whether or not the characterization of bond structures and textures of the reactants and products is to be properly regarded as part of a stoichiometric study is largely a matter of the definition of this term. However, such information may be useful in formulating a reaction mechanism and/or in gaining insight into the factors controlling reactivity in the chemical changes of interest.

Complete removal of water is not necessarily achieved in a single process, as many as seven (unequal) steps may be involved in the dehydration [29] of $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$ (333–583 K). Behaviour may be strongly influenced by the prevailing pressure of water vapour and its accumulation leads to incongruent melting [49]. The textures of product $\text{MSO}_4 \cdot 6 \text{H}_2\text{O}$ ($\text{M} = \text{Mg}^{2+}$, Ni^{2+} , Zn^{2+}) [50] and the structure of $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ [51] depended on the pressure of water vapour present during dehydration of the appropriate heptahydrate. The availability of water vapour determines [52] whether $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ yields the trihydrate or the monohydrate. Water of crystallization may undergo hydrolytic reactions on heating, as in the decomposition of $\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$ [53]. Water appears to stabilize nickel squarate [54].

(ii) Simple salts

The significance to be attached to secondary reactions depends on the objectives of the stoichiometric study. To identify and measure the final products of a reaction completed under specified conditions may be sufficient for many purposes. However, the formulation of a reaction mechanism usually requires the unambiguous identification of the primary products evolved. For example, the high yield of carbon monoxide evolved during nickel promoted formic acid decomposition [55] has been interpreted as evidence for the intervention of nickel formate. The high yield of the same product (CO) from nickel squarate decomposition [54] was discussed with reference to the transitory intervention of nickel carbonyl. Both heterogeneous and homogeneous reactions are believed to participate in the decomposition of copper(II) formate [56]. The possible complexity of secondary reactions, involving primary volatile products, is exemplified by consideration [57] of the mechanism of NH_4ClO_4 decomposition.

(iii) Complex salts

The possibilities of secondary reactions between primary products are

obviously increased when the number of component groups in the reactant increases. In addition, there are alternative types of transformations, not found in simple salts, for isomerization reactions through movements of ligands between coordination sites [26].

(d) Miscellaneous studies

Articles not containing kinetic measurements or stoichiometric studies, but concerned with the decomposition of solids, were placed in this group (48). Many of these were located from the Chemical Abstracts searches, manual (12) and computer (7) and also from *Thermochimica Acta* (9) and the combined search of journal indexes (7). Eleven papers were available in the form of abstracts only. This limitation and the absence of unifying features in the group possibly restricted the detailed content analysis to a small extent.

The largest group of articles classified under this heading refers to phase transitions (23) and sublimations (4), processes which resemble decompositions by involving bond redistributions between the crystal components. While we accept that there is an argument for classifying such processes as stoichiometry, we regard the differences to be sufficiently great to warrant separate listing. X-ray diffraction measurements were the most widely applied technique (25) particularly used in studies of phase transitions or the topochemical features of decompositions.

Other papers of the group were apparently concerned with the decomposition of a solid but it was evident, on closer examination, that the rate limiting step involved some dependence on the water vapour present [50,51,58–60] (5) or that a melt was involved [61–63] (3). Further articles were concerned (inter alia) with annealing [64], solid-state polymerization [65], ion production for mass spectrometry by thermal methods [66], decomposition on a support [67], the prediction of decomposition temperatures from ionic radius [68] or structural factors [69].

The most widely stated, or implied, reason for embarking on these studies was the continuation of previous work by the authors (28) and in 19 instances this was the only reason mentioned. No objective was stated in 13 papers, though this is probably an overestimate since it included all of the studies which were available as abstracts only. Other reasons cited included the absence of previous work (6), commercial interests (4), inconsistencies in the literature (2), biological interest (2), etc., and combinations of these (2).

The most frequently investigated reactants were simple anhydrous salts (19) together with some dehydrations. Oxides (5) appeared as the most favoured reactant followed by sulphates (4), hydroxides (3) and nitrates (3). Many studies were concerned with a single reactant, though one article reported the investigation of 22 different compounds [68] and another referred to a series of reactants [70].

These investigations used diverse experimental techniques (average 2.46 techniques/article) including X-ray diffraction (25), thermogravimetry (20) and DTA (16). Thermoanalytical techniques were generally used less frequently than in the kinetic or the stoichiometric studies. In contrast, microscopic observations (19) were used almost twice as frequently as in the other groups, thus providing a direct route to the elucidation of reaction geometry, without recourse to kinetic measurements.

8. CLASSIFICATION OF REACTANTS

Several criteria were considered for the chemical classification of reactants studied in the articles comprising our source set: the most satisfactory was used to prepare Table 3. Dehydrations refer to rate processes in which the loss of water only was investigated. Simple salts include binary compounds, the salts and double salts of mineral and other acids, salts of organic acids (including metal carboxylates), intermetallic compounds, etc. The other headings are self-explanatory. The range of compounds for which decomposition studies were reported included virtually all possible types of reactant solid.

The relatively small number of reactants listed as organic compounds is a consequence of our regarding metal carboxylates as simple salts and compounds containing an organic ligand as complex salts. The number of decomposition studies concerned with solid organic compounds was small, many such substances melt before or during breakdown.

Table 3 confirms that a majority of the isothermal kinetic studies were concerned with simple and well characterized chemical changes: dehydrations (8) or decompositions of anhydrous simple salts (32). While simple salts also appeared frequently (69) in the stoichiometric investigations these were more often concerned with complex salts (102).

Our intention to correlate reasons for reactant selection with the stated aims of that particular study could not be achieved because research objectives were not always made clear. About half of the studies explicitly mention, or at least imply, that the paper continues work already contributed to the field by the authors. We were, however, surprised at how little information was provided about the aims and objectives of the work in many of the reports we considered.

9. NUMBER OF REACTANTS STUDIED IN EACH ARTICLE

The numbers of different solid compounds investigated in each article are summarized in Table 4. Almost exactly half (182/368) of the articles were concerned with the decomposition of a single substance and a further 56

TABLE 3
Reactant classification of source set articles

Content classification of article	Dehydration	Simple salts		Complex salts		Organic compounds		Minerals	Others	Total
		Hydrates	Anhydrous	Hydrates	Anhydrous	Monomer	Polymer			
Isothermal kinetics	8	5	32	2	5	5	6	1	1	65
Non-isothermal kinetics	7	12	8	8	12	4	2	4	2	59
Stoichiometry (complete)	8	21	19	21	29	0	0	7	1	106
Stoichiometry (incomplete)	4	15	14	21	31	2	2	1	0	90
Miscellaneous	7	7	19	2	5	0	6	2	0	48
Total	34	60	92	54	82	11	16	15	4	368

TABLE 4
Numbers of reactant compounds studied in individual source set articles

Content classification of article	Number of compounds studied in each paper										Total	Mean: solids/article
	1	2	3	4	5-6	7-10	11-15	16-20	> 20			
Isothermal kinetics	50	5	4	1	3	0	1	1	1	0	65	1.92
Non-isothermal kinetics	28	10	4	5	2	4	1	1	1	4	59	5.47
Stoichiometry (complete)	43	24	12	7	9	10	1	0	0	0	106	2.85
Stoichiometry (incomplete)	30	11	11	5	13	13	3	2	2	2	90	4.44
Miscellaneous	31	6	3	2	1	2	1	0	2	2	48	2.94
Total	182	56	34	20	28	29	7	4	4	8	368	3.48

reported observations for two compounds. A relatively small proportion (48) described the behaviour of more than six reactants and 8 could be regarded as comprehensive surveys concerned with groups of more than 20 reactants.

It is evident from Table 4 that the more precise studies (isothermal kinetics and complete stoichiometry) were, on average, concerned with relatively fewer compounds than the non-isothermal kinetic and incomplete stoichiometric studies. All classified groups, however, contained a high proportion of single-compound investigations. Most isothermal studies were concerned with three or fewer reactants. The average for non-isothermal investigations is 5.47 compounds/paper though, if the distorting influence of the four comprehensive studies involving an aggregate total of 167 reactants is removed, this average is reduced to 2.84. This value is almost identical with that found for complete stoichiometric studies (2.85) but less than that found for incomplete stoichiometric studies (4.44).

10. EXPERIMENTAL TECHNIQUES APPLIED

Experimental techniques finding the most widespread applications in the different studies are summarized in Table 5. Each number records the number of articles in which the use of the technique is mentioned. The row "other methods recorded" refers to ten other measurements applied too infrequently to warrant individual tabulation and included the following: Mössbauer spectra (mentioned 10 times for studies classified as complete stoichiometry); manometric pressure measurements (used in 10 of the isothermal kinetic studies); surface area determinations (7); NMR (6); and ESR (5).

Not surprisingly, perhaps, the smallest numbers of experimental techniques were used in isothermal kinetic studies (average 2.12). Such investigations were often concerned with relatively simple reactions and rate processes of already established stoichiometry. Those investigations using the rising temperature kinetic method enjoyed rather greater support from alternative experimental methods (average 2.71). Not unexpectedly, Table 5 also shows that stoichiometric investigations usually exploited a more diverse array of laboratory measurements to characterize the chemical changes involved than those employed in kinetic studies.

Thermogravimetry, mentioned in three-quarters of these studies, was the most widely used experimental method. DTA and X-ray diffraction measurements were mentioned in about half the papers but DSC was much less generally employed. We were surprised at just how infrequently microscopic measurements were made, appearing, on average, in less than one in seven papers and even for the isothermal kinetic studies the proportion was low (21.5%).

TABLE 5
Experimental methods used in articles included in the source set

Experimental techniques used	Isothermal kinetics	Non-isothermal kinetics	Stoichiometry (complete)	Stoichiometry (incomplete)	Miscellaneous	Total	% of total papers using the method
Thermogravimetry	45	53	89	69	20	276	75.0
DTA	11	31	77	50	16	185	50.3
DSC	10	8	9	4	4	35	9.5
Chemical analyses	7	20	63	41	2	133	36.1
X-ray diffraction	20	17	72	50	25	184	50.0
IR Spectra	8	19	61	52	11	151	41.0
Other spectra	1	2	10	11	0	24	6.5
Microscopy	14	2	8	8	19	51	13.9
Evolved gas analysis, MS, Chromatography	9	3	13	11	6	42	11.4
Magnetic susceptibility	1	4	3	7	4	19	5.2
Other methods recorded	12	1	23	12	11	59	16.0
Total	138	160	428	315	118	1159	
Mean $\left\{ \frac{\text{number of methods used}}{\text{number of papers}} \right\}$	2.12	2.71	4.04	3.50	2.46	3.15	

Table 5 emphasizes the diversity of experimental methods currently being used to study decomposition reactions of solids. Clearly the value of exploiting alternative and complementary techniques is widely appreciated and applied.

11. CONTENTS OF INDIVIDUAL JOURNALS AND ABSTRACTS CONTRIBUTING TO THE SOURCE SET

The following subsections discuss the contents of the individual journals, or group of journals (the classes in Table 1) that contribute to the source set. In contrast with the organization of material elsewhere in this article, the present section is not given in a standardized format. This introduces a flexibility into the presentation which permits a more meaningful depiction of significant trends and characteristic features (the "flavour") of the group of articles found in each source class.

(a) Journals of the Academy of Sciences of the U.S.S.R.

(i) Russian Journal of Inorganic Chemistry, 26 (1981)

This journal provided the largest contribution to our source set (79) of all those examined. The solid-state decomposition interest, however, often represented a subsidiary or contributory feature in a study of the stability or reactivity of one or more inorganic compounds. These investigations usually characterized the stoichiometry (Table 2) and/or the reaction temperature of the chemical change observed.

Reasons for undertaking individual studies or for the choice of particular reactants were not always explained. From examinations of the literature citations, however, we concluded that 30 papers, which gave no reason for the study, continued topics on which the authors had already published. Additional or alternative reasons given were that no previous work on the topic had appeared in the literature (19), a practical or commercial interest (12), to resolve a doubt or perceived inconsistency between published articles (9) or to increase understanding of the properties of a known reactant (4). In 5 other papers no reason for the study could be identified.

Classification (Table 3) of the reactants as largely composed of anhydrous salts, complex (30) and simple (21), does not sufficiently emphasize the diversity of the compounds studied in this group of articles. The scope of current interests is more realistically illustrated by the following alternative classification: Anderson-type rearrangements [71] and related reactions (14); salts of oxyacids (13); phosphates and borates (10); lanthanides (8); mixed oxides (7); complex halides and related salts (6); uranium salts (4); phthalates (4); graphite halogen compounds (3); and others (10).

Most papers were relatively short. Many, including all the kinetic reports,

were concerned with either one (30) or two (19) reactants, though one single article investigated 14 reactants [72]. Interest was largely directed towards reaction stoichiometries, complete or partial, though 11 papers reported some kinetic observations.

A well developed uniformity of experimental approach was evident throughout this group of articles. Six measurement techniques were used more widely than others: thermogravimetry, DTG, DTA, X-ray diffraction, IR spectra and chemical analysis. In the 79 papers, all six were used in 23, and five in 25 (the most common omissions being X-ray diffraction (13) and IR spectra (9)). Thermogravimetric and DTA measurements were most widely used, a solely non-isothermal method being employed in 51 papers, a solely isothermal method used in 4, (including only two of the kinetic studies [73,74]) and the remainder applied both. Every paper used at least one of the experimental methods listed above, 15 used three or less. Other techniques applied included crystal optical analysis (7), mass spectrometry (6), evolved gas pressure measurements (6), chromatography (5), solubility determinations (5), density determinations (4) and NMR (4).

(ii) *Russian Journal of Physical Chemistry*, 55 (1981)

Of the 13 articles listed for this journal, 7 continued previously published work by the authors, 2 extended knowledge of a particular reaction, 2 were undertaken because there was little or no previous work on the topic, 1 developed a technical or commercial interest and the reason for 1 was not clear.

Most of these studies described the reactions of simple anhydrous salts or dehydrations, and the remaining 3 papers were concerned with a mineral [75], an organic polymer [76] and a phase change in elemental selenium [77]. As in the sister journal (Section 11(a,i)) these papers were usually concerned with a small number of reactants (one (7), two (4)) and a similar range of experimental techniques were employed. The present journal, however, contained a higher proportion of articles reporting isothermal kinetic studies (6) whereas only 5 were concerned with stoichiometry.

(b) *Thermochimica Acta*, 43–51 (1981)

(i) *Isothermal kinetic studies*

Sixteen articles included isothermal rate measurements, 9 being exclusively or largely devoted to reporting and discussing kinetic phenomena. Eleven papers were concerned with the decomposition of a single reactant substance. Reaction stoichiometries could be regarded as having been satisfactorily characterized in 9 articles, some of these being simple or already known. Reactants studied were diverse, including sulphates (3), amine compounds of cobalt and of chromium (2), tetrazole compounds (2), phosphonium compounds (1), polysaccharides (1), $\text{Cu}(\text{H}_2\text{PO}_2)_2$ (1), and

others. Reasons for reactant selection were not always stated but were often the continuation of previous work or were of commercial interest. Almost every article included thermogravimetric measurements and the supporting techniques used included DSC (6), spectra (6) and/or X-ray diffraction studies (4).

In most articles the kinetic observations were satisfactorily represented by obedience to those rate equations which were listed previously [19]. In two unusual applications of these expressions [78,79] the role of diffusion in sulphate decompositions was considered and another report [80] included a modified form of the Prout-Tompkins equation [19]. Mechanistic discussions were often brief. Reaction geometry was considered in the interpretation of kinetic behaviour in 12 articles but only 4 exploited microscopic observations in confirming such conclusions. The significances of the magnitudes of E values were discussed in 11 papers but A values were less frequently considered.

Isothermal kinetic studies were compared with parallel rising temperature measurements in 6 reports. In one such quantitative comparison [20] the dynamic and the constant temperature observations gave satisfactory agreement. In all the others [13,14,23,24,26], however, the calculated activation parameters showed significant inconsistencies, dependent on such variables as (inter alia) the rate of temperature rise, sample mass and disposition, and the rate equation used in the kinetic analysis. Interpretation of non-isothermal rate data must, therefore, include due consideration of all the parameters that can influence kinetic characteristics.

Three articles [20,23,81] provided relatively comprehensive mechanistic interpretations of both stoichiometric and kinetic observations: in others the conclusions were less extensive or essentially qualitative. Interpretation problems were acknowledged as restricting the value of conclusions reached in three of the papers.

(ii) Non-isothermal kinetic studies

Twenty-four articles reported only non-isothermal rate measurements, about half of these being almost exclusively concerned with kinetic analyses and discussions. Reaction stoichiometries had already been established or were fully characterized in 10 papers but we regard product identification as incomplete in the others (14). Most papers were concerned with four or fewer reactants, but 3 comparative studies involved large numbers of related compounds: 73 organic polynitro compounds [32], 26 cobalt amine complexes [43] and many metal carbonates and carboxylates [33].

Motivations mentioned for undertaking these studies included the extension of a previous interest (9), the investigation of a novel substance and, more rarely, the possible technical importance of the reaction. Almost every paper reported thermogravimetric measurements (23), with supporting experimental observations from DTA (13), DSC (6), spectra, X-ray diffraction and other methods.

Most authors used a single rate equation for the analysis of the rising temperature kinetic data and the calculation of activation parameters (18) but a few described the parallel application of two (3), three (2) or five (1) analytical approaches. The most frequently cited methods were those due to Coats and Redfern [34] (12) and to Freeman and Carroll [35] (5): seven further methods were mentioned, some more than once. Some articles (5) introduced a novel feature into their method of kinetic calculation.

Every paper in this group reported at least one value of E (24), some listed multiple values calculated by alternative analytical methods but the magnitudes of A were given less frequently (11). Variations in apparent values of the activation parameters were discussed with reference to differences in reaction conditions (3), or in calculation procedures (2). The significance of observed magnitudes of E were discussed, usually briefly, in 11 articles and trends in E values found between chemically related reactants were considered in 6 more. Eight papers provided little mechanistic interpretation and in no paper of this group were conclusions concerning reaction geometry supported by microscopic observations.

(iii) Stoichiometric studies

These studies (22) usually reported the temperature interval within which the chemical change of interest took place. The detail in which such reactions were characterized varied considerably, ranging from quantitative determinations of the yields of all products, both residual and volatile, to more qualitative inferences based on limited experimental data. In 15 papers reactions observed are reported in the form of balanced stoichiometric equations and in some others the results were only slightly less comprehensive. Many of the decompositions of interest proceeded to completion through two or more distinguishable steps: in 17 papers intermediate compounds were identified. Studies not including kinetic observations did not usually discuss the factors controlling reactivity.

Reasons given for embarking on studies of the diverse reactants within this group included the continuation of previous work (7), a reactant with interesting properties (7), to identify intermediates or a reaction sequence (6), the reactant was of commercial interest (1) or to develop an analytical method (1). Each report tended to be concerned with a larger number of individual reactants than the kinetic studies. Two articles [82,83] considered the influence of additives on a range of solid reactants.

Stoichiometric studies usually applied a larger number of different experimental techniques than was found for the kinetic investigations. Thermogravimetry (18) again was widely used, weight losses often being used to characterize the chemical changes occurring, also (inter alia) DTA (17), X-ray diffraction (17), spectra (8) and chemical analyses (7).

(iv) Miscellaneous studies

These studies included the phase transformations that occur on heating

TiNO₃ [58] and Na₂SO₄ [59] (the natural mineral thenardite), which were examined by thermal methods and microscopy. Behaviour was irreproducible, but some progress was made towards explaining variations in transition temperatures by the influences of impurities, notably water.

(Additional articles (7), not accepted into the source set, reported a limited amount of information concerning the decompositions of solids but were excluded from further consideration due to the onset of reactant melting or dissolution in released water. Compounds in this diverse group included (inter alia) Ba(NO₂)₂ · 2 H₂O, NH₄F, hydrated Ba(OH)₂, antimony oxides and fluorides.)

(c) Journal of Thermal Analysis, 20–22 (1981)

Many of the 36 articles located were concerned with the elucidation of reaction stoichiometries.

About half the papers continued earlier studies by their authors. The reactants could be classified as inorganic salts (10), complex salts (9), salts of oxyacids (9), minerals (4), organic compounds (3) and a ferrocene polymer (1). Several papers (5) were concerned with metal oxalates, 4 provided mainly stoichiometric information and 1 measured the influence of cation radius on the reaction temperature [68]. No other large group of reactants was discussed though the compounds investigated included sulphates (2), perchlorates (2) and vanadates (2). Most articles were concerned with a single reactant (15) of which 10 used a single preparation.

Four papers discussed the effects of variations of reactant crystallite size, crystallinity or structure and 1 investigated changes in component units in a ferrocene polymer [84]. Ten papers observed the effects of variation of cation on decompositions. Others were concerned with reactions of various polyphosphonates [85], substituted trinitroanilines [86] and polyurethanes [70].

Three studies of isothermal decompositions described the behaviour of a single compound (NH₄ClO₄ [6], Pb₃O₄ [25] and Ni(N₃)₂ [87]) using a single experimental technique (thermogravimetry (2) or EGA (1)) upon which mechanistic conclusions were based. Non-isothermal kinetic papers (7) investigated the decompositions of (inter alia) minerals (3) and polymers (2) but we were able to base no useful generalizations on these observations.

(d) Journal of Inorganic and Nuclear Chemistry, 43 (1981)

Articles in this journal (32) were usually concerned with aspects of inorganic chemistry (reactivity, bonding, structures, etc.). Many discussed complex salts (21), and there were relatively few kinetic studies (7) or discussions of reaction mechanisms.

Two of the 3 isothermal kinetic studies were concerned with the photolyses [10,11] of Sr(N₃)₂ and Ba(N₃)₂, discussed with reference to the thermal

reaction. The third mechanistic study concerned the dehydration, racemization and deamination reactions [21] of optically active $[\text{Cr}(\text{en})_3]\text{Cl}_3 \cdot 2 \text{H}_2\text{O}$ alone and admixed with NH_4Cl catalyst. All 4 non-isothermal kinetic studies were concerned with decompositions of complex salts, for which reaction stoichiometries were incompletely characterized. In one of these papers [88] comparable E values were obtained by five different methods of kinetic calculation, α ranges, usually for zero order obedience, reported and a mechanistic explanation of the observations given.

Stoichiometric observations were often only qualitative or incomplete in those studies concerned with aspects of the inorganic chemistry of the reactants. Interest was generally directed towards crystallographic, thermochemical, solution or properties other than solid-state chemistry of the reactants. No useful classification of compounds studied could be found since no particular component, ligand or structural feature was identified as predominating.

Two studies, concerned with the chemistry of iron, applied Mössbauer spectroscopy (and other techniques) to investigate the decompositions of iron(II) formate and malonate [89] and of iron(III) in the decomposition of neodymium trioxide [90]. Two further studies investigated textural changes during $\beta\text{-FeOOH}$ [91] decomposition and during microcrystalline cellulose [92] pyrolysis. In these last two studies, microscopic observations were supplemented by measurements of surface area, densities and other structural features but not kinetic data.

(e) Indian Journal of Chemistry, 20A (1981)

Source set articles (21) from this journal included (Table 2) isothermal kinetic measurements (5) and stoichiometric investigations (13). Isothermal studies included rate measurements for the pyrolyses of variously pretreated celluloses [93,94] and for the influences of γ -irradiation [95] and Th^{4+} addition [96] on the decompositions of calcium and barium bromates, respectively.

Stoichiometric investigations were usually intended to characterize the properties of new or novel compounds, these substances also being defined by chemical analyses, spectra, etc. The single miscellaneous study was concerned [97] with phase transformations in hydrogen bonded organic compounds.

(f) Combined search of journal indexes (1981)

Of the 42 articles located from the 34 journals searched, 11 reported isothermal kinetic measurements and only a single article reported a rising temperature rate study. Since these papers are fairly widely dispersed in the literature, we have documented the material in somewhat greater detail than

seemed necessary for the individual journals considered above.

Many of the isothermal kinetic studies reported a continuation of previous work and often concerned relatively simple reactants, undergoing an already well-characterized chemical change. Constant temperature decomposition rate measurements were made for the following reactants: α - AlH_3 [98], $\text{Al}_2(\text{SO}_4)_3$ [99], certain alums [47], caffeine hydrate [22], $\text{BaSiO}_3 \cdot \text{H}_2\text{O}$ [100] and the $\beta \rightleftharpoons \gamma$ transition in $\text{Li}_2\text{ZnSiO}_4$ [101]. Studies were also made of the effect of CO_2 pressure on CaCO_3 dissociation [9] and mechanical pretreatment and γ -irradiation on $\text{Ag}_2\text{C}_2\text{O}_4$ decomposition [5]. Thermomagnetic measurements were made of the solid state structural (monomeric/polymeric) transformations of nickel complexes [102]. Rate measurements for Si_3N_4 decomposition constituted a part of a study of textural changes [103]. Observations of dehydration kinetics were used to investigate intracrystalline site preferences of hydrogen isotopes in $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ water of crystallization [15].

Many of the articles reporting some stoichiometric information for solid decompositions made a relatively small contribution to the subject and are not, therefore, individually cited here. These were usually concerned with aspects of structures and bonding in complex compounds.

Articles providing mechanistic discussions of solid-state decompositions which were not primarily based on kinetic evidence considered the reactions of complex tungstic acids [104], $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ [105], $\text{FeC}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$ [106], hydrates of $\text{Al}_2(\text{SO}_4)_3$ [107], and derivatized lamellar phosphates and phosphonates of M(IV) ions [108]. Five papers were concerned with pyrolyses of molybdates and tungstates, 3 of which [109–111] investigated crystal structure changes from X-ray diffraction measurements.

Papers classified as miscellaneous include those concerned with a high temperature phase transformation of AgNO_3 [112], the $\beta \rightarrow \alpha$ transition in polycrystalline SiC [113], the vaterite to calcite phase change [114] (using Mn^{2+} tracer ions), the thermal effects of heating chrysotile [115] and for silica adsorbed on $\text{Mg}(\text{OH})_2$ [67], and the volatilization of quaternary cations [66] and of a lanthanum complex [116].

(g) *Chemical Abstracts (manual search)*, 94–97 (1981–1982), Sections 65–67, 78

Isothermal rate measurements were reported in 19 articles, from the 48 located, a relatively high proportion compared with the contents of other sources. The diverse group of reactants for which kinetic and mechanistic investigations were reported included: $\text{Al}(\text{AlH}_4)_3 \cdot \text{Et}_2\text{O}$ [117], AlH_3 [118], a La/Ni/Al alloy hydride [119], Al_2TiO_5 [120], sodium perborate [121], some arsenates [122], chrysotile asbestos [123], cellulose [124] (with additives) and NH_4ClO_4 (two papers concerned with the effects of ageing [8] at $\sim 400 \text{ K}$ and of the addition of NH_4MnO_4 with irradiation [7]). Two kinetic investi-

gations of phase transformations were concerned with SnF_2 [125] ($\alpha \rightarrow \gamma$ and $\beta, \gamma \rightarrow \alpha$) and with GeO_2 [126] (α -quartz \rightarrow rutile at high pressure). The chemical reaction step was identified as controlling the decompositions of MnCO_3 [127] and of MnSO_4 [128]. The role of liquefaction during decompositions of $\text{Ca}_3(\text{PO}_4)_2$ [129] and of alkoxyfuroic acids [130] were discussed.

Fewer papers (5) were concerned with non-isothermal kinetic studies. These included studies of the decompositions of hydrated inorganic sulphates and of yttrium and lanthanide diphenates [131].

Again the range of reactants used in stoichiometric studies (12) was diverse and no meaningful classification was possible. These articles included investigations of the decomposition of lead formate [132] and the role of iron in $\text{Fe}(\text{IO}_3)_3$ [133] breakdown. In a detailed study of the dehydration and other properties of hydrated strontium nitroprussides [134] the structural characteristics of water in the solids were characterized.

Classified as miscellaneous is a group of articles by Boldyrev and co-workers [50,51,60] concerned with dehydrations in which the nucleation and growth reactions were studied by microscopic and X-ray diffraction measurements. The sizes of product crystallites formed during the dehydrations of $\text{MSO}_4 \cdot 7 \text{H}_2\text{O}$ [50] ($\rightarrow \text{MSO}_4 \cdot 6 \text{H}_2\text{O} + \text{H}_2\text{O}$, $\text{M} = \text{Mg}^{2+}$, Ni^{2+} or Zn^{2+}) varied markedly with the prevailing water vapour pressure. The role of incongruent melting in these water elimination reactions was considered [50,60]. Related work [51] concerned the effect of water availability on dehydrations of $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ and the severity of reaction conditions on the dehydrations [69] of $\text{Na}_4[\text{Fe}(\text{CN})_6] \cdot 3 \text{H}_2\text{O}$ and $\text{K}_2[\text{CuL}] \cdot 3 \text{H}_2\text{O}$ (H_4L is EDTA). The same school applied a similar approach to study [135] the development of growth nuclei during AlH_3 decomposition.

Other papers of this group were concerned with the identification of phases formed during decompositions of the alloy systems: Cu/Sn/Ni [136], Ti/Mo/Zr/Sn [137] and Al/Cu [138]. The structures and textures of residual MgO [139] and Al_2O_3 [140,141], formed by the decomposition of oxyacid salts, were investigated. The crystal structures of barium hydrogen oxalates [142] were discussed with reference to the lattice transformations that occur during solid-state decompositions [143].

(h) Chemical Abstracts (computer search), 94-97 (1981-1982)

The 26 articles located from this source included only 6 kinetic studies and these were largely qualitative. Rate measurements were made for the decompositions of trona [144,145] (a phase in NaHCO_3 breakdown), $\text{AlF}_3 \cdot 3 \text{H}_2\text{O}$ [146], the vioform complex of barium [147] and the sodium salt of tribuzone [148,149] in solution and as a solid.

The 13 papers concerned with reaction stoichiometries included the following reactants: simple hydrated salts ($\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$; $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$); various (NH_4Ln , NH_4Cu and basic $\text{Fe}(\text{III})$) chromates; several

phosphates; complex tungstates; and the mineral bayldonite [150].

Miscellaneous studies (7) included 4 papers reporting phase transformations (including that of KCl at high pressure [151]) and the properties of alloys. The others concerned the behaviour of polymers including thermal *cis/trans* isomerization in polyacetylene [152], crystallization of thermoplastic polyurethanes [153] and polymerization in a diacetylene crystal [65].

(i) 2nd European Symposium on Thermal Analysis

This [3] was the only major international conference on a relevant subject to be published during the review period, 1981. This volume contains 147 short articles, normally four, but sometimes two pages of typescript. This restriction on length made it necessary for authors to report or to discuss only a small number of points. According to the criteria applied in the collection of our source set 38 papers would have been regarded as acceptable here. These were not, however, incorporated in our totals since there was strong evidence that many represented duplicate publications. We adjudged, from a specific search to establish this point, that the contents of at least 17 of these papers had been published completely or partially elsewhere by the end of 1982.

To permit a comparison of the contents of this publication [3] with the general literature, as represented by our source set and without distorting the contents of the latter, the remainder of this section reports an appropriate specific survey. A closely comparable pattern of content distribution is found.

A majority of the articles [3] (32) were concerned with the decomposition of a single or a small number of related reactants. Thermogravimetry (26) and DTA (22) were the most widely applied experimental techniques (Table 5) with fewer papers reporting the use of DSC (2). Other experimental techniques used included X-ray diffraction studies (7), IR (4) and surface area measurements (3) to characterize residual products or mass spectrometric analyses (4) of volatile products. Microscopic examinations of reactants and products were described in seven articles and photographs reproduced in three.

Many of the kinetic studies (21) were concerned with simple reactions of established stoichiometry. The difficulties inherent in determining the rate equation $\{f(\alpha) = kt\}$ and the activation parameters (A and E) from rising temperature-rate measurements, particularly for reversible reactions, were recognized and discussed. Indeed the brevity of these individual papers evidently tended to encourage authors to emphasize the strengths and weaknesses of the methods of thermal analysis, the theoretical bases of the equations applied were discussed and possible modifications considered.

Values of E were reported in 20 papers. Fourteen provide some discussion of reaction mechanisms and, of these, 6 refer to the geometry of interface

development and 12 provide some discussion of factors controlling the bond rupture step. The relative reactivities of compounds containing similar constituents were considered in 8 papers, in some of which the parameters determining the onset of reaction were examined.

(j) Literature reviews

It had been our original intention to incorporate appropriate review material into our source set. However, very few reviews were found and, since these were peripheral to our main theme, it was decided only to record their existence in this subsection.

Two reviews were concerned with various hydrides of intermetallic compounds [154,155]. Also noted, as possibly being of related or of specific interest, were articles concerned with the microanalysis of solids [156], the use of mass spectrometry to study coordination compounds [157], the chemical consequences of the polar axis in organic solid-state chemistry [158], the rates of phase transitions and their role in catalysis [159] and inorganic applications of thermogravimetry and DTA [160].

It is appropriate to mention here the difficulties we experienced in locating survey material, since this is another aspect of the search problems already described above. Review entries in Chemical Abstracts are often restricted to a title and the number of references cited. This evidently has the undesirable consequence of resulting in relatively few index entries for those books, reviews and articles which contain systematic presentations of the contents of earlier literature. We accept that the comprehensive indexing of all reviews would present considerable problems (e.g., the present article) but would argue that critical abstracting of review material, constituting, as it does, a most important component of the literature, would increase the value of Chemical Abstracts and its indexes. It seems unreasonable that comprehensive and authoritative surveys should receive less space and fewer index entries than the individual articles upon which these have been based.

12. DISCUSSION

The contents of the source set demonstrates a strong and continuing interest in decomposition reactions of solids. Our impression is that the rate of output, 368 articles in 1981 (or about 1 article/day), is probably not very different from that of other recent years. These papers together represent a considerable total research investment and a continuing commitment to solid-state chemistry by both industrial and academic institutions. Such interest is to be expected since solid reactants are involved in many economically important technological processes, from the extraction of raw materials in ores, through the manufacture of numerous useful articles, to corrosion

and the disposal of waste. Industrial problems are often solved, or otherwise circumvented, by fundamental laboratory investigations, which may also directly, or indirectly, initiate related academic studies. It is also quite evident that the chemistry of solids is an interesting subject per se and many mechanistic studies have been undertaken to characterize the factors controlling the chemical changes that occur in crystalline reactants. However, we were often surprised at just how little introductory explanation some authors give of the reasons for making the study that they are reporting. Many such justifications were vague, sometimes it was apparently assumed that an earlier study was worth continuing or that the solids were "of interest", without further elucidation. Published introductions cannot always be expected to trace the detailed history of development of ideas during completion of a particular study or to list the changes in direction that became necessary during its implementation. We did consider, however, that a positive expression of the original motivation for a project was a helpful feature for its initial presentation to the reader. Relatively few studies were described as being of actual or potential commercial importance.

Many aspects of the trends perceived in the present analysis have been discussed in the foregoing sections. This section is concerned with our more general conclusions and the less quantitative impressions reached during our literature scrutiny, considered in the context of currently accepted theory and future outlook. The following four general, but obviously interdependent, topics are the subjects of the following sub-sections. Outstanding recent articles: we attempt to identify the most significant papers in the source set. Form of the literature: we draw attention to the problems encountered in making comprehensive literature reviews for the subject which arise due to the wide dissemination of articles. Theory of solid-state chemistry: we believe that the time is overdue for the critical reappraisal of the use of certain theoretical concepts, developed for homogeneous rate processes, in the elucidation of mechanisms of heterogeneous reactions. Non-isothermal kinetic studies: fundamental problems of interpretation remain. Our treatment here is intended to stimulate constructive debate in areas of current interest and controversy so that the factors controlling the reactivity of solids may be identified with certainty and the basis of the formulation of solid-state reaction mechanisms examined in the context of recent advances.

(a) Outstanding recent contributions to the subject

We regard the literature period reviewed, 1981, as constituting a time of general scientific progress and consolidation without an obvious challenge or disturbance to the accepted theory or the appearance of novel phenomena likely to result in immediate changes to the directions of development of this field. We identify very few individual papers as being of sufficiently out-

standing merit to warrant particular mention here. Indeed the references already cited above were usually selected because we regarded the paper concerned as constituting an important contribution within a specific topic. The one development that we regard as a positive indication of a probable direction of future progress (though we should also mention our own interest in this proposal [2]) is the suggestion that a liquid phase may participate in nucleation and growth reactions, as discussed by two groups of workers [47,50,51].

We identify isothermal kinetic measurements as providing the most reliable information about the mechanisms of solid-state decomposition, particularly when deductions concerning reaction geometry are supported by microscopic observations. Two types of study were distinguished here. The first of these reported continued investigations of reactions, already the subject of extensive previous work, for example, the decompositions of NH_4ClO_4 , and $\text{Ag}_2\text{C}_2\text{O}_4$, and the dehydration of alums. The second extended the scope of rate studies to include new compounds. We also attach considerable importance to the several papers concerned with non-isothermal rate measurements which critically considered the accuracy and significance of quantitative kinetic interpretations of such data.

(b) Form of the literature

We have emphasized above that articles describing decompositions of solids are widely disseminated in the chemical literature. The words "decomposition" and "solid" are not particularly effective index references since both enjoy common usage, as well as more general chemical applications. This was particularly convincingly demonstrated by our computer index search which omitted many of the papers sought while listing numerous irrelevant citations (Table 1). Some improvement of index search methods would undoubtedly follow wider statements by authors in article titles, or key words, that the reactant is a solid. (We have suggested above that these reactions may be termed *crystolysis*.)

Other methods of tracing relevant publications, not tested quantitatively here, would be through: (i) authors active in the field and exploiting the Science Citation Index; or (ii) relevant compounds, using Registry Numbers to search Chemical Abstracts. The large number of potential reactants would, however, make the latter method very laborious since any general survey could include, in addition to simple and complex salts, diverse substances such as zeolites, alloys, polymers, glasses, etc.

Our present experience leads us to commend searches of indexes and abstracts of selected journals, as the most effective method of locating articles in this field. Such searches may then be complemented by examination of the texts of promising articles to locate relevant material incorporated as a minor contribution in articles primarily concerned with a different objective.

These problems found in compiling a comprehensive list of relevant papers may have been a factor in deterring potential authors from preparing reviews, since relatively few are available concerned with the decompositions of solids. Some of those that have appeared, however, have notably contributed towards the advancement of the subject and are frequently cited. The systematic treatments of kinetic characteristics of solid-state reactions by Jacobs and Tompkins [161] and later by Delmon [162] are probably largely responsible for the acceptance of that group of rate equations now in general use [19]. Similarly, the mechanistic discussions by Garner [163] and by Young [52] provide general background sources that include many of the theoretical concepts that are applied in the formulation of reaction mechanisms.

Another literature source is the proceedings of conferences, some of which are held at regular intervals. The material presented at successive meetings, in such a series, reflects the organizers perception of the current levels of interest and activity in different branches of the subject. Plenary lectures, at such meetings, sometimes critically assess progress in a selected topic at greater length than is possible in the papers contributed. Records of discussions may draw attention to areas of controversy in the subject, though such exchanges may often be of greater value to the participants themselves than to the reader unfamiliar with details of recent progress in the specific topic under debate.

We believe the literature on this subject would benefit considerably from general but critical reviews. It is stimulating to those active in a field to update theoretical concepts, clarify and systematize the information available, identify areas where disagreements, uncertainties and gaps exist and indicate possible directions of profitable future progress.

(c) Theory of solid state chemistry

Obedience of yield-time data to a particular rate expression is often accepted as sufficient evidence to identify the geometry of reaction interface development. The rate limiting step is often characterized from a comparison of the magnitude of E with various bond strengths within the reactant, the dissociation enthalpy (see discussion of the Polyanyi-Wigner equation [1]), etc. As pointed out above, some authors discuss both these aspects of reaction, reaction geometry and interface chemistry, some discuss one or other and a few provide little or no theoretical explanations or interpretations of their observations. It seems to us that when theoretical explanations of chemical observations are sought, it is appropriate to consider both these interdependent facets of behaviour when formulating a reaction mechanism. This was advocated previously [2] and our appreciation of the value of this approach has increased during the present literature survey.

Characterization of the geometry of interface development, through inter-

pretation of kinetic obedience, is the aspect of decompositions of solids that has achieved greatest success. Numerous acceptable kinetic analyses of this type have been reported [1], though many are not supported by microscopic evidence. Little use has so far been made in this field of the advances in observational techniques which, despite limitations arising when reactant particles are small, imperfect and/or opaque, is often capable of providing detailed information concerning the shapes and distributions of nuclei, not always obtainable from measured total yield-time data.

Since reactant-product contact zones are often inaccessible to direct study [2], inferences about interface chemistry have frequently to be deduced from analogies with homogeneous reactions. The Arrhenius equation is usually obeyed by solid-state decompositions and, in consequence, the parameters A and E have been taken as measures of the frequency of occurrence of the reaction situation and the enthalpy for transition complex formation, respectively. While not discounting this approach, we believe that no general and satisfactory theoretical foundation for its application to breakdown of solids has, as yet, been provided. Indeed, the two factors mentioned below differ in important respects from the factors controlling the apparent magnitudes of A and E in homogeneous rate processes. Firstly, the energy distribution function, for participating reactants bonded to a solid surface, or in a solid [164], is not necessarily expressed by the Maxwell-Boltzmann equation [1]. Secondly, unlike many homogeneous reactant mixtures, the concentrations of participants at the active reaction interface may be temperature dependent, due to the influence of this parameter on adsorption or dissociation equilibria [41,165,166].

The operation of alternative kinetic controls provides an explanation for the occurrence of compensation behaviour observed in some groups [41] of heterogeneous rate processes. It is suggested that this may arise where there is an isokinetic onset of reactions within the group due to the operation of the same rate determining feature [166], e.g., rupture of identical, or closely similar, bonds in the reactant, onset of mobility of a participant, local melting (perhaps of a common impurity), etc.

Theoretical considerations tend to support the view that decompositions may proceed more rapidly in a melt than in a crystalline solid. On fusion, the stabilizing lattice forces on the components are relaxed and so also are the stereochemical constraints so that reactants may adopt the most effective reaction conformation leading to bond redistributions. It has been shown in several systems that reactivity increases on melting [167,168] or on dissolution [169,170]. From such considerations it has been suggested that the chemical activity associated with nuclei in some solid-state reactions may reside in the ability to retain a proportion of a volatile product and thereby provide a liquid medium in which chemical changes occur [47,169]. (This model directly conflicts with the earlier view [163] that residual components of the nucleus did not impede volatile product escape.) Another possible

explanation of the sigmoid shaped kinetic curves (characteristic of many solid decompositions [1]) is the restricted development of a melt as the reaction proceeds. These representations of interface phenomena are based on a more "chemical" interpretation of the participating reactions than has hitherto found general favour. Such interpretations require microscopic examinations to elucidate the internal structures of nuclei and the textures of products in addition to confirming the geometry of interface dispositions.

The unambiguous establishment of whether or not melting occurs should be an essential feature of any mechanistic study of a reaction involving a solid. Melt formation is not, however, always evident or easily detected, even when specifically sought. Fusion to form a viscous fluid may be restricted in extent and the homogeneous active reaction zone progressively moves through the reactant, such behaviour is believed to occur during decompositions of ammonium dichromate [168] and of copper(II) malonate [171]. Many papers, evidently reporting the decomposition of a solid, do not explicitly state that melting is absent but imply this by basing mechanistic proposals upon theoretical foundations applicable to the reactions of a solid.

(d) Non-isothermal kinetic studies

Whereas criteria for the distinguishability of obedience for isothermal kinetic data to rate equations have been provided [46], we are aware of no such analysis applicable to the more difficult consideration of the quantitative examinations of rising temperature data. Such analyses are complicated by the requirement to identify $\{f(\alpha) = kt\}$ and also to calculate A and E from a single set of measurements. It is surprising, therefore, that such a small proportion of articles in our source set use microscopic observations to confirm or to supplement geometric conclusions from the exclusively non-isothermal rate studies (2 out of 59, a much smaller proportion than for isothermal studies, 14 out of 65). Mechanistic discussions were often brief and the reliability of kinetic parameters (A and E) and conclusions can only be ascertained by comparison with isothermal measurements.

We find it difficult to understand the reasons sustaining the current considerable and continuing interest in non-isothermal kinetic investigations. No agreed methods of interpreting measurements have yet emerged. Many recent studies have not yielded unambiguous conclusions, indeed, in some of these, similar results could have been more easily obtained by a limited microscopic study. The time now appears to be opportune for a general and critical reappraisal of the aims, methods and achievements of the non-isothermal method of kinetic investigation, assessing realistically both the benefits and limitations of this approach.

13. CONCLUSIONS

Our semi-quantitative content analysis of published articles concerned with decompositions of solids reveals a considerable and wide-ranging interest in the subject. A high proportion of the articles appeared in relatively few journals, some of which specialize in the field. The compilation of a complete list of relevant papers was difficult and not, at present, amenable to computer index searching.

The range of reactants encompassed within the articles of our source set included virtually every type of solid. Some of these studies attempted limited objectives, those classified as stoichiometric characterized the sequence of changes that occurred on heating and/or identified the reaction products. Discussions in these papers did not always include the consideration of the possible complexities of behaviour. Other studies investigated reaction mechanisms through kinetic analyses. Constant temperature rate measurements were tested for obedience to a limited range of equations based on quantitative consideration of the geometry of interface development. Conclusions were not always confirmed by microscopic observations. Mechanistic interpretations based on non-isothermal rate measurements were considered less reliable. Certainly the field of rising temperature kinetics has not developed as rapidly as at one time seemed probable.

We hope that this approach to content analysis will be helpful in providing some perspective in the field to enable contributors to appraise the value of their work in the context of other recent publications. Others may perceive methods for the development of this approach for its generalization and applications in other subjects.

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SOURCE SET

The following list of articles constitutes the source set examined in the literature content analysis. Citations are classified under the headings given in Table 1.

Articles considered of interest in the present survey have been accorded full references in the text. The references given below, in abbreviated form, are summarized only to provide access for the interested reader to our complete source material.

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47 (1981) 15, 71, 113, 149, 179, 189, 213, 271, 309, 359, 375.
48 (1981) 61, 137, 147, 375.
49 (1981) 207, 219, 247, 333, 371, 385.
50 (1981) 17, 41, 93, 105, 111.
51 (1981) 97, 105, 153, 169, 199, 233, 245, 269, 277, 307, 353, 381.

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