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The significance of "compensation effects" appearing in data published in "computational aspects of kinetic analysis": ICTAC project, 2000

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Abstract

Examination of the results reported for the recent International Congress on Thermal Analysis and Calorimetry (ICTAC) kinetics project [Thermochim. Acta 355 (2000) 125] shows that, from kinetic analyses of identical sets of numerical data measurements, different workers, using different computational procedures, obtained significantly different kinetic parameters. The reported Arrhenius parameters, A (frequency or pre-exponential factor) and E (activation energy), calculated from the data sets supplied, showed apparent (approximate) compensation trends. Thus, when reviewing or applying the values of Arrhenius parameters reported for innumerable and diverse rate processes in the literature, the uncertainties in the magnitudes of A and E (often not even estimated or discussed) cannot be regarded as arising only from differences in the sample or experimental conditions, but must also include consideration of the mathematical and computational methods used. Variations of either type can lead to compensation effects and the recognition of compensation can be a valuable indication of a need to explore the source of this behavior. An observed kinetic compensation effect (KCE) can, thus, be a result of differences in the sample or experimental conditions, be an indication of complex reaction controls, or, as shown in this survey, may be a computational artifact.

Keywords: Kinetic compensation effect (KCE); Activation energy; Pre-exponential factor; Arrhenius parameters; Kinetic analysis

1. Introduction

One dominant conclusion from the recent comparative study [1] of "*Computational aspects of kinetic analysis: The International Congress on Thermal Analysis and Calorimetry* (*ICTAC*) *kinetics project*" is that, from the kinetic analyses of identical sets of numerical data measurements, different workers, using different computational procedures, obtained significantly different kinetic parameters. The Arrhenius parameters, A (frequency or pre-exponential factor), E (activation energy) and, to a less-noticeable extent, the conversion function (rate equation, kinetic model), $g(\alpha)$ or $f(\alpha)$, (making up the conventional "kinetic triplet": α is the fractional reaction) showed important variations when contributors to this study applied their choice of kinetic analysis from the computational methods widely employed in this field [2]. This has serious implications for all kinetic investigations of solid state reactions because the wide range of conclusions (kinetic triplets), reported for each of the

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rate processes compared in [1], may be generally applicable, throughout the field.

If the conventional approach to kinetic and mechanistic investigations of thermal reactions of solids is to be sustained as an acceptable method of interpreting and exchanging quantitative information, reasons for these substantial divergences of conclusions (the kinetic triplets) must be established. Inconsistent results are usually attributed to variations in the properties between the different samples of a selected reactant, and are known [2] to arise, for example, due to the presence of impurities, defects, residual solvent, etc. or from variations in the experimental conditions, including ineffective removal of gaseous products during reversible reactions, incomplete heat transfer in different sample masses, particle sizes, etc.

In the study reported in [1], however, all participants started with identical sets of (product yield, α, time, temperature) numerical data. Data sets for the decompositions of calcium carbonate (in vacuum and in nitrogen) and of ammonium perchlorate were obtained from both isothermal and programmed temperature experiments and the remaining sets were simulated data calculated for an equally-weighted pair of concurrent first-order reactions. The origins of the data sets analyzed were irrelevant for the purposes of the comparative analysis 'round robin' project [1], but the simulated sets were the only ones for which a "correct answer" was (in principle) available.

2. Compensation behavior

The variations of the Arrhenius parameters reported for the kinetic data analyzed in [1] were presented and discussed at the Kinetics Workshop held at the 12th ICTAC, held in Copenhagen in September, 2000. During the discussion at the Workshop, P. Gallagher asked whether these variations could be described by a compensation plot? This had not been explored by the presenters, but it turned out that one of us (AKG), who had not been present at the Workshop, had already begun to do so from the published results [1]. Here, we show that the variations of the Arrhenius parameters can, as suggested, be conveniently summarized for discussion through a kinetic compensation effect (KCE), for each system. There is a vast literature on the KCE and this paper is not intended to review this literature, see [3–6]. The KCE is a linear relationship between the magnitudes of $\ln(A)$ and E within the set of Arrhenius parameters calculated for each of a series of related or comparable rate processes. Such a comparison traditionally ignores, or assumes constant, any effect of the third component of the kinetic triplet, the conversion function, $g(\alpha)$ or $f(\alpha)$. An important property of a KCE is that all reactions constituting the set exhibit an equal (isokinetic) rate constant at the isokinetic temperature, T_i [4]. A theoretical model capable of explaining the KCE has yet to be agreed. Several interpretations of this behavior pattern have been advanced, but none has yet received general recognition. In the usual presentation and discussion of the theoretical foundations for the Arrhenius equation, no feature connecting the magnitudes of the frequency of occurrence of the reaction situation (A) and the energy barrier to reaction (E) has been identified.

KCEs have been reported for numerous and diverse sets of related rate processes [5–8], each composed of a group of similar chemical changes for closely comparable reactants, such as variously substituted derivatives of a constant parent molecular species, or differently treated samples of crystalline reactants that, therefore, contain differences in defect and/or impurity contents. The reactions may be solid state decompositions or heterogeneous catalytic processes on the same solid catalyst; KCEs have also been described for a wide variety of other types of reactions [3]. Such effects could be classified as Type 1 KCE and are assumed to originate from common features, and, thus, reactivities, within each group of comparable chemical changes that comprise a set.

When samples of the same reactant are used, but the conditions during the experiment (such as atmosphere, sample mass, etc.) are varied, a KCE may also be observed [4]. These kinetic patterns have been attributed to changes in the relative influences of mass and heat transfer, including the possible participation of the reverse reaction. The same heterogeneous process carried out on a series of different solid catalysts could also be accommodated within this Type 2 KCE. Little mention is made of the influence of possible simultaneous changes in the conversion function.

An examination of the data in [1] (discussed with reference to Figs. 1–4 in the following sections) shows that compensation behavior can also be observed where identical sets of numerical data are subjected

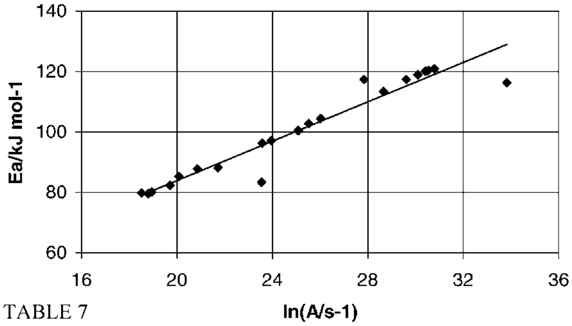
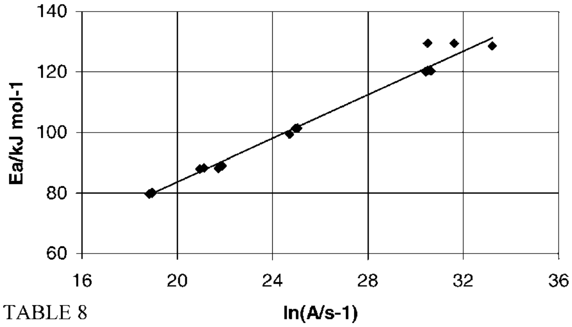


TABLE 7



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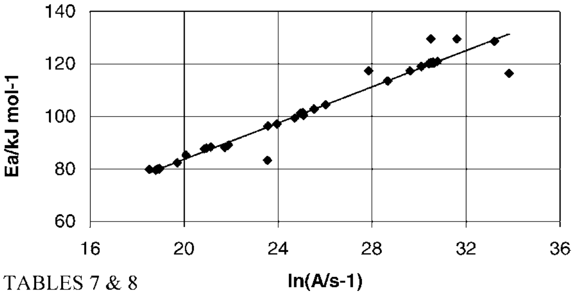


TABLES 7 & 8

Fig. 1. Compensation plots for Arrhenius parameters reported by different workers from kinetic analysis of data in Tables 7 and 8 of [1]. The sets of simulated rate measurements are composed of two equally-weighted, concurrent, first-order reactions with Arrhenius parameters: $\ln(A_1) = 18.93\,\mathrm{s}^{-1}$, $E_1 = 80\,\mathrm{kJ\,mol}^{-1}$ and $\ln(A_2) = 30.45\,\mathrm{s}^{-1}$, $E_2 = 120\,\mathrm{kJ\,mol}^{-1}$.

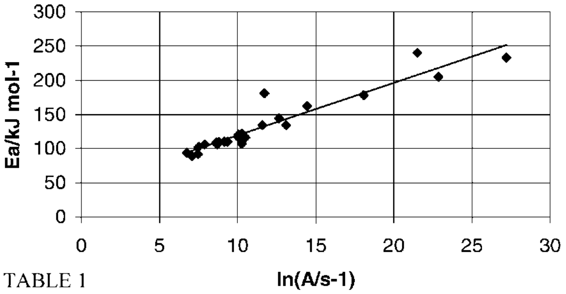
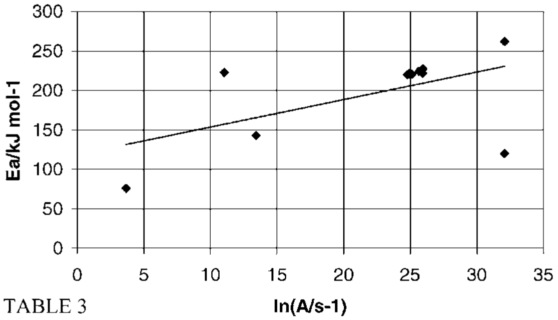


TABLE 1



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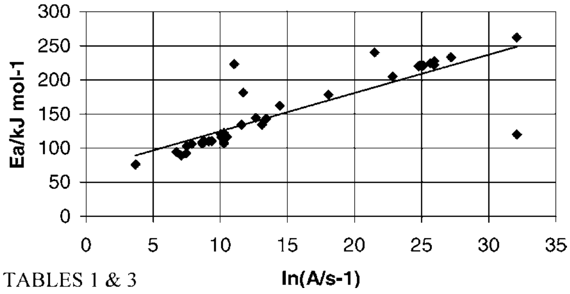

TABLES 1 & 3

Fig. 2. Decomposition of calcium carbonate in vacuum: compensation plots for Arrhenius parameters reported by different workers from kinetic analysis of the same data from Table 1 (programmed temperature) and Table 3 (isothermal) in [1].

to different computational procedures in the kinetic analyses (which also usually lead to identification of different conversion functions). Should this be distinguished further as a Type 3 KCE? Is it an artifact simply of mathematical or computational origin, or does it arise from neglect of any influence of the choice of conversion function, or could it have a physical significance? Norwisz and Plewa [7] and Criado and Gonzalez [8] have shown that KCEs were observed when the Arrhenius parameters, forming part of the non-unique triplets, obtained by kinetic analysis of single-heating-rate experiments were compared. In the kinetics project [1], however, data sets obtained at different heating-rates were provided. Vyazovkin and Lesnikovich [9] have clearly shown that incorrect identification of the conversion function leads to errors in the values obtained for the Arrhenius parameters. In spite of these demonstrations, similar kinetic analyses continue to be published.

In preparing compensation plots from Tables 1–8 [1], values of E without an accompanying $\ln(A)$ value

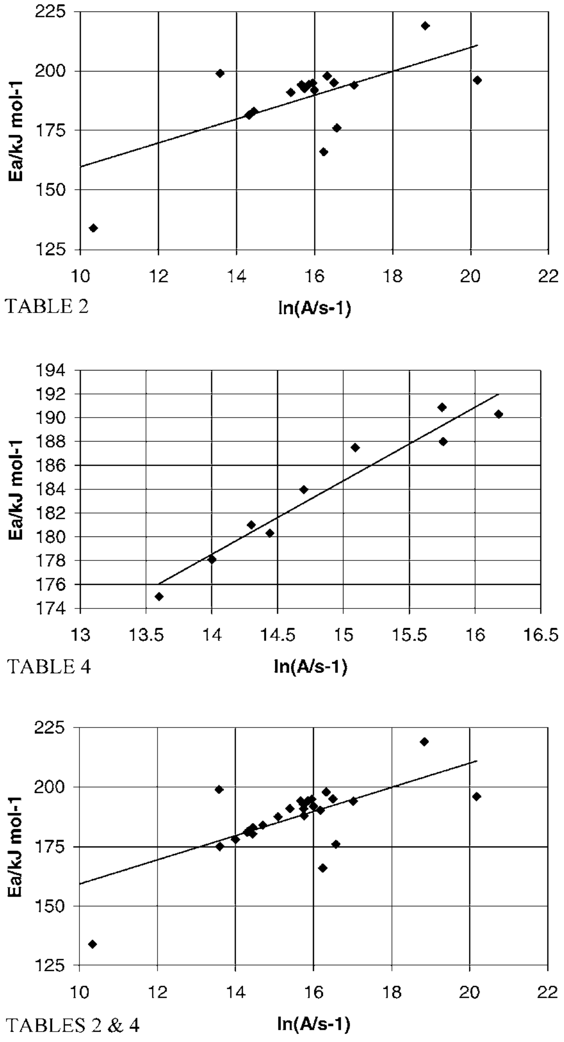

Fig. 3. Decomposition of calcium carbonate in nitrogen: compensation plots for Arrhenius parameters reported by different workers from kinetic analysis of the same data from Table 2 (programmed temperature) and Table 4 (isothermal) in [1].

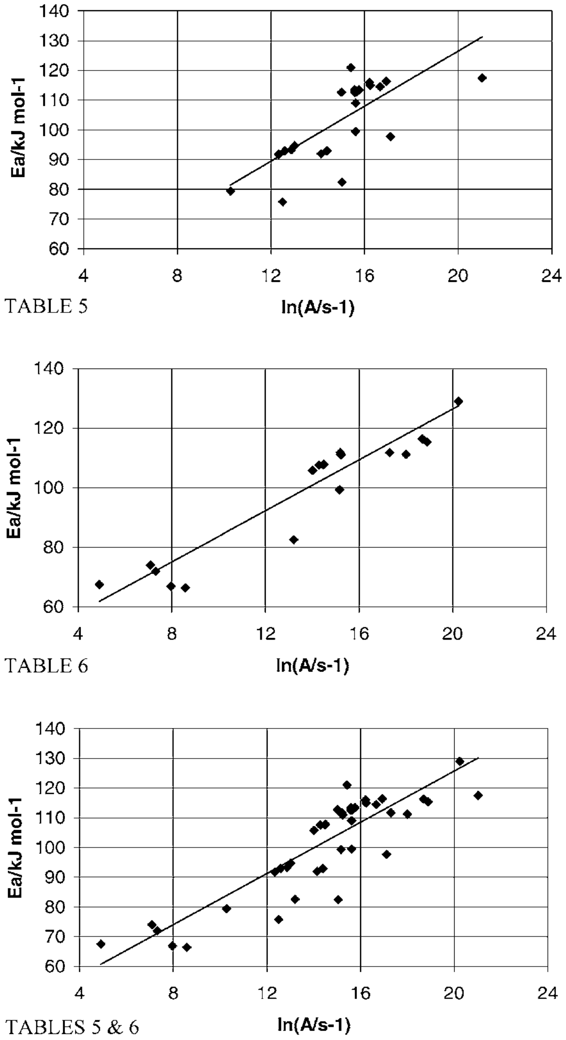

Fig. 4. Decomposition of ammonium perchlorate in nitrogen: compensation plots for Arrhenius parameters reported by different workers from kinetic analysis of the same data from Table 5 (programmed temperature) and Table 6 (isothermal) in [1].

were obviously omitted, as were—Tables 1 and 2: Desseyn from the negative ln(*A*) values on; Tables 3 and 4: Desseyn range and only one of the Roduit pairs; Table 5: only one of the Burnham pair 116 and 16.21; Table 6: only one of the Roduit pair 111.76 and 15.10. Apart from these values, omitting the few which were either incomplete or exceptionally distant from the points forming the KCE set, all data from [1] were included in the comparative analysis. No consideration was given to the possibility of selective deletion of reported results because no scientific criteria appear to us to be available for such a judgment (this point is made here because a referee has stated "The results obtained by faulty computational procedures should be ignored and not included in KCE plots". Who is to decide, and for what reason, that some results are to be identified as 'faulty'?).

The slopes, intercepts and r^2 values from linear regression, and the isokinetic temperatures, T_i = slope/0.008314, for each of the data sets are given

Table 1
Compensation parameters

Table [1]	Slope = RT_i	Intercept	r^2	T_i (K)
1	7.677	42.6	0.89	923
3	3.492	118.5	0.30	420
1 and 3	5.612	68.4	0.68	675
2	5.012	109.6	0.48	603
4	6.175	92.1	0.94	743
2 and 4	5.083	108.4	0.50	611
5	4.628	34.0	0.53	557
6	4.278	40.9	0.88	515
5 and 6	4.304	39.6	0.75	518
7	3.259	18.7	0.93	392
8	3.593	11.8	0.99	432
7 and 8	3.447	14.7	0.96	415

in Table 1. No conclusions are drawn from these values, other than an indication of the quality, or otherwise, of the compensation plots.

The values of r^2 in Table 1, confirm the considerable scatter of data apparent in Figs. 1–4, with the exception of the simulated data. The variation seems to be very much larger than might have been anticipated for parameters obtained from calculations based on the sets of common data. Not only do the Arrhenius parameters vary with compensation but results also exhibit other types of deviation. This is an important conclusion from the present comparisons that could benefit from further investigation to understand more completely the factors that are involved in kinetic analysis and the errors inherent in the results from such calculations. It could be relevant in understanding the present patterns of behavior that the (experimental-error-free) simulated data showed the most satisfactory compensation behavior, scatter being mainly within the clusters ("clusters" is used in its descriptive, non-statistical sense).

3. The simulated data sets

The simulated data sets in Tables 7 and 8 of [1] were calculated for the model system: two equally-weighted, parallel, first-order reactions with Arrhenius parameters—reaction (1): $\ln(A_1) = 18.93\ \mathrm{s}^{-1}$, $E_1 = 80$ kJ mol^{-1} and reaction (2): $\ln(A_2) = 30.45\ \mathrm{s}^{-1}$, $E_2 = 120\ \mathrm{kJ\ mol}^{-1}$. Separate consideration of the individual contributions from these assumed component rate processes showed that, at 360 K, the first reaction (1) was largely completed (92%) by 100 min and the rate thereafter was due effectively to reaction (2). At 380 K, both processes contributed significantly during the early stages. It seems that the contributory reactions are capable of separation by the kinetic analysis of data for different α ranges, as is indicated by the distribution of points on Fig. 1. Under each figure the table referred to is in [1].

A pronounced compensation trend was found (within the ranges for E of 70–130 kJ mol^{-1} and for $\ln(A/\mathrm{s}^{-1})$ of 18 to 34) with all, except six, of the points on the graph being close to the line joining the points defined by the Arrhenius parameters for the contributory reactions. From the 46 reported pairs of E and $\ln(A)$ values, 11 were located, within a ±5% error limit, at the point characteristic of reaction (1) alone and a further 13 similarly corresponded with expectation for reaction (2). Seven additional values corresponded with expectation (i.e. ±5%) to the middle point of the line joining the two contributory rate processes and for a further seven points the $\ln(A)$ values were outside this range. Thus, about half of the results of kinetic analysis characterized, within acceptable limits, the Arrhenius parameters for the individual contributory reactions, and most (altogether 40 out of 46) of the others were close to the "compensation" line joining these points (Fig. 1). The most probable explanation of these results is that they arise through different weightings given in the calculation methods to the two component rate processes, combined with different emphases in different intervals of the overall α–time or α–temperature curves. We have no explanation for the three values of E greater than the reactions considered or for the other three points that were at significant distances from the line on the composite plot (Fig. 1). The clustering (used only in a descriptive, non-statistical sense) appears to be evidence of some ability of the computational methods used to separate the individual contributions that constitute this overall complex process.

4. Decomposition of calcium carbonate in vacuum

The compensation plot, Fig. 2, for the decomposition of $CaCO_3$ in vacuum, shows the appreciable spread of Arrhenius parameters recorded in Table 1 (programmed temperature) and Table 3 (isothermal) from [1]. Most points were close to a well-defined KCE. The isokinetic temperature, $T_i = 803$ K, was calculated from the slope [3,4] (and is towards the lower end of the temperature ranges investigated [1], File 1: approximately 790–930 K and File 3: 788–823 K). This is somewhat lower than previously reported values, 815–1250 K [3], for this (conditions-sensitive) reaction.

The scatter of points observed in Fig. 2 is capable of a variety of alternative explanations. However, the most important conclusion is that the different computational methods, applied to the same data set, have yielded an unexpectedly wide range of apparent values of E and A (E: 70–265 kJ mol^{-1} and ln(A): 3–32 s^{-1}). It is well known [10] that the rate of this reaction is highly sensitive to conditions within and in the immediate vicinity of the reactant. It is probable, therefore, that the different weightings given by the alternative approaches to kinetic analyses for the reactions within different α ranges and at different heating rates yield Arrhenius parameters that are influenced by variations in the effective pressures of CO_2 within the reaction zone [2]. Some workers have reported results for 'low α' and 'high α' ranges and, because the calculations refer to different heating rates, the effective product pressures and their influence on the overall rate are expected to be different. We conclude that the diverse methods of kinetic analysis used focus on partial ranges of reactions that effectively proceed under appreciably different conditions, with consequent variations in magnitudes of the apparent Arrhenius parameters.

An alternative interpretation is to regard the composite compensation line in Fig. 2 as connecting two clusters of points that are characteristic of the two sets of data (programmed temperature and isothermal). Many values of E for the programmed temperature experiments are between 105 and 120 kJ mol^{-1} and ln(A) from 8 to 11 s^{-1}, with some others more widely dispersed. Isothermal measurements, in contrast, gave values that were mainly much larger, many were 220–230 kJ mol^{-1} and ln(A) was usually close to 25 s^{-1}. A reasonable explanation of these two sets of results is that during programmed temperature experiments the contribution of the reverse reaction is relatively small because the effective product pressure always lags behind that required for equilibration. In contrast, at constant temperature, a greater pressure relative to equilibrium may be achieved within the pores of initially formed solid product (see [11]), during the progress of dissociation, if CO_2 removal is not effective.

5. Decomposition of calcium carbonate in nitrogen

The thirty points represented by the pairs of Arrhenius parameters listed in Table 2 (programmed temperature, Set 2) and Table 4 (isothermal, Set 4) [1] are shown in the compensation plot, Fig. 3 (from which two entries have been discounted because of exceptionally low values of ln(A)). A large proportion of these points are clustered. Most values of E were 187 ± 12 kJ mol^{-1} (35 of the 48 reported, 73%) and ln(A) values were 15.2 ± 1.6 ($(0.8-20) \times 10^6$ s^{-1}: 23 of the 32 reported, 72%). The disposition of points on Fig. 3 indicates a slight compensation trend, from which T_i was estimated to be about 1000 K, within the temperature intervals used in both sets of kinetic studies (Figs. 2 and 4 of [1]). This was also within the range of previously reported T_i values for the decomposition of calcium carbonate in air or nitrogen, 815, 927, 1058 and about 1100 K [3]. Arrhenius parameters for the programmed temperature experiments tended to be generally larger than those for the isothermal measurements, but the ranges overlapped. Mean values of the Arrhenius parameters for experiments of two types were not calculated, because interest here was more directly concerned with the spread of values derived from the same original experimental data, moreover some of the effects of such variation were offset by the compensation.

Probably the most important conclusion from the comparative analysis [1] is the relatively wide range of magnitudes of Arrhenius parameters (E: 70–265 kJ mol^{-1} and ln(A): 3–32 s^{-1}) that arises through the use of different computational methods applied to identical original data. Most of the values of E were (see Fig. 3) within ±8 kJ mol^{-1} of the median, a variation of about ±4%, although a number of other values were outside this range by a significant margin. Here, again, it appears, as suggested for the simulated data above, that different data analysis procedures may emphasize the different kinetic contributions within an overall complex reaction. The 'preferred' value of E from the distribution on Fig. 3 of around 187 kJ mol^{-1} is well within the range of values that Beruto and Searcy [11] associate with diffusive escape of product CO_2 gas participating in dissociation equilibrium inside pores of product CaO, that forms the outer layers of residual, partially reacted, calcium carbonate. This is slightly larger than the decomposition enthalpy, 173.5 kJ mol^{-1}. Almost all of the magnitudes of E reported in Tables 2 and 4 [1] were below the value, 205 kJ mol^{-1}, reported for the dissociation reaction in a good vacuum [11]. Some of the variation in kinetic parameters may, thus, arise from different weighting of those portions of the decomposition curve where the reverse reaction exerts significant kinetic control. Although the inhibiting influence of gas present on the dissociation rate has been repeatedly reported in the literature, very few *systematic* studies of the quantitative, specific influences of gas pressure, particle sizes, and other procedural variables on reaction kinetics have been reported.

6. Decomposition of ammonium perchlorate

The kinetics of thermal decomposition of ammonium perchlorate are complicated by the phase transformation that occurs at 513 K [12], a factor that was avoided here because all rate data were collected above this temperature. However, there is the possibility that decomposition was accompanied by reactant sublimation, opposed by the nitrogen atmosphere present. This can influence measured rate data, particularly at the higher temperatures [12].

The distribution of points (E: 60–130 kJ mol^{-1} and ln(A): 4–22 s^{-1}) on the compensation plot, Fig. 4, for these reactions, from [1] (programmed temperature, Set 5, and isothermal, Set 6) shows the clustering of about half the entries, from both types of kinetic studies, in a group for which E is between 105 and 117 kJ mol^{-1} and ln(A/s^{-1}) from 14 to 17. In approximately half of the remainder of the kinetic triplets, one or other Arrhenius parameter was within these ranges. However, overall there is significant scatter of reported results and any compensation trend is so weak as to be barely discernible (an estimated line drawn through the points gave an isokinetic temperature of 560 K, which is roughly intermediate between the ranges of the two rate studies). The only deduction drawn from Fig. 4 was that there was significant scatter of reported Arrhenius parameters.

Inspection of the figures and data in [1] indicates that the overall changes proceed to completion in (at least) two steps, as accepted in the kinetic analyses. It would appear that these data are the set that were later analyzed in a more comprehensive study of this reaction by Vyazovkin and Wight [13]. The conclusions were that E values for the exothermic first step (about 30% reaction) decreased with increasing α from about 130–95 kJ mol^{-1}. E values during the second step (30% to completion) increased across approximately the same range. This analysis identifies systematic changes in E during the progress of reaction which is identified as complex, composed of both concurrent and consecutive steps, including sublimation. This mechanistic interpretation, goes far beyond the more limited analyses reported in [1]. However, most values of E in Fig. 4 are within the range mentioned in [13] (130–95 kJ mol^{-1}), with a small number falling below this interval. Some 45% of the points are significantly outside the clusters, which themselves represent a much greater degree of uncertainty than the error limits usually mentioned in literature reports for solid state reactions.

7. Discussion

7.1. The significance of the present comparative analysis

The data sets used in this comparative study [1], meet the essential requirements for reliable kinetic analysis because all were obtained for a series of different heating rates or for a series of different isothermal temperatures. It has been clearly demonstrated [14], and is generally accepted, that a set of measurements obtained at a single-heating rate (and, even more obviously, from a single isothermal experiment) does not give a unique kinetic triplet.

The distributions of points, and their deviations from each line on the compensation plots, Figs. 1–4, provide a measure of the consistency of the results (a KCE expresses isokinetic behavior, there is identical reactivity at T_i) but not of the absolute accuracy of the methods, because the magnitudes of the Arrhenius parameters for the contributing processes are only known for the data in Fig. 1. It is well established that the kinetic triplets for calcium carbonate decomposition are markedly dependent on the transfer within the reactant of heat [10] and of mass (carbon dioxide) [11]. The present analyses, Figs. 2 and 3, demonstrate that the magnitudes of A and of E also vary with calculation methods. In all four compensation plots, Figs. 1–4, there are clusters of data points, which represent values preferred within the present survey. These plots are a useful method of displaying the patterns of relative variations of calculated parameters, but the relationships cannot be regarded as possessing any chemical significance because each set of Arrhenius parameters was derived from identical measurements. These compensation trends appear, therefore, as a mathematical consequence of calculation methods that have yielded wide ranges of A and E values (while any influence of the conversion function is ignored), obtained from the same data, for each of several reactions.

The difficulties of the kinetic resolution of complex processes were particularly exemplified through the results for the simulated (two) parallel first-order reactions. The relative contributions, in different α ranges from the two processes, change considerably with temperature. The result found is that the apparent Arrhenius parameters obtained from the kinetic analyses range (mainly) between the extremes of the individual processes (Fig. 1 and text). This is an encouraging feature of the project provided that this type of variation is recognized as an indication of complex behavior and this aspect is examined further [15].

In all four figures, the scatter of data obtained by non-isothermal measurements was approximately the same as that from isothermal studies. There was no convincing evidence to confirm that one type of experiment gave more consistent calculated parameters than the other. Even within the data clusters, there was significant dispersal of values about each mean, confirming that the calculated magnitudes of $\ln(A)$ and of E were not precisely reproducible, many of the variations in these reported data ranged up to around ±5%. This was unexpectedly large for parameters calculated from identical data sets.

More serious, however, are the much greater divergences of a relatively small proportion of values which are more remote from the clusters, found in all the tables from [1] and indicated on the figures in the earlier sections. Reasons for these variations may be inherent in the kinetic analytical expressions used or in the definitions of the quantitative terms employed. An explanation of these scattered values would make an important contribution to advancement of the subject by eliminating a source of considerable inconsistency and uncertainty.

The observation that values of E and of A vary significantly, when calculated by different researchers using the conventional methods of kinetic analysis from identical measurements (for each of eight sets of α, t, T data), is potentially the most important conclusion from this comparative study [1]. The results raise doubts about the acceptability of some aspects of the theory, the significances of E and A values, which depend upon the definition of k, and/or some of the computational methods used in the kinetic analyses of rate data obtained from both isothermal and programmed temperature experiments. Precise reasons for these inconsistencies are not discussed in detail here but this problem is identified as being fundamental to the subject of kinetic analysis and requires urgent critical assessment. Because the comparative approach was applied to the common data analyses considered in [1], it must be concluded that the much, if not all, of the variations apparent in Figs. 1–4 arise through differences inherent in the computational procedures employed. The discussion in the following sections considers some implications of this problem, including possible reasons why it has appeared, what action may be required in response to its detection and its significance in already published material.

7.2. Aspects of kinetic analysis

Conventionally in solid state kinetic analyses, α, the fractional reaction, quantitatively expresses the extent of a particular process at a given time and temperature. Measured values, for a single rate process, can then be tested for fit to a rather limited set of rate equations [2]. Where two, or more, concurrent or overlapping reactions contribute to the measured yield–time data, the contributions from each should, ideally, be distinguished and the separate data sets subjected to individual kinetic analysis. Kinetic analysis of complex reactions cannot be based on total product yields and techniques such as continuous evolved gas analyses are needed to distinguish each contributory process. Even if the definition of α is valid, the range of α values across which the kinetic analysis has been implemented must be identified and reported because some approaches to kinetic analysis refer only to limited α ranges. By focusing attention on the maximum rate, for example, aspects of the overall pattern of behavior may be missed.

The systems considered in [1] vary in their complexity. The endothermic, reversible calcium carbonate decomposition is likely to have a simpler chemical mechanism than the multi-reaction steps during the exothermic, irreversible decomposition of ammonium perchlorate, but neither can be described as simple (i.e. single-step) reactions.

It is also well known that different definitions of rate constants can influence the magnitudes of Arrhenius parameters calculated by these alternatives [2]. The rate constant is conventionally expressed in units $(\text{time})^{-1}$, from which rate expressions for solid state reactions take the form [2]: $g(\alpha) = k^n t^n$. The alternative (and incorrect) definition: $g(\alpha) = kt^n$ leads to magnitudes of $\ln(A)$ and of E both in error by a factor $\times n$ and to uninterpretable time dimensions for A. If the kinetic model $g(\alpha)$ is not correctly identified [9], however complex the function may turn out to be, this will also result in an incorrect definition of the rate coefficient, k.

There are many examples in the literature where the use of alternative rate equations leads to different E values from kinetic analyses of the same rate measurements. Such studies have, however, been shown to be incorrect in their attempts to obtain consistent kinetic triplets from single experiments [8]. Consequently, all Arrhenius parameter values reported in the crystolysis literature require reappraisal, because many are mentioned as varying with the kinetic model used in their calculation. In the theory of homogeneous kinetics, the magnitudes of the Arrhenius parameters, particularly E [16], have been regarded as (constant) properties of a controlling chemical process. It is expected that identical values (within experimental-error) of these parameters should be obtained by other researchers studying the same process, provided that the correct rate equation (however complex) has been identified to describe that process. In considering crystolysis reactions, if different workers identify different kinetic models as describing the process, the resulting Arrhenius parameters will usually differ at least slightly, and often greatly, from each other. A criterion for comparison of computational methods should, thus, be that all three components of the kinetic triplet should be unambiguously identified. Reporting E values without associated A values is clearly misleading and, because the method of calculation of A and E is dependent upon the choice of rate equation, it is essential to report complete kinetic triplets (together with the definition of α and the range of α considered). There is a real danger that the description of some of the more reliable methods of kinetic analysis, based on data obtained at different heating rates, as "model-free", could undermine the importance of the conversion function in the kinetic triplet. Perhaps the recognition of compensation behavior might be taken as evidence of the possibility that such reported Arrhenius parameters do not necessarily represent the unique set of kinetic characteristics of the process under consideration.

Reasons for the inconsistencies of rate parameters for all eight of the systems of interest here have yet to be characterized. It is already well established that kinetic parameters calculated from single-heating rate data show variations (representative references can be provided by AKG). The above analysis (and see also [17], discussed further in the following sections) shows that similar variations arise in alternative analyses of multiple-heating rate data, demonstrating a more general problem in interpreting the significance of reported kinetic conclusions. This must be addressed to ensure consistency in future work and in reconsideration of many results in the recent literature.

The comparative evaluation of kinetic data for the dehydration and decomposition stages of calcium oxalate monohydrate, measured under similar conditions in 13 European laboratories and reported by Anderson et al. [17], cannot be directly compared with the (later) study of interest here [1]. This is because the earlier calculations were based on different sets of measurements, each obtained by the participants themselves, for standardized experimental methods. Nevertheless, as in the present article, these results similarly [19] exhibited pronounced KCEs, indicative of (the expected) comparable levels of reactivity within the sets of reactions for which the calculated Arrhenius parameters showed significant variations. There is, however, the strong possibility that such variability of calculated A and E values could (again) arise as a result of changes in the influences of calculation method, including possibly the rate equation, used in the kinetic analysis, as discussed in the earlier sections.

If the magnitudes of A and E are dependent upon the choice of rate equation, then any compensation plot is a two-dimensional projection of a higher (at least three-) dimensional relationship [18]. The simplest such projection would be a compensation plot on a plane with constant conversion function (or kinetic model). The simplest three-dimensional relationship would be when the magnitudes of A and E are not dependent upon the choice of rate equation, thus, resulting in a stack of identical compensation plots. At the other extreme, a complicated surface would result when comparison of magnitudes of A and E involved non-vertical movement from one conversion-function plane to another (however, the influence of the conversion function is represented). The validity of such a multi-dimensional explanation remains to be explored. If the method of calculation of A and E is dependent upon the choice of rate equation, then all Arrhenius parameters reported in the literature require careful appraisal and, in the absence of suitable supporting information, cannot be accepted at face value. This applies especially to all the non-unique kinetic triplets that have been obtained from single-heating rate experiments.

Some of the methods of kinetic analysis used in [1], were based upon linear regression, whereas others used more sophisticated non-linear techniques. Many reports of kinetic fit by linear regression identify the rate equation, and express quantitatively the precision of fit through the correlation coefficient (r). Frequently several values of r, referring to fits by different equations for the same data set, are close to unity, which makes it difficult to decide which is 'best'. However, the extent of fit, the range of α across which the equation is regarded as applicable, is rarely (if ever) specified. Without identification of this α-interval of acceptability, the reported accuracy of fit is hardly meaningful: for example, do different equations 'fit' across different α ranges? Even more rarely implemented is the ultimate test of the kinetic analysis, namely the comparison of the experimental data with the equivalent set of data calculated from the estimated kinetic triplet, carried out after linear regression, whereas this procedure is the basis of non-linear regression. The significance of small alterations to the estimated parameters is seen most easily using non-linear methods. The implied accuracy with which calculated Arrhenius parameters are reported (for example, values of E reported to ± 0.01 kJ mol^{-1}) is frequently unrealistic.

Some approximate equations have been devised to simplify calculations of the desired kinetic parameters, for example, use of finite differences instead of derivatives, and, even more particularly, approximate solutions for the 'temperature integral'. Flynn [19] states: "in this age of vast computational capabilities, there is no valid reason not to use precise values for the temperature integral when calculating kinetic parameters". Certainly, kinetic parameters should be able to be calculated more reproducibly than appears from the spread of values found in [1]. It is probable that the use of computational procedures based on different approximations by different workers [2] has contributed, at least in part, to the variations in the Arrhenius parameters found here.

The results in [1], together with the behavior patterns described in the earlier sections, could provide a valuable resource to the participants themselves. They alone have access to the calculation methods and detailed computer programs used in their kinetic analyses. From these they may be able to establish reasons for the variations of the Arrhenius parameters described in the earlier sections, such as the use of approximations, inconsistent definitions of terms, or a dependence of A and E on the kinetic model. Individual results could then be compared in the context of the different conclusions found by other participants in the project. If uncertainties, errors and unsuitable or ambiguous definitions of terms could be identified, characterized and eliminated, the credibility, and value in theory development, of results of kinetic analyses could be substantially increased.

8. Conclusions

Current methods of kinetic analysis, as used by different workers interpreting the same data [1], have achieved some measure of agreement in calculating

Arrhenius parameters (the clusters shown in Figs. 1–4), but the variation found overall is greater than can be regarded as acceptable. Reasons for this variation, possibly inherent in some of the kinetic analysis programs, need to be identified and modification of methods made where appropriate. Project participants themselves [1] need to identify the reasons for the present unacceptable discrepancies, by comparisons of the methods used and establishment of the essential differences between the various calculation procedures used. Possible reasons for these variations include inconsistent definitions of terms such as the power law exponents, the definition of α and the α ranges to which an interpretation applies, the incorrect choice of conversion function from alternative possibilities, and approximations made to simplify calculations, such as evaluation of the temperature integral [19]. The distributions of points on the compensation plots, expressed by r^2 values in Table 1, were much wider than might have been expected from calculations based on identical data sets, with the interesting exception of the simulated data. Establishment of the individual reasons for the compensation and for the scatter are both of interest. Assessment of the roles and magnitudes of errors in characterizing the kinetic model, together with calculation of the magnitudes of A and of E, are essential prerequisites to increasing the reliability of data interpretation. Such studies could also usefully identify possible reasons for the patterns of results and the several problems raised for discussion in the present paper.

It follows that uncertainties, similar to those shown in Figs. 1–4, must apply to all (or most) Arrhenius parameters reported for solid state reactions, thus, increasing the difficulties of comparison of values of A and E reported by different researchers. Presumably an even greater scatter of kinetic triplets would have been obtained if the analyses had been based on measurements obtained by different workers, using different experimental techniques (e.g. as in [17]).

Constancy of the magnitudes of Arrhenius parameters and the conversion function identified, from one data set using different calculation methods, provides the major criterion of consistency in kinetic analysis. The same reasoning suggests the possibility that compensation trends, as here, could identify the possibility of incorrect computational procedures and/or assumptions.

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