

# Arrhenius parameters and compensation behaviour in solid-state decompositions

Andrew K. Galwey, Michael E. Brown\*

Department of Chemistry, Rhodes University, Grahamstown, 6140, South Africa

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## Abstract

Many instances of compensation behaviour (i.e. conformity of the Arrhenius parameters to a relationship of the form:  $\ln A = bE_a + c$ , where  $b$  and  $c$  are constants) reported for solid-state decompositions, refer to reactions that are at least partially reversible under reaction conditions used in the kinetic studies. Arrhenius parameters calculated for such processes are sensitive to the prevailing pressure of volatile product and heat transfer controls that may vary appreciably between successive experiments. Thus, compensation effects have been reported for various single reactions (e.g. the decomposition of  $\text{CaCO}_3$ , the dehydroxylation of  $\text{Ca}(\text{OH})_2$  and the dehydration of  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ) where, for each solid, the reactivity of the starting material can be regarded as constant.

Compensation has also been reported for sets of chemically comparable reactants that (are expected to) decompose in the same temperature interval. Compensation may then arise either from the aforementioned variation of reaction conditions, or from differences in the reactants, such as particle sizes, packing, etc.

Because of the variety of compensation effects reported, the phenomenon is often regarded as an experimental artefact. It is of interest to examine the reasons for the concurrent changes of Arrhenius frequency factors and activation energies. The significance of activation energies in solid-state decompositions is discussed briefly and three classes can be distinguished. The accuracy of measurement of activation energies needs to be increased so that their sensitivity to prevailing reaction conditions can be established, investigated and understood. © 1997 Elsevier Science B.V.

## 1. Introduction

The compensation effect is a widely reported pattern of kinetic behaviour for which no accepted theoretical explanation has yet been provided. The existence of a relationship between the Arrhenius parameters (reaction frequency factor,  $A$ , and activation energy,  $E_a$ ) of the following form has been reported for many different types of rate processes [1]:

$$\ln A = bE_a + c \quad (1)$$

where  $b$  and  $c$  are constants. Each group of rate processes that constitutes a *compensation set*, identified as the fit of  $A$  and  $E_a$  values to Eq. (1), contains common chemical characteristics. Compensation is sometimes regarded as a unifying feature, perhaps even including similar rate controlling steps, within the set of reactions so related. A further property of a set of reactions for which  $A$  and  $E_a$  values fit Eq. (1) is the existence of an isokinetic temperature,  $T_i$ , at which all reactions proceed at equal rates [2] (and equal rate constants= $k_i$ ).  $T_i$  is often close to, or within, the temperature interval of the measured kinetic data [3,4]. Perhaps the greatest interest in compensation phenomena has been for heterogeneous catalytic reac-

\*Corresponding author. Tel.: INT-461-318-254; fax: INT-461-25109; e-mail: chmb@warthog.ru.ac.za.

tions [1–3], but compensation has also been widely reported and discussed for solid-state decompositions [4–7], with which the present review is concerned.

The effect appears to have been recognised mainly in observations obtained for other reasons. Few studies have been specifically directed towards understanding the effect itself. Chemical processes exhibiting this behaviour may be a set of virtually identical reactions, as in the earliest work by Constable [8], who studied the rates of reaction of ethanol on a series of copper catalysts that had been subjected to different heat treatments. In contrast, a compensation effect has been reported [1] for different chemical changes proceeding on the same metal catalyst.

The important question of identifying the factors that control the changes in magnitudes of  $A$  and  $E_a$  and why these parameters should rise or fall in relation to each other for the reactions that comprise the set, still remains unanswered. Agrawal has mentioned [4] that “the validity of the compensation effect has been heatedly debated.” Measurements of compensatory fits on both the sides of  $T_i$  have not always confirmed that there is an inversion of relative rates for reactions having different  $A$  and  $E_a$  values. This kinetic feature was demonstrated in an early study by Cremer [3] of formic acid decomposition on samples of MgO that had been subjected to different heat pre-treatments. Agrawal [4] has pointed out that the data giving linear compensation plots may not, however, show acceptable constancy of reaction rate at an identifiable  $T_i$  value, when the same rate measurements are displayed on a composite Arrhenius plot. This is regarded as the critical test of isokinetic behaviour [9].

In the absence of any mechanistic interpretation of compensation behaviour, applications of Eq. (1) seem to be ‘theoretically sterile’ (borrowing a descriptive conclusion applied by Laidler [10] to a different, but related problem) in that the equation provides no predictive capacity and remains an empirical observation that leads to no useful insights into the controls of reactivity.

This article surveys reported instances of compensation behaviour for solid-state decompositions and discusses theoretical explanations for the pattern of variations among the Arrhenius parameters reported for representative sets of reactions. Compensation behaviour may arise because all decompositions of the set proceed in very similar temperature intervals.

Establishing the isokinetic character of the data, from which the compensation effect is recognized, inverts the usual interpretative approach. Qualitatively, however, this perspective accepts the view that bonds of similar reactivities control the rates of the reactions that constitute the set for which Eq. (1) provides the comparative test. Precursors to the rate determining step are activated at closely similar temperatures. Conditions prevailing within the different reactants constituting the set, particularly the influence of volatile products in reversible reactions, may contribute more towards controlling the temperature coefficient of reaction rate (hence  $A$  and  $E_a$  [1]) than the temperature at which the reaction occurs. Although this is a qualitative consideration, it may have some value in discussions of compensation by focussing attention on the magnitudes and variation trends of Arrhenius parameters within the sets of reactions related through Eq. (1).

Two extreme positions in the ongoing debate about the validity and significance of the compensation effect are (i) that it may arise as a computational artefact [4], and (ii) that it may have a ‘real’ chemical significance. If (ii) is true, the apparently dominant position of the Arrhenius relationship as a unifying feature throughout chemical kinetics is weakened. The *independence* of the parameters  $A$  and  $E_a$  is interpreted, through the absolute reaction rate theory, as an acceptable basis for the formulation of reaction mechanisms at the fundamental level of bond-breaking and bond-formation steps. The recognition, therefore, of a direct, but theoretically unexplained, relationship between the Arrhenius parameters appears, at best, as an omission from accepted theory or, at worst, as evidence that the theory is in error.

A further problem remains unresolved in considering the kinetics of reactions proceeding in the solid state. For such reactions, values of  $A$  and  $E_a$  calculated from linear Arrhenius plots are often accepted as possessing the same theoretical significance as those envisaged in the transition state model. The theory of reaction rates developed for homogeneous rate processes is not, however, generally applicable to reactions of solids without a critical comparison of the underlying assumptions. It has been pointed out [11] that the distribution function for energy in crystals is different from those applicable to homogeneous reactants. More recently [12], it has been argued from a

theoretical standpoint that the rates of reactions of solids will exhibit a similar pattern of temperature dependence to that applicable in homogeneous processes under most conditions. Much less is known about detailed mechanisms and rate controlling factors for reactions at interfaces and the uncertainty about bond redistribution models inhibit the development of quantitative explanations of reaction rates. Reactant concentrations at interfaces may be subject to controls, as well as to temperature variations, which are different from those in homogeneous systems [1]. However, the rates of the vast majority of reactions of solids are well-expressed by the Arrhenius equation [13] and it is useful to discuss the magnitudes of reported  $E_a$  values before proceeding to consider compensating behaviour.

## 2. The significance of Arrhenius parameters in solid-state decompositions

Reactions proceeding within an active reactant-product contact zone [13] are usually inaccessible to direct observation. Mechanistic inferences concerning the factors which control the rate of the limiting bond redistribution step, or steps (assuming the applicability of this 'homogeneous' concept) are frequently based on indirect evidence, including inferences deduced from the magnitudes of  $A$  and  $E_a$ . For many reactions of interest, independent knowledge of the properties or concentrations (or the total amounts within the reaction zone) of the precursors to chemical change is not available. Thus, the 'frequency of occurrence of the reaction situation' can be inferred (or guessed) only approximately through consideration of textural evidence, chemical analyses and crystallography. In the absence of a precise reaction model, any quantitative theoretical treatment of reaction rates becomes impossible.

### 2.1. Reaction frequency factor

If the number of precursor reactant species participating in the interface process is not known, rate constants, and hence  $A$  values, cannot be expressed in terms of concentrations/time (or sites per unit area/time, as commonly used in heterogeneous catalysis [2]). Because of the use of a dimensionless fractional

decomposition, the dimensions of  $A$  values for reactions of solids are  $(\text{time})^{-1}$ .  $A$  values thus provide a measure of reactivity, but they cannot be related to individual chemical steps without additional assumptions that include consideration of reaction geometry [13].

### 2.2. Activation energy

Values of  $E_a$  for numerous solid-state decompositions have been reported [13], but the reliability and/or significance of a high proportion of these values remains in doubt. For many reactants only one reported value of the activation energy may be available, so that in a field where agreement is not always achieved, the reliability of such results could be considerably increased by confirmatory studies.

### 2.3. $E_a$ values for irreversible decompositions

For a limited number of irreversible solid-state decompositions, several studies of the same reaction have been completed and consistent values of  $E_a$  are available. Kinetic characteristics of these rate processes are entirely or largely independent of reaction conditions. For example, many published values of  $E_a$  for the decomposition of  $\text{NH}_4\text{ClO}_4$  are in the 100–140  $\text{kJ mol}^{-1}$  range [13], though there is also a reported compensation trend extending slightly beyond this range. Values of  $E_a$  reported for the decomposition of nickel oxalate are  $135 \pm 12 \text{kJ mol}^{-1}$ .

Under this heading, the results from groups of closely related compounds could also be included. For example, the reactivities of the three solids  $\text{KMnO}_4$ ,  $\text{RbMnO}_4$  and  $\text{CsMnO}_4$  are similar and activation energies for the decompositions of these three solids are between 160 and 170  $\text{kJ mol}^{-1}$  [14,15]. Decomposition is probably determined by the stability of the  $\text{MnO}_4^-$  ion (though  $E_a$  values for  $\text{LiMnO}_4$  and  $\text{NaMnO}_4$  are somewhat less, 135  $\text{kJ mol}^{-1}$ , evidence of a contribution from, or influence of the constituent cation).

### 2.4. $E_a$ values for reversible decompositions

The kinetics of many reversible solid-state rate processes are influenced by local reaction conditions

and some are very sensitive to the prevailing pressure of the volatilized product. Kinetic studies of the decomposition step, in the absence of any contribution from the reverse process, require careful control of reaction conditions. For example, when the decomposition of  $\text{CaCO}_3$  was studied [16] at pressures that were sufficiently low ( $< 0.1$  Pa) to ensure that all product  $\text{CO}_2$  was effectively removed from the reaction zone, the activation energy measured ( $205 \text{ kJ mol}^{-1}$ ) was appreciably larger than the dissociation enthalpy ( $178 \text{ kJ mol}^{-1}$ ), a result that differs from many other values reported in the literature for the  $\text{CaCO}_3$  decomposition [13]. In another example, the dehydration of  $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  was similarly studied in vacuum [17] and rate measurements for small samples (0.2–3 mg) were extrapolated to zero mass to remove contributions from the rehydration step. The magnitude of  $E_a$  determined was larger than other reported values for this reaction.

In most kinetic studies, experiments are designed to obtain data specifically relating to reactant decomposition only. Many articles do not discuss the influence of reversibility on kinetic behaviour, including the possibility that a volatile product may influence, contribute to, or possibly even control the calculated magnitudes of  $A$  and  $E_a$ . These influences from reversibility are expected to be significant in many non-isothermal experiments, where reaction can be rapid and product escape from the reaction zone is opposed by the presence of an inert atmosphere. The magnitudes of Arrhenius parameters are sensitive to reaction conditions and, measured under ill-defined reaction conditions, can have no fundamental significance because they are not reliably related to the chemical controlling step. For such data and reaction conditions, compensation effects are often identified.

In discussing the kinetics of decomposition of  $\text{CaCO}_3$ , Beruto and Searcy [16] point out that  $\text{CO}_2$  may be retained within the pore system of the product  $\text{CaO}$ , behind the advancing  $\text{CaO}/\text{CaCO}_3$  interface. Adsorption within this zone reverses the desorption step ( $\text{CaO} + \text{CO}_2$ )  $\rightarrow$   $\text{CaCO}_3$ ) and this results in the establishment of the equilibrium dissociation pressure of  $\text{CO}_2$  within the coherent reacting particle. The rate of  $\text{CO}_2$  release beyond the crystal is thus determined by the pressure of  $\text{CO}_2$  within the particles. The apparent value of  $E_a$  is then equal to the dissociation enthalpy. The participation of these secondary pro-

cesses must be eliminated before the kinetics of the decomposition can be determined. This important condition is not fulfilled in many studies. The reliability of  $A$  and  $E_a$  values for this reaction has been discussed by Maciejewski and Reller [18]. Compensation trends are considered in the following.

### 3. Single reaction compensation behaviour

For certain rate processes (usually reversible and endothermic), the magnitudes of Arrhenius parameters reported by different workers, and/or values obtained under different reaction conditions, exhibit compensation. If the apparent  $A$  and  $E_a$  values show variation, it is hardly surprising that (at least approximately) isokinetic behaviour should appear, because data refer to the same chemical change that can be expected to occur within a characteristic (reactivity controlled) temperature range. There is, however, little quantitative information available on the factors that determine changes in reaction rate and the values of  $A$  and  $E_a$  within the compensation range.

#### 3.1. The decomposition of calcium carbonate

The literature concerned with this decomposition is extensive [18–23] and the study referred to earlier [16] is important in characterizing only the dissociation rate. There have been several studies of the influences of procedural variables on the decomposition of  $\text{CaCO}_3$  [19,20]. These variables include: the heating rate in dynamic experiments, physical properties of the reactant mass (crystallite sizes, dispersion and geometric shape), the influence of atmosphere (particularly the partial pressure of  $\text{CO}_2$  and the flow rate), etc. Such investigations of reactivity may be of value in identifying the controls of reaction rate for industrial processes. The uncertainties in measuring the relative kinetic influences make such observations unsuitable for determining details of the rate limiting step.

During non-isothermal kinetic studies, inhomogeneities are developed within the reactant mass with local variations in temperature and prevailing  $\text{CO}_2$  pressure. For example, during  $\text{CaCO}_3$  decomposition [21] the shape of the  $\text{CO}_2$  yield vs. time curve can be determined by the heat supply to the reactant.

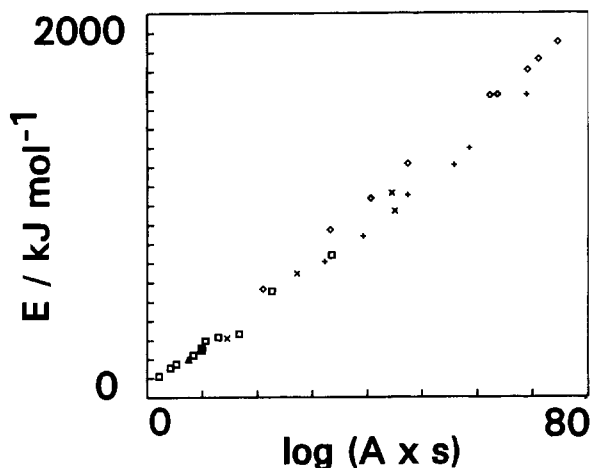


Fig. 1. A compensation plot showing  $A$  and  $E_a$  values reported from non-isothermal studies of  $\text{CaCO}_3$  decomposition. Data from: Zsakó and Arz [22] for reactions in ( $\square$ ) 'air' and (+)  $\text{CO}_2$  (no pressure units recorded); Gallagher and Johnson [23] for reactions in ( $\diamond$ )  $\text{CO}_2$  (higher values continue the straight line off the graph given here) and a single (mean) value for reaction in ( $\triangle$ )  $\text{O}_2$ ; Wei and Luo [20] – (x) (mean values from Table 1; values for 7–13 and 7–09 from Table 3 have been omitted due to uncertainty about the magnitude of  $A$  values recorded).

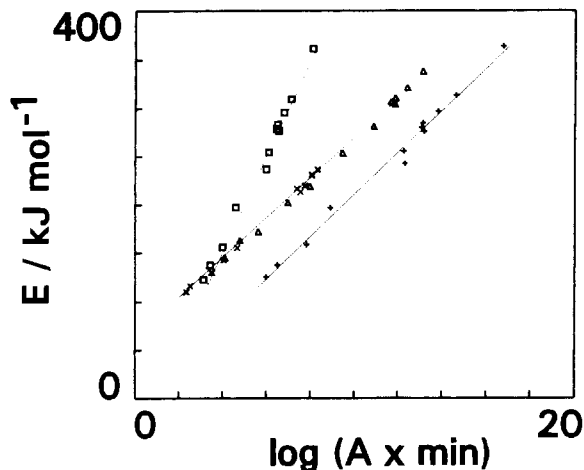


Fig. 2. A compensation plot for the second reaction ( $\text{MgO} \cdot \text{CaCO}_3 \rightarrow \text{MgO} \cdot \text{CaO} + \text{CO}_2$ ) during the decomposition of six Turkish dolomites [24]. The authors used different methods in the kinetic analyses of non-isothermal measurements and did not report compensation. The middle line, using the ( $\triangle$ ) Horowitz–Metzger and (x) Dharwadkar–Karkhanavala methods, is close to the main trend in Fig. 1. The other lines were obtained using the ( $\square$ ) Coats–Redfern and (+) Doyle–Zsakó methods. The first reaction ( $\text{MgCO}_3 \cdot \text{CaCO}_3 \rightarrow \text{MgO} \cdot \text{CaCO}_3 + \text{CO}_2$ ) shows generally similar behaviour.

Although kinetic behaviour is recognized to be influenced by heat and/or mass ( $\text{CO}_2$ ) transfer, the individual relative significances of these factors under well-defined conditions have not been established.

Compensation plots from two studies of calcium carbonate decomposition [22,23] in 'air' and in  $\text{CO}_2$ , and a recent paper [20], are shown in Fig. 1. A point calculated from data given by Beruto and Searcy [16] has also included ( $\log(A/\text{s}^{-1}) = 6.7$  and  $E_a = 205 \text{ kJ mol}^{-1}$ : on the additional assumption that reaction is completed in 170 min at 1013 K) and is on the same line.

Values of  $A$  and  $E_a$  reported for the second step in the breakdown of some Turkish dolomites [24] ( $\text{MgO} \cdot \text{CaCO}_3 \rightarrow \text{MgO} \cdot \text{CaO} + \text{CO}_2$ ) were within the scatter of the points at the lower end of the line in Fig. 1. (These authors [24] did not report compensation behaviour, but their data are used in Fig. 2. The middle line in Fig. 2, i.e. data from use of different non-isothermal kinetic methods, coincides with the line in Fig. 1.) The first stage of reaction ( $\text{MgCO}_3 \cdot \text{CaCO}_3 \rightarrow \text{MgO} \cdot \text{CaCO}_3 + \text{CO}_2$ ) [24] exhibited a compensation pattern close to that shown in Fig. 2, with a slightly lower, 975 K, isokinetic

temperature. The different compensation lines calculated from the same experimental measurements using different mathematical methods raises questions about these methods of interpretation of data.

The scatter of data in Fig. 1 is appreciable (behaviour is not isokinetic [4]) reflecting some variation in data reported by different workers. The strong compensation trend discerned must, however, derive from the common chemical controlling step. Isokinetic temperatures calculated from the slopes of the individual compensation lines for reactions in  $\text{CO}_2$  were 1244 K [22] and 1250 K [23]. These temperatures are remarkably close to the DTG peak temperature (1243 K) for the reaction [19]. Values of  $T_i$  for  $\text{CaCO}_3$  decomposition in air, or  $\text{N}_2$ , similarly calculated were more scattered, as expected, where there was greater scope for variation of the  $\text{CO}_2$  pressure and reactant inhomogeneity. Calculated magnitudes of  $T_i$  were 1058 K [22], 815 K ([23], Fig. 3), 927 K [20] and  $\sim 1100 \text{ K}$  [24]. The DTG maximum was at  $\sim 1170 \text{ K}$  [19].

The points in Fig. 1 are close to a common compensation line for reactants in the form of powder

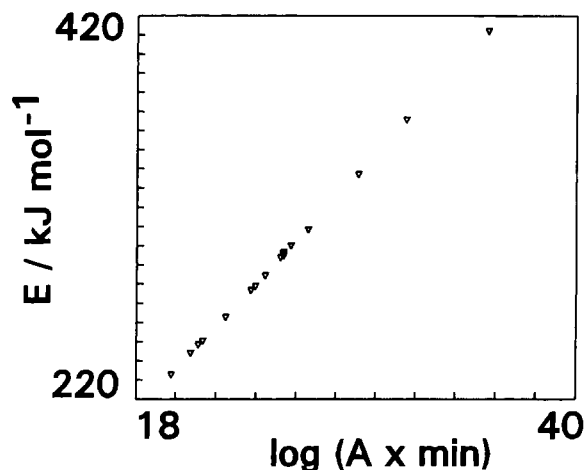


Fig. 3. The compensation trend for decomposition of samples of doped strontium bromate. Taken from non-isothermally determined  $A$  and  $E_a$  values reported by Nair and Sahish [39], who did not discuss compensation.

[20,22,23], crystal [16] and the 'second step' of the dolomite decomposition [24]. The largest values of both  $A$  and  $E_a$  were found for reactions in  $\text{CO}_2$  [22,23], particularly for small reactant samples and at slow heating rates [23]. Magnitudes of  $E_a$  for the second stage of the dolomite decomposition [24] in  $\text{CO}_2$  containing atmospheres were, on average, greater than those in  $\text{N}_2$ , though there were significant variations within each group.

Thus, there are empirical indications that a rise in the prevailing pressure of  $\text{CO}_2$  increases the magnitudes of both Arrhenius parameters. This does not, however, provide a quantitative explanation of the pattern of behaviour observed. The roles of the  $\text{CO}_2$  pressure and of heat transfer, require detailed study before such an explanation is likely to emerge. A general theory would have to be applicable to reactions proceeding under all conditions, including programmed temperature experiments. Qualitatively, compensation appears as a consequence of comparable reactivities of diverse samples in a variety of reaction situations. Much more detailed kinetic studies are required to identify and quantitatively establish the relative contributions from heat transfer, product gas removal and other effects. Influences of reaction-induced inhomogeneities will be more difficult to determine quantitatively.

### 3.2. Decomposition of calcium hydroxide

The compensation pattern found for the reversible and endothermic dissociation of calcium hydroxide ( $\text{Ca}(\text{OH})_2 \rightleftharpoons \text{CaO} + \text{H}_2\text{O}$ ) is similar to that for  $\text{CaCO}_3$  described above. There are, however, fewer reported studies and none under high vacuum to eliminate contributions from the reverse process. Values of  $E_a$  are reported between  $\sim 34$  and  $190 \text{ kJ mol}^{-1}$ . The enthalpy of reaction is  $\sim 100 \text{ kJ mol}^{-1}$ . Recent studies [25,26] concluded that the Arrhenius parameters could not be identified with a specific chemical step in the dissociation. The isokinetic temperature,  $683 \text{ K}$  [25], was within the range of kinetic measurements.

### 3.3. The dehydration of lithium sulphate monohydrate

The dehydration of  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  was briefly considered [27] for use as a 'kinetic standard' for comparison of kinetic measurements obtained by different laboratories. The reaction is reversible and endothermic, but no studies appear to have been done of the dehydration under high vacuum. Reported activation energies ( $60$  to  $120 \text{ kJ mol}^{-1}$  with a few higher values) vary significantly with reaction conditions [27,28]. Compensation behaviour was found and the isokinetic temperature ( $\sim 400 \text{ K}$ ) was within the experimental range. The pattern is generally similar to that of  $\text{CaCO}_3$ . Extension of measurements to include reactions under a range of controlled water vapour pressures, and high vacuum conditions, would be valuable.

## 4. Single reaction: Multiple kinetic analysis compensation behaviour

The 'first step' in the decomposition of  $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$  was studied [29] at five heating rates ( $2.5$ – $20 \text{ K min}^{-1}$ ), complemented by isothermal TG and DTG measurements in dry  $\text{N}_2$ . Arrhenius parameters were calculated for decomposition of this single reactant, using eight different but widely used methods of kinetic analysis. Apparent values of  $A$  and  $E_a$  varied between  $\sim 10^4$ – $10^{19} \text{ min}^{-1}$  and  $60$ – $220 \text{ kJ mol}^{-1}$ , respectively. These data showed a 'compensation effect' which must either derive from the influence of the heating rate, or from inconsisten-

cies in the assumptions of the mathematical methods of analysis. The pattern of observations is consistent with previous observations that Arrhenius parameters calculated from isothermal and non-isothermal data may differ significantly [30]. The same experimental data, used in the alternative calculations, are necessarily and obviously always isokinetic. This is sufficient to explain the appearance of compensation behaviour.

### 5. Related reactions: Compensation behaviour

A group of compounds of similar structures, containing identical or closely comparable bonds, can be expected to react within similar temperature intervals. If the apparent values of  $A$  and  $E_a$  for the decompositions of such a set of (isoreactive) reactants show variations then there is usually compensation. For example, the thermal decompositions of seven cobalt halide amine complexes,  $(\text{CoX}_2(\text{amine})_2)$ , were studied [31] in the 400–450 K range. The composite Arrhenius plot shows that the reactions of the set were not strictly isokinetic [4] (at  $T_i = 460$  K, rates varied  $\times 20$ ), but the trend was accepted as a compensation effect [31]. Compensation has been observed for other groups of closely related reactants [32,33]. This kind of compensation effect is closest to that encountered in heterogeneous catalysis and is ascribed to the kinetic consistency of rate processes which involve rupture of bonds of similar strengths in comparable reactants and measured within similar temperature intervals. Details of the factors determining the appreciable variations in the Arrhenius parameters have not been determined, but this category of compensation is fundamentally different from that resulting from differences in conditions prevailing during decomposition of an otherwise identical reactant, although both behaviours may be described by Eq. (1) with different constants.

If all related reactants in a group decompose by reversible and endothermic reactions [34,35], it will be difficult to determine whether the observed compensation results from the differences in the bonding situations, from the differences in the prevailing reaction conditions, or from both. For example, compensation behaviour was reported for a series of clay dehydroxylations [36] ( $75 < E_a < 195$  kJ mol<sup>-1</sup>;  $T_i = 528$  K and the temperature range was 420–550 K).

### 6. Mechanism change: Compensation behaviour

Ball [37,38] has drawn attention to the occurrence of compensation behaviour when solid-state decompositions exhibit a change of mechanism. The point of change in slope on the Arrhenius plot is an isokinetic temperature for the two different rate processes. For example, the dehydration ( $-4\text{H}_2\text{O}$ ) of  $(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  proceeds as a nucleation and growth reaction below 350 K ( $A = 2.1 \times 10^{21}$  s<sup>-1</sup> and  $E_a = 170$  kJ mol<sup>-1</sup>), whereas above 350 K the contracting area model applicable ( $A = 2.2 \times 10^8$  s<sup>-1</sup> and  $E_a = 82$  kJ mol<sup>-1</sup>). A similar pattern of behaviour was found for the dehydration of copper(II) acetate monohydrate [37].

It is possible that the changes in Arrhenius parameters across this discontinuity could be related to changes in the structure of the transition complex.

### 7. Reactant doping: Compensation behaviour

#### 7.1. Decomposition of doped strontium bromate

Arrhenius parameters obtained in a non-isothermal study of the decomposition of doped  $\text{Sr}(\text{BrO}_3)_2$  samples showed a compensation effect, Fig. 3, not mentioned in [39]. For the pure reactant,  $A = 3.8 \times 10^{23}$  s<sup>-1</sup> and  $E_a = 295$  kJ mol<sup>-1</sup>. The temperature at maximum reaction rate remained constant (578 K) for all 17 samples studied, but calculated values of  $A$  and  $E_a$  increased for crystals containing  $\text{K}^+$  or  $\text{Mg}^{2+}$  and decreased due to the incorporation of  $\text{Al}^{3+}$  or  $\text{KBr}$ . The values of  $A$  and  $E_a$  varied systematically with the amount of dopant. TG curves showed mass losses in closely similar temperature intervals, confirming the occurrence of acceptable isokinetic behaviour.

This reaction has promise as a model system, because it may be possible to relate concentrations of dopants to the concentrations of the precursors to chemical change [1]. This could be of value in identifying the theoretical significance of  $A$ . It would be interesting to know whether isokinetic behaviour is shown by isothermal kinetic measurements for these reactions.

## 7.2. Decomposition of copper(II) oxalate

Compensation was also found in the reported results for different preparations of copper(II) oxalate [40]. The temperatures at maximum reaction rate, on heating at  $2 \text{ K min}^{-1}$ , were between 587 and 613 K and  $E_a$  values were between 141 and  $274 \text{ kJ mol}^{-1}$ . This variation could arise from changes in imperfection or impurity concentrations in the reactants.

## 8. Conclusions

### 8.1. Activation energy values for solid-state decompositions

Although determination of the activation energy is a major objective of most kinetic studies of solid-state decompositions, the accuracy of such reported  $E_a$  values is frequently difficult to assess. Reproducibility of measurements is not always good and relatively few values have been confirmed independently.  $E_a$  values are often reported to several significant figures, without provision of realistic estimates of the uncertainties in the measurements. Arrhenius plots are generally assumed to be linear for solid-state reactions [12] and few tests are made for possible deviations. This assumption is fundamental to most methods of non-isothermal kinetic analysis where the consequences of deviation (or mechanism change [37,38]) are often ignored. The precision achievable in measurement of  $E_a$  values for reactions of solids is unlikely to match that routinely achieved in homogeneous rate processes.

We distinguish three classes of  $E_a$  values reported for solid-state decompositions:

1. The controlling activation step in an irreversible reaction – values of  $E_a$  are largely independent of prevailing conditions as in the decompositions of  $\text{NH}_4\text{ClO}_4$ ,  $\text{KMnO}_4$ ,  $\text{NiC}_2\text{O}_4$ , and values reported by different workers are in good agreement.
2. The controlling activation step in a reversible (and usually endothermic) decomposition – particularly careful experimental measurement is essential to exclude any contribution from the reverse process as convincingly demonstrated for the decomposition of  $\text{CaCO}_3$  [16] and the dehydration of  $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  [17].

3. The overall temperature coefficient in reactions which are kinetically sensitive to reaction conditions – probably, most values of  $E_a$  in the literature refer to the reactions of this type, though the possibility of reversibility and the factors influencing kinetic behaviour are not always characterized.

Surprisingly, a few tests of the reproducibility of reported  $E_a$  values for decompositions of types (i) and (ii) are to be found in the literature. Interdependent variations of  $A$  and  $E_a$ , fitting Eq. (1), for processes that can be classified as type (iii), may arise as a consequence of isokinetic behaviour or a close approximation to this condition. This provides evidence for the suggestion that the same mechanism may occur in all reactions included in a compensation set [35,41]. The identification of a controlling vibrational frequency, related to the isokinetic temperature, may be of value in recognizing the common pathway for reactions of any particular set [41]. Compensation may also be a consequence of temperature or reactant inhomogeneities within the decomposing solid [4,42].

It is important that efforts should be made to generally increase the accuracy of measured  $E_a$  values for solid-state decompositions, together with the provision of realistic quantitative assessments of uncertainty limits. Only then a theoretical interpretation of the significance of the activation energy will become possible.

### 8.2. Compensation effects

Compensation effects have been reported for several reversible and endothermic reactions. For these rate processes kinetic characteristics are sensitive to local conditions, the most important being the heat transfer and availability of volatilized product within the reactant mass. Such pseudo-isokinetic behaviour may be found in the reversible breakdown of a selected reactant ( $\text{CaCO}_3$ , etc.), or in a series of compounds containing almost identical bonds and reactivity. Arrhenius parameters determined under these rate-dependent conditions do not possess fundamental significance and may not be of any value in mechanistic interpretations. It could be useful, nonetheless, to investigate further the factors that determine the magnitudes of  $A$  and  $E_a$ . At present, however, compensa-



tion effects appear as an empirical relation and a more complete understanding is difficult without a precise model that explains the magnitude of *A*.

The identification of compensation with mechanism change [37,38] and the appearance of interesting trends in doped reactants [39,40] offer promising directions for future progress. At present, no theory is accepted as explaining the compensation effect adequately, though in some systems it may be regarded as a consequence of isokinetic behaviour.

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