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THE USE OF THE RISING TEMPERATURE TECHNIQUE TO ESTABLISH KINETIC PARAMETERS FOR SOLID-STATE DECOMPOSITIONS USING A VACUUM MICROBALANCE*

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ABSTRACT

There are certain experimental aspects concerning the effect of rising temperature on the apparent weight of a substance which have been extensively studied. The theoretical treatment of the kinetics of decomposition under rising temperature conditions rests largely on a combination of equations one of which is the Arrhenius equation. One thus has to combine the kinetic law;

$$\frac{d\alpha}{dt} = kf(\alpha)$$

the law describing the temperature coefficient of the rate (usually the Arrhenius equation);

$$k = Af(T)$$

and the equation describing the imposed temperature (T in degrees Kelvin) against time (t);

$$T = T_0 + \beta f(t)$$

where α is the fraction decomposed, k is the specific rate constant, A is a constant (the pre-exponential term in the Arrhenius equation), T_0 is the initial starting temperature in the rising temperature experiment, and β is the heating rate.

The combination of these three equations carries certain implications. The Arrhenius equation is almost invariably assumed to hold over the entire temperature range. The assumption may not hold and the most common deviation is the occurrence of two or more linear plots when plotting log k against $1/T$. It is held that this would apply when there is a discontinuous alteration in "reaction site distribution" when a common compensation plot of log A against E (the activation energy) should result. Another matter which is essential to the calculation is the correct choice of the

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specific reaction rate incorporated in the Arrhenius expression. It is concluded that E and A values for solid-state decompositions are environmentally dependent and that values calculated from rising temperature experiments should not necessarily agree with those obtained from the more traditional isothermal experiments.

INTRODUCTION

The theoretical treatment of the kinetics of decomposition under rising temperature conditions rests largely on a combination of equations one of which is the Arrhenius equation. The justification for the use of this equation in all solid-state reactions without reservation is difficult but if this is accepted then the establishment of kinetic parameters from the rising temperature technique is theoretically possible.

One thus has to combine various relationships. There is the differential form of the kinetic law,

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

where α is the fraction decomposed at time t, and $f(\alpha)$ is the appropriate function of α, k is a constant which is temperature-dependent. The temperature-dependence of the constant k is usually described by the Arrhenius equation,

$$k = Ae^{-E/RT} \tag{2}$$

where k is the specific reaction rate constant, A is the pre-exponential factor, E is the activation energy, T is the temperature in degrees Kelvin and R is the gas constant. The temperature programme imposed on the system can be represented by,

$$T = T_0 + \beta t \tag{3}$$

where T_0 is the initial temperature, and a linear heating rate has been assumed with a heating rate of β. Combination of these three equations will enable the kinetic parameters to be established.

In past papers, the problems attendant on experimental aspects have been presented especially the temperature-dependent buoyancy effects[1-3]. In this paper, problems raised in interpreting the kinetic parameters by the combination of the above three equations are described. The algebra involved in the combination of these equations especially the methods of integrating the data have been reviewed by Šesták et al.[4]. Here, the use of the Arrhenius equation is investigated, particularly the use of the correct specific reaction rate term, and the interpretation of the meaning of the Arrhenius parameters discussed.

THE DEPENDENCE OF THE RATE OF DECOMPOSITION WITH TEMPERATURE

The generally recognised phenomena is that the rate of reaction is faster at higher temperatures than at lower temperatures. This generalization is not specific enough to be useful and is not necessarily true. Most thermogravimetric plots show a rate of reaction which increases initially as the temperature is raised but decreases towards the latter stages of decomposition at the higher temperatures. One therefore chooses a reaction rate constant so that solid-state decompositions can be represented in the form given in eqn (1) and the temperature dependence of the constant k then determined.

Assuming that k is defined correctly (see later) then one cannot necessarily assume the correctness of the Arrhenius expression, i.e.,

$$\log k = a - \frac{b}{T} \tag{4}$$

(or usually in the form given in eqn (2)) where a and b are constants. An alternative representation would be another series expression of the form used in thermodynamics to show the variation of the heat of reaction with temperature. To establish this latter idea on a formal basis would give more substance to some of the integral methods of evaluating kinetics from rising temperature methods[5-10].

However, the Arrhenius expression is usually assumed and the point must be made that, although many systems show a linear relationship between $\log k$ and $1/T$, there are two very common deviations from this relationship found in many solid-state decompositions. The first deviation from normal behaviour in these plots is the existence of two or more linear regions instead of a single linear plot. Another behaviour often found is that the plot of $\log k$ against $1/T$ is a continuous curve. An example of the first group is the oxidation of carbon samples containing metal oxide catalysts[11, 12]. An example of the last group that may be quoted is the thermal decomposition of cadmium carbonate doped with various ions[13].

There are other points to notice about the Arrhenius equation. The first is that the units of energy (KJ mol^{-1}) for E only arise because the slope of the line in the Arrhenius plot is divided by the gas constant R. The temperature coefficient for the plot of $\ln k$ against $1/T$ is simply reciprocal degrees. The problem also arises in solid-state chemistry that the term "mole" refers to a quantity which is not immediately apparent.

Redfern[14] has defined the activation energy as the average excess energy a reactant molecule must possess in order to react. Anderson[15] however prefers to regard both the pre-exponential term A and the activation energy as mathematical parameters describing the reaction on an empirical basis.

It must be noted that, by the theory of absolute reaction rates, the constant k in the Arrhenius equation is given by;

$$k = \frac{RT}{Nk} K^{*} \tag{5}$$

where h is Planck's constant and K^{*} is the equilibrium constant for the activated complex. Then as for other equilibrium constants;

$$\Delta G^{\ddagger} = -RT \ln K^{\ddagger} \tag{6}$$

and

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \tag{7}$$

The terms in the Arrhenius equation may now be identified, i.e., E with $\Delta H^{\ddagger}$ and A can be written as

$$\frac{RT}{Nh} e^{\Delta S^{\ddagger}/R} \text{ where } \Delta S^{\ddagger}$$

is the entropy change associated with the change to the activated complex. Alternatively A can be written in terms of the partition functions; i.e.,

$$A = \frac{RT}{Nh} \cdot \frac{Q^{\ddagger}}{Q} \tag{8}$$

where $Q^{\ddagger}$ is the complete partition function for the activated complex excluding that for the reaction coordinate and Q is the complete partition function for the reactant. Both forms of the equation have been utilised in solid-state reactions[16, 17].

THE TEMPERATURE-DEPENDENT FUNCTION k

In solid-state reactions the temperature-dependent function k (eqn (1)) has not necessarily the same meaning as in homogeneous reaction kinetics. In the latter case, the specific reaction rate k used in the Arrhenius equation is the reaction rate for unit concentration. Concentration terms are not present in solid-state decompositions which are governed by the movement of a reaction interface. The definition of the specific reaction rate in homogeneous processes is therefore represented by;

$$\frac{dC}{dt} = kf(C) \tag{9}$$

where C is the concentration, such that when $C = 1$, then;

$$\frac{dC}{dt} = k \tag{10}$$

The analogous condition for solid-state decompositions is that;

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

such that when $\alpha = 0$, then

$$\frac{d\alpha}{dt} = k \tag{11}$$

It will be shown later that not all solid-state kinetic equations obey this simple concept and there may be some doubt as to the use of the constants in Arrhenius type equations. It is also a common practice to use the constant appearing in integrated forms of the rate expressions rather than that appearing in the differential form which is strictly required for the Arrhenius equation.

Thus if the integrated expression is taken as;

$$k_I t = f_I(\alpha) \tag{12}$$

then

$$\frac{d\alpha}{dt} = k_D f_D(\alpha) \tag{13}$$

(the subscripts indicating the integral (I) nature of the equation in which the constant or the function appears and similarly for the differential (*D*) expression) and

$$\left[\frac{k_I}{n_I}\right]^{1/n_2} = k_D \tag{14}$$

or

$$k_I = n_I (k_D)^{n_2} \tag{15}$$

The constants in the integral equations and the corresponding differential equations are only identical in certain cases. It is the constant in the differential equation which must be used in the Arrhenius equation. If the relationship between the two forms is:

$$k_I = n_I k_D \tag{16}$$

then the use of the integral constant will produce the correct analytical value for E but an incorrect value for A. If the relationship is;

$$k_I = (k_D)^{n_2} \tag{17}$$

then the value of both E and A will be affected. The difference this makes can be seen by taking a specific example, viz.,

$$kt^n = \alpha \tag{18}$$

$$\frac{d\alpha}{dt} = nk^{1/n}\alpha^{n-1/n} \tag{19}$$

and

$$nk^{1/n} = A\,e^{-E/RT} \tag{20}$$

when

$$k = \left(\frac{1}{n}\right)^n A^n\,e^{-nE/RT} \tag{21}$$

TABLE 1

KINETIC EXPRESSIONS FOR SOLID-STATE DECOMPOSITIONS WHICH PRODUCE "ORDER" TYPE EQUATIONS IN THE DIFFERENTIAL FORM

Integral form	*Differential form*	*n*
$Kt = -\ln(1-\alpha)$	$\frac{d\alpha}{dt} = K(1-\alpha)$	1
$Kt = (1-\alpha)^{-1}$	$\frac{d\alpha}{dt} = K(1-\alpha)^2$	2
$Kt = 1-(1-\alpha)^{\frac{2}{3}}$	$\frac{d\alpha}{dt} = \frac{3}{2}K(1-\alpha)^{\frac{1}{3}}$	$\frac{1}{3}$
$Kt = 1-(1-\alpha)^{\frac{1}{2}}$	$\frac{d\alpha}{dt} = 2K(1-\alpha)^{\frac{1}{2}}$	$\frac{1}{2}$
$Kt = 1-(1-\alpha)^{\frac{1}{3}}$	$\frac{d\alpha}{dt} = 3K(1-\alpha)^{\frac{2}{3}}$	$\frac{2}{3}$

Notes

1. The traditional 1st and 2nd order expressions are included because experience indicates their occurrence in polymer degradation reactions.
2. The form of the 1st order expression is found in many solid-state reactions with a particular type of mechanism involved.
3. To a *first approximation* all deceleratory processes may be represented by the 1st order decay equation.

and the error involved by putting k directly into the Arrhenius equation is at once apparent.

The argument can now be extended to cover the actual "form" of the kinetic expressions. There are of course a large number of kinetic expressions which are based on models reflecting various combinations of nuclei appearance, reaction interface change, and diffusion conditions. Some of these have a differential form which allows the temperature-dependent constant k to meet the specific limitations set out above which allow it to be regarded as a formal specific reaction rate constant (see eqns (1) and (11)) but others do not meet this condition. The occurrence of "order" expressions in solid-state decompositions is purely coincidence and has no special significance. Those kinetic expressions which do show an order equation in the differential form do however meet the formal requirement just mentioned that when

$$\alpha \to 0, \frac{d\alpha}{dt} = k,$$

and these are illustrated in Table 1.

Three general types of differential equation describing the rate of decomposition arise in solid-state chemistry. These are:

$$\frac{d\alpha}{dt} = k\,\alpha^m \tag{22}$$

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{23}$$

and

$$\frac{d\alpha}{dt} = k(-\ln(1-\alpha))^p \tag{24}$$

These may be combined into one general expression[18],

$$\frac{d\alpha}{dt} = k\alpha^m(1-\alpha)^n(-\ln(1-\alpha))^p \tag{25}$$

The form corresponding to eqn (23) has been shown to meet the formal requirement for use in the Arrhenius equation but eqns (22) and (24) do not, and neither does eqn (25). However, the k term in these equations although not fulfilling the requirements for a true specific rate constant is temperature-dependent. It is still advisable however to use the constant appearing in the differential form of the equation and to test for obedience to an Arrhenius type expression. Equations not showing an order dependence are shown in Table 2.

Since there are two parameters in the Arrhenius equation, both E and A should be reported and even if the calculation is assumed to be empirical both are necessary to enable the kinetics to be properly described.

Possibly the easiest treatment to understand is that of Shannon. He uses an equation based on the earlier Polanyi-Wigner treatment[19]. Shannons treatment[17] is to use the activated complex theory of reaction rate kinetics when,

$$k_r = \frac{RT}{Nh}\cdot\frac{Q^*}{Q}\exp\left(\frac{-E}{RT}\right) = A\exp\left(\frac{-E}{RT}\right) \tag{26}$$

where k_r is a nominal first order type reaction rate constant (all the terms have already been defined), which he rearranges as;

$$k_r = \frac{RT}{Nh}\,a\exp\left(\frac{-E}{RT}\right) \tag{27}$$

where,

$$a = A\Big/\frac{RT}{Nh} = \frac{Q^*}{Q} = \exp\left(\frac{\Delta S^*}{R}\right) \tag{28}$$

It is then possible to take the experimental kinetic data and use the above equation to calculate "a". The evidence produced by Shannon shows that, in the cases quoted, "a" covers a wide spectrum of values which he finds convenient to classify as;

(1) Reactions with "a" values less than unity

TABLE 2

DIFFERENTIAL FORMS FOR SOLID-STATE KINETIC EQUATIONS NOT SHOWING TRADITIONAL ORDER FORM

Integral form	*Differential form*	*m*	*n*	*p*
		for $\frac{d\alpha}{dt} = K\alpha^m(1-\alpha)^n(-\ln(1-\alpha)^p$		
$Kt = \alpha^2$	$\frac{d\alpha}{dt} = \frac{1}{2} K\alpha^{-1}$	-1	0	0
$Kt = \ln\alpha$	$\frac{d\alpha}{dt} = K\alpha$	1	0	0
$Kt^2 = \alpha$	$\frac{d\alpha}{dt} = 2K^{\frac{1}{2}}\alpha^{\frac{1}{2}}$	$\frac{1}{2}$	0	0
$Kt^3 = \alpha$	$\frac{d\alpha}{dt} = 3K^{\frac{1}{3}}\alpha^{\frac{2}{3}}$	$\frac{2}{3}$	0	0
$Kt^4 = \alpha$	$\frac{d\alpha}{dt} = 4K^{\frac{1}{4}}\alpha^{\frac{3}{4}}$	$\frac{3}{4}$	0	0
$Kt = -\ln(1-\alpha)^{\frac{1}{2}}$	$\frac{d\alpha}{dt} = 2K(-\ln(1-\alpha)^{\frac{1}{2}}(1-\alpha)$	0	1	$\frac{1}{2}$
$Kt = [-\ln(1-\alpha)]^{\frac{1}{3}}$	$\frac{d\alpha}{dt} = 3K(-\ln(1-\alpha)^{\frac{2}{3}}(1-\alpha)$	0	1	$\frac{2}{3}$
$Kt = (1-\alpha)\ln(1-\alpha)$	$\frac{d\alpha}{dt} = K(-\ln(1-\alpha)^{-1}$	0	0	-1

Note

There are alternative expressions for
$Kt = -\ln(1-\alpha)1/n$, namely $d\alpha/dt = K\alpha^m(1-\alpha)^n$

Table 2 *(cont.)*

n'	m	n
2	$^1/_2$	0.774
3	$^2/_3$	0.700
4	$^3/_4$	0.664
5	$^4/_5$	0.642
.	.	.
.	.	.
.	.	.
α	1	0.556

(2) Reactions with "a" values approximately unity

(3) Reactions with "a" values more than one.

The calculation of "a" can therefore be achieved from the kinetic data as indicated above, but by using the idea that the reaction is governed by a decomposition process at the reaction interface then the assumption of various models for the activated complex allows "a" to be calculated from spectroscopic data. In carbonate decompositions "a_k" is less than unity in most cases (the subscript k indicating that its calculation is based on kinetic experiments whilst a subscript s indicates that the calculation owes its origin to spectroscopic data). The spectroscopic estimate of Q^* can be made on the assumption that the cation is involved only in minor changes of position with no change in energy whilst the carbonate ions are those involved in major alterations in the transition to the activated complex. Shannon concludes that Q^* is more similar to Q_{reactant} in exothermic reactions and to Q_{product} in endothermic reactions. Carbonate decompositions are always endothermic, so it follows that in this case Q^* is more like Q_{product}. Shannon was able to show that there was reasonable agreement between values of "a" calculated from a basis of spectroscopy and those calculated from the kinetic data for calcite and magnesium carbonate. The theoretical treatment at present put forward however makes the result independent of the position of the reactant species in the reactant interface. Obviously an "edge" position or a "corner" position would be a more active site with a different energy content than a more protected position in the centre of a reaction interface. Incorporation of this idea into the theory would lead to the Q^* value possessing different values according to the position of the activated complex with respect to the geometry of the reaction interface.

THE COMPENSATION EFFECT

Inspection of the data available especially in carbonate decompositions shows that the same chemical material may show various values of E and A dependent upon the conditions of the material and the nature of the experiment. This has caused many arguments regarding the true or most dependable value of E and A which should be selected from those available in the literature.

However the compensation effect covers the phenomena whereby a change in the activation energy is reflected by a compensating change in the pre-exponential term and allows the above position to be rationalised. It is essentially a series of related experiments in which there is a linear relationship[20] between $T\Delta S^*$ and ΔH^*. It has been applied to both homogeneous and heterogeneous reactions and the data calculated from the use of the Arrhenius equation. The concept that a linear relationship exists between log A and E is also called the compensation effect. From these two statements of the compensation effect, it follows that:

$$T\Delta S^* = RT\left(\log A - \log \frac{RT}{Nh}\right) \tag{29}$$

and the difference between $T\Delta S^{\ddagger}$ and log A can be calculated. At constant temperature, it is seen that the log A term differs by a constant term and a factor which would justify the alternative representation of the compensation effect. It follows however that to preserve a constant value of A, any change with temperature in log RT/Nh must be compensated by a change in $\Delta S^{\ddagger}/R$ and the product $T \exp(\Delta S^{\ddagger})$ must be constant. It can however be shown that A is not strictly constant and is a function of temperature but that the change in A is very small and to within the usual limits imposed by plotting log k against $1/T$ may be regarded as a constant term.

The compensation effect is merely an experimental observation and many reports have been published on its significance[21-24]. Garn[21] suggests that obedience of data to the compensation equation may be a consequence of the operation of a common dominant rate-controlling factor. Zsako[23] stresses that the existence of the linear relationship is indicative of a more general characteristic. However, the experimental linear relationship recorded whether of fundamental significance or not is very valuable in describing reacting systems and specifying reactor designs. It would seem that to avoid suspicion regarding the values of A and E used in the calculations the $\mathrm{d}\alpha/\mathrm{d}t$ term must be related with the rate of advance of the reaction interface and this is implicit in the use of the Polanyi-Wigner equation and its subsequent development by Shannon and Cordes. The compensation effect takes the form;

$$\log A = mE + C \tag{30}$$

where m is the slope and C the intercept. Cremer[25] and Constable[26] suggest that the compensation effect will be shown in a heterogeneous model where the reaction will occur at different reaction sites. They allow for a "reaction site" distribution by the use of an equation of the form;

$$\text{Rate} = k \sum_i n_i \exp\left(\frac{-E_i}{RT}\right) \tag{31}$$

Each type of reaction site is characterised by its own activation energy. Such a distribution can be imagined in solid-state kinetics where sites on a "corner" would obviously give rise to different activation energies to sites on "edges" or in the "faces" of the reaction interface. It is the combination of individual Arrhenius equations applied to each of these sites together with a "weighting" due to site distribution which produces an overall value found for A and E in each experiment and which upon comparison of experiments in which the site distribution varies produces the observed compensation effect. The matter is outlined in the papers by Cremer[25], Constable[26], Heuchamps and Duval[27] and Sosnovsky[28]. This question of the distribution of sites of varying energy arises again when considering kinetic parameters calculated from rising temperature experiments.

RISING TEMPERATURE TECHNIQUES FOR CALCULATING KINETIC PARAMETERS

The detailed treatments for rising temperature methods of calculating kinetic parameters have already been reviewed[4], but the matter is raised here with regard to the values obtained for the Arrhenius parameters.

The three basic equations have been set out at the beginning (eqns (1), (2) and (3)). Combination of eqns (1) and (3) gives;

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{k\,\mathrm{f}(\alpha)}{\beta} \tag{32}$$

whence,

$$k = \left[\frac{\frac{\mathrm{d}\alpha}{\mathrm{d}T}\cdot\beta}{\mathrm{f}(\alpha)}\right] \tag{33}$$

Such a combination would allow a plot or table to be constructed of k against T. Most investigators however proceed by incorporating the Arrhenius equation to give;

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \left(\frac{A}{\beta}\right)\cdot\mathrm{f}(\alpha)\cdot\exp\cdot\left(\frac{-E}{RT}\right) \tag{34}$$

which can be rearranged to give;

$$\frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \left(\frac{A}{\beta}\right)\cdot\exp\cdot\left(\frac{-E}{RT}\right)\cdot\mathrm{d}T \tag{35}$$

or

$$\log\left[\frac{\frac{\mathrm{d}\alpha}{\mathrm{d}T}}{\mathrm{f}(\alpha)}\right] = \log\left(\frac{A}{\beta}\right) - \frac{E}{RT} \tag{36}$$

when a plot of log

$$\left[\frac{\frac{\mathrm{d}\alpha}{\mathrm{d}T}}{\mathrm{f}(\alpha)}\right]$$

against $1/T$ gives A and E. However this is not strictly an Arrhenius plot, but a slight rearrangement gives;

$$\log\left[\frac{\frac{\mathrm{d}\alpha}{\mathrm{d}T}}{\mathrm{f}(\alpha)}\cdot\beta\right] = \log k = \log A - \frac{E}{RT} \tag{37}$$

This equation is directly analogous to the Arrhenius equation and so plots of log k against $1/T$ can be made and a direct comparison attempted with Arrhenius plots established from a series of isothermal experiments.

Here we concern ourselves with the decomposition of carbonates as an example. Detailed publications on various carbonate systems will be published. However, the

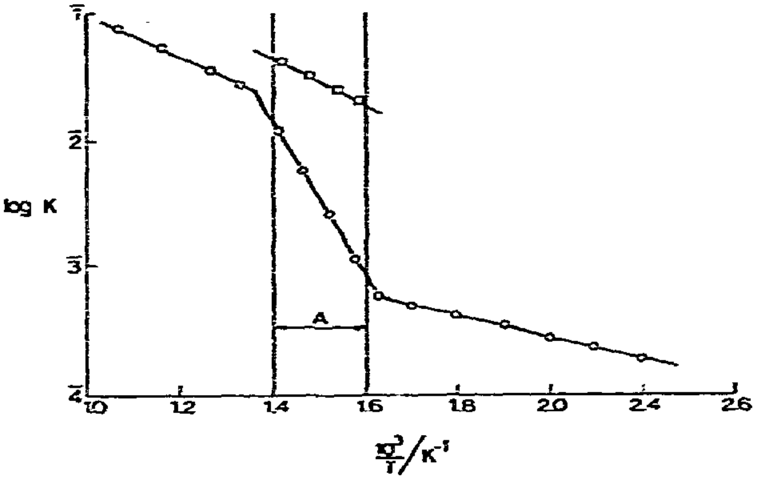

Fig. 1. Arrhenius plots for carbonate decompositions. Schematic representation of data for isothermal and rising temperature experiments. —□—□—, Isothermal experiments—Range A; —○—○—, rising temperature experiments. Ordinate: log k — log of specific reaction rate constant; abscissae: $(10^3/T)/k^{-1}$.

results of these data are schematically portrayed in Fig. 1. The data are calculated as a series of Arrhenius plots. The rising temperature experiments often produce two or more linear regions over a much wider temperature range than the isothermal series of experiments. All these linear regions each produce characteristic values of E and A, which all lie on a common compensation plot.

There are certain points which need clarification. The first point is that an appropriate choice must be made of f(α). In general, most carbonates and many endothermic oxysalt systems (i.e., in which the decomposition stage is endothermic) follow a deceleratory mechanism which results in the calculation of a specific reaction rate constant which does not differ significantly to that calculated by making the assumption that the process is first order. Provided therefore that the process is deceleratory no great error will be involved by proceeding on this assumption but this can be checked by a single isothermal experiment.

It has also become customary to interpret non-linearity in the appropriate plot for the rising temperature experiment necessary to calculate E and A as being due to the incorrect choice of the kinetic expression and hence f(α). Non-linear and two-line Arrhenius plots however also arise from isothermal data[11-13]. The kinetic data leading to two or three linear regions in the Arrhenius plot for the rising temperature plots (Fig. 1) in this instance therefore arise from a change in the conditions of the experiment and are related to the Arrhenius parameters themselves. It is also clearly seen that the rising temperature E and A values do not agree with the isothermal experiments, but it must be stressed do lie on a common compensation plot. The most logical explanation would appear to be that a particular distribution of sites is involved in the isothermal experiments and another distribution of sites is initially operative in the rising temperature experiments. These site distributions alter discontinuously as one goes from one linear Arrhenius region to another. This has been established for carbon oxidations[11, 12] and also in some oxides[29]. It would seem to be operative in oxysalt systems and particularly for carbonates. It is probable that the prime factor in altering the distribution of sites of varying energy content, is the sintering phenomena whereby particles are only fritted together at low temperatures, are subject to surface diffusion in a higher temperature range and are subject to bulk diffusion in the highest temperature range. These temperature ranges can be established quite firmly in terms of the Tammann temperature[30]. It is also possible that the effect of water vapour being evolved with the carbon dioxide in certain carbonates would also alter the sintering phenomena (usually to accelerate the process) and cause a change in the distribution of sites of varying energy content. The acceleratory effect of water vapour on zinc oxide sintering has been firmly established[29].

From this, it can be seen that we should not necessarily expect rising temperature experiments to produce E and A values which agree with the same parameters established from isothermal experiments. They may be regarded as the operative parameters under the conditions of investigation. Further, we should not expect a single A and E value to be established from a single TG experiment in all cases. It is also instructive to plot the data from rising temperature data as an Arrhenius plot as this facilitates comparison and interpretation. Finally, it is possible that the connection between the various A and E values collected on a particular series of compounds may be established by a compensation plot indicative of changes in the distribution of sites of varying energy.

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