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Activation energy determination for linear heating experiments: deviations due to neglecting the low temperature end of the temperature integral

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Abstract Model-free isoconversion methods which use approximations of the temperature integral are generally reliable methods for the calculation of activation energies of thermally activated reactions studied during linear heating. These methods generally neglect the temperature integral at the start of the linear heating, $I(T_o)$. An analytical equation is derived which describes the deviations introduced by this assumption. It is shown that for most reactions encountered this assumption does not have a significant influence on the accuracy of the method. However in cases where T_o is within about 50 to 70 K of the reaction stage to be investigated and activation energies are relatively low, significant deviations are introduced. It is shown that some of the published thermal analysis work on activation energy analysis of reactions occurring at relatively low temperatures is affected by these deviations. Examples are specific cases of dehydration reactions, cure reactions and cluster formation in Al alloys.

Introduction

A general objective of the analysis and prediction of thermally activated reactions is the derivation of a complete description of the progress of a reaction that is valid for any thermal treatment, be it isothermal, by linear heating or any other non-isothermal treatment [1–3]. As any given reaction might progress through a range of mechanisms and intermediate stages, all of which can have a different temperature-dependency, this aim can be difficult to achieve. Hence, many researchers make the simplifying assumption that the transformation rate during a reaction is the product of two functions, one depending solely on the temperature, T, and the other depending solely on the fraction transformed, α [4, 5]:

$$\frac{d\alpha}{dt} = f(\alpha)k(T) \tag{1}$$

The temperature dependent function is generally assumed to follow an Arrhenius type dependency [6, 7].

$$k = k_o \exp\left(-\frac{E}{RT}\right) \tag{2}$$

Thus, to describe the progress of the reaction at all temperatures and for all temperature-time programmes within these assumptions, the function $f(\alpha)$, and the constants k_o and E need to be determined. For non-isothermal experiments, the reaction rate at all times depends on both $f(\alpha)$ and $k(T)$, and the determination of $f(\alpha)$, k_o and E (the so-called kinetic triplet) is an interlinked problem (see e.g. [8]). A deviation in the determination of any of the three will cause a deviation in the other parameters of the triplet. Reliable analysis methods generally start by deriving the activation energy using a model-free analysis method [9], i.e. a method which makes no presumptions of $f(\alpha)$.

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It has been shown that for analysis linear heating experiment (heating at constant rate), highly accurate and reliable activation energy analysis methods can be obtained by applying accurate approximations of the temperature integral [10]. This derivation can be formulated as follows. Equation (2) is inserted in Eq. (1) and this is integrated by separation of variables [10]:

$$\int_{T_o}^{T_f} \frac{d\alpha}{f(\alpha)} = \frac{k_o}{\beta} \int_{T_o}^{T_f} \exp\left(-\frac{E}{RT}\right) dT = \frac{k_o}{\beta}\left[\int_0^{T_f} \exp\left(-\frac{E}{RT}\right) dT - \int_0^{T_o} \exp\left(-\frac{E}{RT}\right) dT\right] \tag{3}$$

where T_f is the temperature at an equivalent (fixed) state of transformation, T_o is the start temperature of the linear heating experiment, and β is the heating rate. The integrals on the right hand side are generally termed temperature integrals (or 'Arrhenius integral'). We can write Eq. 3 as:

$$\int_{T_o}^{T_f} \frac{d\alpha}{f(\alpha)} = \frac{k_o}{\beta}[I(T_f) - I(T_o)] \tag{4}$$

where $I(T_o)$, $I(T_f)$ are the temperature integrals on the right hand side of Eq. 3.

The derivation proceeds by noting that of the last two terms, one is much smaller than the other

$$\int_0^{T_o} \exp\left(-\frac{E}{RT}\right) dT \ll \int_0^{T_f} \exp\left(-\frac{E}{RT}\right) dT \tag{5}$$

or $I(T_o) \ll I(T_f)$. And hence $I(T_o)$, the smaller term in Eq. 4, is neglected. Thus it follows that:

$$\int_{T_o}^{T_f} \frac{d\alpha}{f(\alpha)} \cong \frac{k_o}{\beta}\left[\int_0^{T_f} \exp\left(-\frac{E}{RT}\right) dT\right] \tag{6}$$

Through applying a suitable approximation for the temperature integral on the right of the latter equation a range of well-known and lesser known isoconversion methods for activation energy analysis can be derived [10]. These methods include the Kissinger method [11], the Kissinger–Akahira–Sunose (KAS) method [12, 13] (also termed the generalised Kissinger method), the Flynn–Wall–Ozawa (FWO) method [14, 15], a method described by Vyazovkin and co-workers [16, 17] and 3 highly accurate methods developed by the present author [10, 18, 19]. All of these methods involve the plotting of $1/T_f$ vs. a logarithmic function which depends on the heating rate and often the temperature and all of these methods neglect the last integral term in Eq. 3 ($I(T_o)$ in Eq. 4). The general equation is:

$$\ln\frac{\beta}{T_f^{\kappa}} = -A\frac{E}{RT_f} + C \tag{7}$$

where κ is a constant depending on the approximation of the temperature integral employed [1], and A and C are constants. For the above mentioned methods κ equals 0 (FWO method), 2 (KAS method) and 1.9 to 1.95 for the methods by Starink. Whilst all of these works [9–18] (and a vast range of other works) imply that the approximation involved in neglecting $I(T_o)$ is appropriate, it appears that the actual influence of this approximation on the analysed activation energy values has never been quantitatively determined. The aim of the present short paper is to investigate the accuracy of this approximation.

Analysis

In derivation of isoconversion methods it is generally assumed that $I(T_o) \ll I(T_f)$ and $I(T_o)$ is subsequently neglected. However, it can be shown that in a limited number of cases this is not justified, and in this section we will derive an expression for the deviations in measured E introduced as a consequence of neglecting $I(T_o)$.

We will specifically analyse the case where two experiments at two different heating rates, β_1, β_2, are conducted. If a larger range of experiments are performed the analysis should be valid in good approximations provided $\beta_1\beta_2$, are taken as the upper and lower heating rate considered. From Eq. 4 follows that if a certain fixed state of the reaction is attained at the two different heating rates:

$$\frac{k_o}{\beta_1}[I(T_{f1}) - I(T_o)] = \frac{k_o}{\beta_2}[I(T_{f2}) - I(T_o)] \tag{8}$$

Where T_{f1} is the temperature at which the fixed state is reached at heating rate $\beta_1$and T_{f2} is the temperature at which the same fixed state is reached at heating rate β_2. From the latter equation follows:

$$\frac{\beta_2}{\beta_1} = \frac{I(T_{f2}) - I(T_o)}{I(T_{f1}) - I(T_o)} \tag{9}$$

and

$$\frac{\beta_2}{\beta_1} = \frac{I(T_{f2})}{I(T_{f1})} \frac{1 - I(T_o)/I(T_{f2})}{1 - I(T_o)/I(T_{f1})} \tag{10}$$

For further evaluation of the temperature integrals, we will employ Doyle's approximation:

$$\int_0^T \exp\left(-\frac{E}{RT}\right) dT \approx \frac{E}{R}\left(0.00484 e^{-1.0516\frac{E}{RT}}\right) \tag{11}$$

(The accuracy of the latter equation has limitations [7, 10]. However, its relative simplicity is here exploited to obtain mathematically tractable solutions. Small inaccuracies introduced are in this case considered to be acceptable.) From the latter equation, we can obtain an expression for the ratio of two temperature integrals:

$$\ln\frac{I(T_{f2})}{I(T_{f1})} \approx 1.0516\frac{E}{R} \times \left[\frac{1}{T_{f2}} - \frac{1}{T_{f1}}\right] \tag{12}$$

combining the latter equation with Eq. 10 provides:

$$\ln\frac{\beta_2}{\beta_1} - \ln\frac{1 - I(T_o)/I(T_{f2})}{1 - I(T_o)/I(T_{f1})} = \ln\frac{I(T_{f2})}{I(T_{f1})} \cong 1.0516\frac{E}{R} \times \left[\frac{1}{T_{f2}} - \frac{1}{T_{f1}}\right] \tag{13}$$

the aim of this paper is to investigate the consequences of neglecting $I(T_o)$, using $I(T_o) \ll I(T_{f1}), I(T_{f2})$. If we were to do this the latter equation would simplify to:

$$\ln\frac{\beta_2}{\beta_1} = \ln\frac{I(T_{f2})}{I(T_{f1})} \cong 1.0516\frac{E_u}{R} \times \left[\frac{1}{T_{f2}} - \frac{1}{T_{f1}}\right] \tag{14}$$

where E_u stands for the activation energy obtained from an analysis in which $I(T_o)$ is neglected. (The latter equation is essentially the Flynn–Wall–Ozawa method [14, 15].) Taking the difference of the latter two equations provides:

$$\ln\frac{1 - I(T_o)/I(T_{f2})}{1 - I(T_o)/I(T_{f1})} \cong 1.0516\frac{\Delta E}{R} \times \left[\frac{1}{T_{f2}} - \frac{1}{T_{f1}}\right] \tag{15}$$

where $\Delta E = E_u - E$, the error in E introduced by neglecting $I(T_o)$. As long as $I(T_o)$ is small compared to $I(T_{f1})$ and $I(T_{f2})$ it is justified to make a first order approximation:

$$\begin{aligned} &\ln\frac{1 - I(T_o)/I(T_{f2})}{1 - I(T_o)/I(T_{f1})} \\ &\cong \ln\left[1 + \frac{I(T_o)}{I(T_{f1})} - \frac{I(T_o)}{I(T_{f2})}\right] \cong \frac{I(T_o)}{I(T_{f1})} - \frac{I(T_o)}{I(T_{f2})} \\ &\cong \exp\left(-1.0516\frac{E}{R}\left[\frac{1}{T_{f2}} - \frac{1}{T_o}\right]\right) \\ &\quad - \exp\left(-1.0516\frac{E}{R}\left[\frac{1}{T_{f1}} - \frac{1}{T_o}\right]\right) \end{aligned} \tag{16}$$

where the last step of the above derivation is achieved by employing Eq. 12.

Thus we obtain:

$$\frac{\Delta E}{R} \cong \frac{\exp\left(-1.0516\frac{E}{R}\left[\frac{1}{T_{f2}} - \frac{1}{T_o}\right]\right) - \exp\left(-1.0516\frac{E}{R}\left[\frac{1}{T_{f1}} - \frac{1}{T_o}\right]\right)}{1.0516\left(\frac{1}{T_{f2}} - \frac{1}{T_{f1}}\right)} \tag{17}$$

From the latter equation we can see that the deviation ΔE introduced by neglecting $I(T_o)$ can be calculated in a direct and straightforward equation. ΔE is a function of T_o, T_{f1}, T_{f2} and E, where T_{f1} and T_{f2} are a function of β_1 and β_2, respectively.

The temperature differential (T_{f2}–T_{f1}) depends on E, β_1 and β_2, and in practical cases (T_{f2}–T_{f1}) is between about 10 K and 50 K. Analysis of Eq. 17 will show that under these conditions E, T_o and the difference between T_{f1} and T_o are the dominant parameters determining ΔE. Thus, unless otherwise noted, we will generally set (T_{f2}–T_{f1})=30 K, which will limit the number of independent variables that need to be considered.

Experimental

Most of the data presented below is taken from recent literature, and in addition an Al–1.21at%Cu–1.19at%Mg–0.20%Mn alloy has been studied. Details on production route for this alloy are given in Ref. [20]. After solution treatment at 768 K, water quenching and stretching by 2.5%, the alloy was left at room temperature for a few months before further ageing at 423 K. Differential Scanning Calorimetry (DSC) experiments were conducted using a Perkin–Elmer Pyris 1 in nitrogen atmosphere at a constant heating rate of 10 K/min, using disc-shaped DSC samples with a thickness of about 0.9 mm and diameter 5 mm. All runs were corrected by subtracting the baseline of the

DSC, which was obtained from a run with an empty pan as reference. Further baseline correction procedures are outlined in Ref. [1].

Evaluation and application

General assessment of consequences of neglecting $I(T_o)$

The analysis presented above shows that neglecting $I(T_o)$ causes the activation energy measured by the isoconversion method to be increased. In evaluating the potential importance of this deviation we should consider that other sources of mathematic approximation error are typically in the order of 0.1 to 0.5%, for the more accurate methods [1, 10]. But more important sources of measurement error are sample variability and various sources of experimental noise, which combine to produce plots of $\ln\left(\beta/T_f^{\kappa}\right)$ vs $1T_f$ that do not have the predicted perfect straight-line correlation, resulting in an experimental error. These sources of error depend on many factors and can vary wildly, to produce potential errors typically from 0.2% to 5%. In this work we will consider 0.5% as a practical limit below which mathematical errors are mostly irrelevant, but it is noted that even larger mathematical errors can become irrelevant if sample variability and various sources of experimental noise combine to produce large errors.

Evaluation of Eq. 17 for literature reports of determinations of activation energies for linear heating data using an isoconversion method, reveals that $\Delta E/E$ caused by neglecting $I(T_o)$ is negligible for the vast majority reported studies. (About 500 papers were scanned and only about 1% reported on reactions with a combination of T_o, T_{f1}, T_{f2} and E that could introduce a possibly significant deviation.) For instance, for reactions with $E > 70$ kJ/mol and $T_{f1} > 375$ K, $\Delta E/E$ is smaller than 0.5% provided T_{f1}-$T_o > 65$ K, i.e. if the linear heating is started at least 65 K before the reaction stage to be studied, $\Delta E/E$ will be negligible under realistic experimental conditions. (Other factors such as measurement noise, sample variability and baseline variations, will generally combine to introduce more significant errors [1, 10].) And if $E > 100$ kJ/mol, T_{f1}–T_o needs to be larger than 50 K to achieve $\Delta E/E < 0.005$.

Elsewhere [10] it was shown that the approximation of the temperature integral $I(T_f)$ also causes a deviation in the activation energy. The latter deviation can be minimised by choosing an accurate approximation, which leads to one of the more accurate isoconversion methods, and deviations due to approximation of the temperature integral can be limited to less than 0.5%. From the present analysis combined with the analysis in Ref. [10] we can thus conclude that the recently derived variants of isoconversion methods [10] are highly accurate in nearly all experimental conditions. The examples discussed below should be considered as very small class of reactions where some caution should be exerted in applying isoconversion methods that use approximations of the temperature integral.

To evaluate Eq. 17 we will plot $\Delta E/E$ for a number of potentially relevant cases. In Fig. 1 $\Delta E/E$ is plotted for a reaction with T_{f1}=350 K and T_{f2}=380 K, with T_o varying around 300 K. This represents cases where the linear heating experiment is started around room temperature with a reaction occurring within 100 K of the start of the experiment. A start temperature

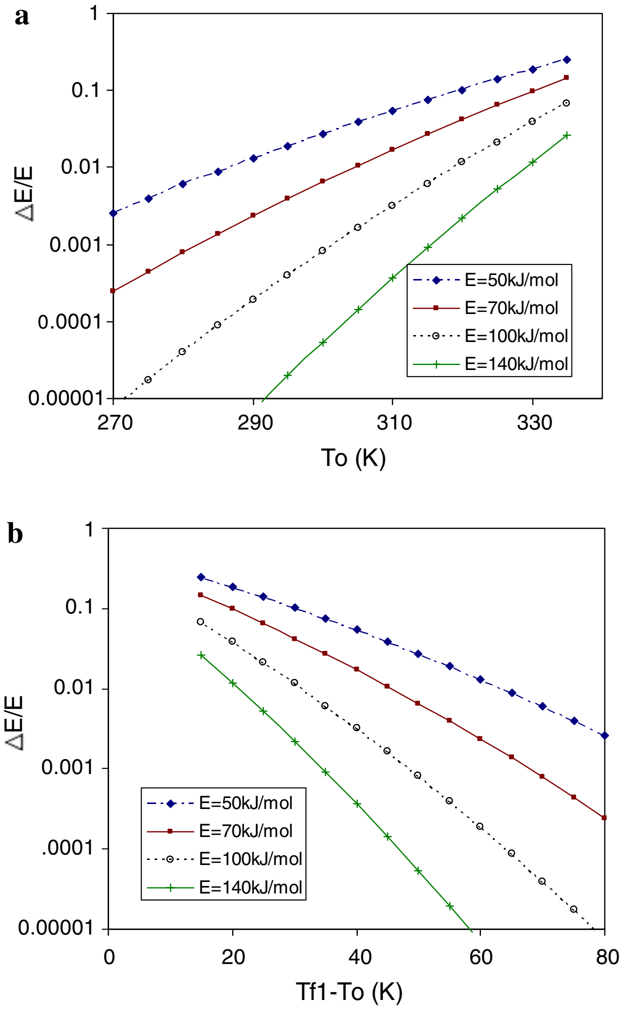

Fig. 1 The relative error in activation energy, $\Delta E/E$ vs. T_o (**a**) and vs. T_{f1}–T_o (**b**) for a reaction with T_{f1}=350 K and T_{f2}=380 K, as obtained from Eq. 17

between room temperature and 325 K is common practice in many types of studies. The relatively low reaction temperatures are commonly encountered for three types of reactions: (i) GP zone or cluster formation in supersaturated Al based alloys [21–25], where E is typically between about 50 and 80 kJ/mol; (ii) dehydration reactions [26, 27], where E can be substantially higher (mostly between 70 and 140 kJ/mol), and (iii) curing reactions, where E is mostly between 50 and 100 kJ/mol [28–30]. (We will consider these reactions in the next section.) Fig. 1 shows that $\Delta E/E$ increases with increasing T_o and with decreasing E. The same data is also plotted as a function of $T_{f1}-T_o$ which represents the temperature interval between the start of the linear heating experiment and the lowest temperature used for obtaining the activation energy (Fig. 1b). Figure 1b shows that $\Delta E/E$ decreases rapidly with increasing $T_{f1}-T_o$. This is a general feature for all values of T_o, T_{f1}, T_{f2} and E and shows that the error introduced by neglecting $I(T_o)$ can be minimised by ensuring that the start temperature of the linear heating experiment is well below that of the reaction to be analysed.

A typical value for the relative error in activation energy determination, $\Delta E/E$, which in most experimental conditions is just about negligible is about 0.5%. Figure 2 provides a plot of the maximum allowable value of $T_{f1}-T_o$ for which $\Delta E/E$=0.005, as a function of the activation energy. Data for various values of T_{f1} is plotted, and $T_{f2}-T_{f1}$=30 K. This plot can be used as a quick reference to identify whether errors in activation energy determination are significant. It should be stressed again, that from a (limited) search through the literature it is believed that for about 99% of the papers reporting activation energy analysis using isoconversion methods on linear heating data, these errors are insignificant.

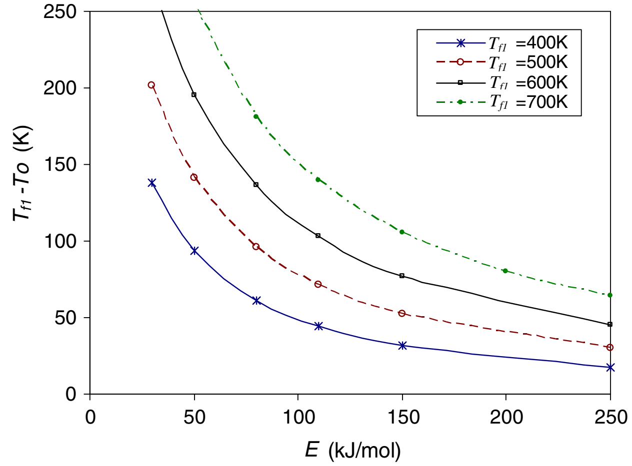

Fig. 2 The maximum allowable value of $T_{f1}-T_o$ for which the relative error in activation energy introduced by neglecting $I(T_o)$ is below 0.5%, as a function of the activation energy. Data for four values of T_{f1} is plotted, $T_{f2}-T_{f1}$=30 K

Low temperature reactions: cluster formation, dehydration reactions, cure reactions

In this section we will consider some of the published data on activation energy analysis of low temperature reactions involving cluster formation, dehydration and curing. The examples are selected from recent literature and aim to provide an overview of possible deviations in activation energy analyses which assumed $I(T_o)$ to be negligible.

We will first consider the DSC analysis of Cu–Mg co-cluster formation in a solution treated and quenched Al–1.9Cu–1.6Mg–0.2Mn (at.%) alloy [25]. The relevant parameters for this reaction (T_o=280 K, T_{f1}=340 K, T_{f2}=370 K, E=75 kJ/mol, see Ref. [25]) indicate a $\Delta E/E$ value of 0.13%, which is in practice negligible. However, it is interesting to note that if the DSC would have been started above room temperature, say 305 K, the relative error $\Delta E/E$ in the activation energy determination would increase to 2.1% and inaccuracies would start to become significant.

Dehydration reactions often have an activation energy that is higher than that of cluster formation, and this will limit the relative error $\Delta E/E$ in the activation energy determination (see Fig. 1 and 2). For instance, the dehydration reaction of hydrated Co(II) methanesulfonate studied by Su et al. [27] the parameters (T_o=310 K, T_{f1}=340 K, T_{f2}=370 K, $E\approx$125 kJ/mol) would provide $\Delta E/E$ value of 0.1%, which is generally negligible. On the other hand, the dehydration reaction in 1,10-Phenanthroline studied by Vechio et al. [27] the parameters (T_o=293 K, T_{f1}=305 K, T_{f2}=340 K, $E\approx$85 kJ/mol) would provide a $\Delta E/E$ value of about 7% for the early stage of the reaction. Thus, the activation energies quoted by Vechio et al. [27] would need to be reassessed in the light of the present findings.

Also in published analyses of cure reactions using linear heating, sometimes significant errors are introduced due to neglecting $I(T_o)$. Analysis shows that in the most severe cases published in Refs. [28–30] (most severe here means samples and analyses with lowest T_{f1} and E), $\Delta E/E$ values of 1.2% to 2.6% are encountered. But in a similar number of papers on analysis of cure reactions $\Delta E/E$ values are always below 1%.

Multi-stage reactions with reversion stage

In addition to the reactions where the start temperature of the linear heating experiment is just below the reaction to be studied, we may also consider cases where the effective T_o for a reaction is defined by prior reactions. This could be the case where during heating a sequence of reactions occurs starting with the formation of a phase or structure stable at low temperature, here termed δ', which is stable only below a certain temperature T_S, and which is followed by the formation of the stable phase or structure, here symbolised by δ. If the original unstable state at the start of the linear heating is α, and the three states are the only ones possible, then we could either see the sequence of reaction on heating (reaction A):

$$\alpha \rightarrow \delta' \rightarrow \delta$$

Or if on passing T_S δ' reverts to α (reaction B)

$$\alpha \rightarrow \delta' \rightarrow \alpha \rightarrow \delta$$

(Also, under fast heating rate condition one could see $\alpha \rightarrow \delta$)

In reaction B, any formation of δ' can only occur after δ' has dissolved, and hence we can think of T_S as the effective start temperature of the linear heating experiment analysing δ formation. Hence we can consider T_o to be given by T_S. There are many reactions in the domains of chemistry, physics and materials science that could be influenced by this, and hence influence the activation energy analysis. Again this can be analysed by Eq. 17, with T_S substituted for T_o. Here we will illustrate this by considering precipitation reactions in Al based alloys.

In Al–Mg based alloys, two main precipitate structures are formed on isothermal ageing below about 360 K and subsequent linear heating to about 310 °C, they are the low temperature $L1_2$ ordered precipitates generally indicated by β'' (other indications: δ', ordered GP zone) [31–33] and the β' phase, which forms at higher temperatures (typically $T > 450$ K) 34]. In Fig 2 we can observe the β'' dissolution reaction in room temperature aged samples; for samples aged very long times at room temperature this reaction is completed at about 110 °C, with the β' phase formation starting at about 220 °C. With an activation energy for β' formation of about 75 kJ/mol ‘[31], Eq. 17 indicates that $\Delta E/E$ is smaller than 0.3%, and hence neglecting of $I(T_o)$ could not have influenced the determination of the activation energy significantly.

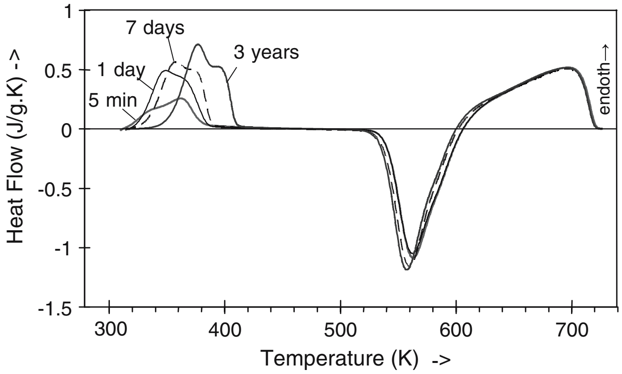

Fig. 3 DSC curves of ice water quenched Al–16Mg samples aged for 5 min, 24 h, 7 days and 3 years at room temperature after solutionising at 713 K. (From Ref [32])

In solution treated Al–Cu–Mg based alloys with compositions in the α+S phase field (at around 500 K), linear heating will cause the formation Cu–Mg co-clusters (also termed GPB zones) [35–37] and S phase [38–40]. If the alloys are aged at low temperature to cause the formation of Cu–Mg co-clusters, subsequent linear heating will cause the reversion of clusters prior to formation of S phase. Estimating T_o as the effective temperature for cluster dissolution (230 °C) and T_f at the peak of S phase formation, the relevant parameters for this reaction (T_o=500 K, T_{f1}=530 K, T_{f2}=545 K, $E\approx$130 kJ/mol, see Ref. [1, 22] and Figs. 3, 4) indicate a $\Delta E/E$ value of ~8%. Thus, the activation energies for S phase formation obtained by linear heating would need to be considered with caution as they may be influenced by neglecting $I(T_o)$.

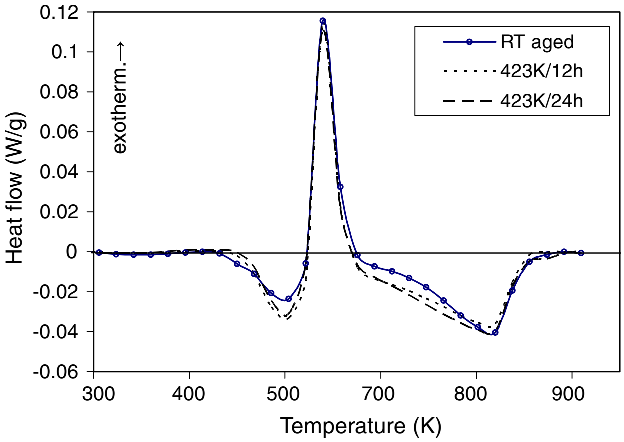

Fig. 4 DSC curves of samples of an Al–1.21at%Cu–1.19at%Mg–0.20at%Mn alloy solution treated, quenched, stretched by 2.5%, room temperature aged for several months and (for two of the samples) aged at 423 K

Conclusions

Model-free isoconversion methods which use approximations of the temperature integral are generally reliable methods for the calculation of activation energies, E, of thermally activated reactions studied during linear heating. These methods generally neglect the temperature integral at the start of the linear heating, $I(T_o)$. In the present work an analytical equation is derived which describes the deviations introduced by neglecting $I(T_o)$. The ΔE is a function of T_o, T_{f1}, T_{f2} and E, where the T_{f1}, T_{f2} are the temperatures of a fixed stage of the reaction achieved at heating rate β_1, β_2, respectively. Evaluation of this equation shows:

- For most reactions encountered, neglecting $I(T_o)$ does not have a significant influence on the accuracy of the isoconversion method. Plots are presented which show the deviations introduced as a function of T_o, T_{f1}, T_{f2} and E.
- In cases where T_o is within about 50 K to 70 K of the reaction stage to be investigated and activation energies are relatively low, significant deviations can be introduced.
- It is shown that some of the published thermal analysis work on activation energy analysis of reaction occurring at relatively low temperatures is affected. Examples are specific cases of dehydration reactions, cure reactions and cluster formation in Al alloys.

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