

On the applicability of isoconversion methods for obtaining the activation energy of reactions within a temperature-dependent equilibrium state

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When the equilibrium state of a reaction depends on the temperature, isoconversion methods for calculating activation energies are no longer valid. In these cases (apparent) activation energies obtained from isoconversion methods vary with temperature and fraction transformed, even if the true activation energy of the thermally activated process is constant. Expressions that describe the influences of the reaction parameters and the equilibrium state on the apparent activation energy are derived. A new method of extrapolating apparent activation energies is introduced that allows the determination of the true activation energy. Verification of this extrapolation method using precipitation in an Al–1 at % Si alloy shows a good correspondence between experiment and calculations. For the Al–1 at % Si alloy the apparent activation energy can deviate by 30% from the true activation energy of the reaction.

1. Introduction

Thermally activated transformation processes in the solid state can be investigated by isothermal experiments or by non-isothermal experiments at a constant heating rate. The latter is the case with, for instance, differential scanning calorimetry (DSC). For isothermal experiments, activation energies are obtained from the slope of a plot of $\ln(t_f)$ versus $1/T_i$, where t_f is the time to obtain a certain fraction transformed and T_i is the temperature. For non-isothermal analysis at a constant heating rate activation energies can be obtained using, for instance, the Kissinger method or the generalized Kissinger method [1–3]. (Kissinger [2] originally derived his method for the state at which the maximum reaction rate was achieved, i.e. the peak in a DSC signal. It was later shown that this method could be generalized to any fixed state of the reaction, see e.g. [1]. The latter will be referred to as the generalized Kissinger method). Both types of analysis are isoconversion methods: given two or more time–temperature programmes only the times to reach a certain fraction transformed are needed. These isoconversion methods are subject to a number of assumptions, most notably that the (metastable) equilibrium state obtained after completion of the transformation is independent of temperature. (The term “equilibrium state” used here refers to the compositions of the phases present in equilibrium and the relative proportions of the phases present in

equilibrium, i.e. “equilibrium state” refers to all the parameters involved in defining the equilibrium.) However, since in phase diagrams the boundaries between the phase fields are generally temperature dependent, it is very rare that this assumption is met. In principle this means that for most solid state reactions isoconversion methods are not valid (see also [4]). Nevertheless, isoconversion methods are often used to derive apparent activation energies for reactions in the solid state. [In this work we will use the term activation energy, E_A , to describe the temperature dependence of the reaction rate, where E_A occurs in an exponential form of the sort $\exp(-E_A/k_B T)$ and k_B is the Boltzmann constant. In all other cases the term apparent activation energy, E_{app} , will be used.]

In this work we will investigate to what extent variation of the equilibrium state with temperature influences the applicability of isoconversion methods for evaluation of activation energies in non-isothermal studies at a constant heating rate. It was shown previously [5] that the generalized Kissinger method and a method developed by the present author are the most accurate methods in this group of analysis methods. After a brief review of activation energy analysis methods in Section 2, in Section 3 the influence of variation of the equilibrium state on reaction kinetics is analysed on the basis of theoretical reaction models. In Section 4 the theoretical

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expressions will be applied to precipitation reactions in an Al–1 at % Si alloy as studied by DSC.

2. Theory and background

2.1. Activation energy analysis methods for constant equilibrium state

In most theoretical analyses (see e.g. [1, 2, 3, 5]) of transformation rates, the transformation rate during a reaction is assumed to be the product of two functions, one depending solely on the temperature, T , and the other depending solely on the fraction transformed, α , i.e.

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

where α is the fraction transformed, i.e.

$$\alpha = x(t)/x_{\text{end}} \quad (2)$$

$x(t)$ is the amount transformed, x_{end} is the total amount that can transform for a given time–temperature program, i.e. is determined by the (meta-) stable equilibrium state. For isothermal experiments x_{end} can depend on the temperature and, as the end temperature of a reaction occurring during linear heating can vary with the heating rate, β , x_{end} can also vary with β . Equation 1 implicitly assumes that a stage of the transformation can be unambiguously defined by the fraction transformed, α . For $k(T)$ usually an Arrhenius expression is chosen, i.e.

$$k(T) = k_0 \exp(-E_A/k_B T) \quad (3)$$

where k_0 is a constant, E_A is the activation energy of the process, and k_B is the Boltzmann constant. Throughout this work it is assumed that E_A is constant, i.e. independent of temperature or amount transformed. Hence, only transformations that involve a single thermally activated process are considered.

In the literature numerous types of expressions for $f(\alpha)$ have been applied. In this work we will consider one that is based on expressions first suggested by Šesták and Berggren [6] and that has been shown [7, 8] to describe precipitation in Al-based alloys quite well

$$f(\alpha) = (1 - \alpha)^p \left[\ln \frac{1}{(1 - \alpha)} \right]^q \quad (4)$$

It is noted that this choice for $f(\alpha)$ can take account of both homogeneous n th-order reaction kinetics ($q = 0$, reaction order $n = p$) and Johnson–Mehl–Avrami (JMA) reaction kinetics ($p = 1$ and Avrami exponent $m = (1 - q)^{-1}$).

From Equation 1–3 it follows directly that for transformation studies performed at constant temperature, T_i , E_A can be obtained from the well known relation (i.e. see [1, 9])

$$\ln t_f = \frac{E_A}{k_B T_i} + C_1 \quad (5)$$

where t_f is the time needed to reach a certain fraction transformed, f ; and C_1 is a constant that depends on

the reaction stage and on the kinetic model. Thus E_A can be obtained from two or more experiments at different T . In transformation studies performed at a constant heating rate, E_A can be obtained by a Kissinger-type isoconversion method or variants thereof. Application of these types of analyses requires data on the temperatures at a fixed state of transformation, T_f , as function of the heating rate, β . Methods for determining E_A can be derived as follows. Equation 1 is integrated by separation of variables

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{k_0}{\beta} \int_0^{T_f} \exp\left(-\frac{E_A}{k_B T}\right) dT \\ = \frac{k_0 E_A}{\beta k_B} \int_{y_f}^\infty \frac{\exp(-y)}{y^2} dy = \frac{k_0 E_A}{\beta k_B} p(y_f) \quad (6)$$

where $y = E_A/k_B T$, $y_f = E_A/k_B T_f$ and T_f is the temperature at a fixed state of transformation. Various ways of approximating the last integral in Equation 6 have been applied in the literature [1, 2, 3, 5]. Integrating in parts and truncating the series by using $y_f \gg 1$ results in the following approximation* for $p(y)$ [1, 5, 10]

$$p(y) \cong p_K(y) = \frac{\exp(-y)}{y^2} \quad (7)$$

that leads to

$$\ln \frac{\beta}{T_f^2} = -\frac{E_A}{k_B T_f} + C_2 \quad (8)$$

where C_2 is a constant that depends on the reaction stage and on the kinetic model. Thus, plots of $\ln(T_f^2/\beta)$ versus $1/T_f$ should result in straight lines, the slope of the straight lines equalling E_A/k_B . This method is usually referred to as the (generalized) Kissinger method. Adoption of a specific reaction model, as various authors have done in the past [11–13], is not required. Alternative methods are Ozawa's method (see e.g. [3]) and Boswell's method [14]. However, in a previous publication [5] it was shown that these two methods are much less accurate than Kissinger's method. It was shown that this is due to approximations of $p(y)$ that are less suitable than Equation 7. In the same publication [5] a new method was derived that is more accurate than Kissinger's method*. This method uses the following expressions

$$\ln \frac{\beta}{T_f^{1.8}} = -A \frac{E_A}{k_B T_f} + C_3 \quad (9)$$

with

$$A = 1.0070 - 0.0012 E_A \quad (E_A \text{ in eV}) \quad (10)$$

*It should be noted that in the range $15 < y < 60$ $p_K(y)$ differs from $p(y)$ by several per cent. Hence, strictly speaking, the accuracy of this approximation is limited. However, it has been shown by the present author [5] and by Criado and Ortega [10] that this shortcoming has little effect on the final accuracy of the generalized Kissinger method that can calculate activation energies to an accuracy of about 0.2%.

where C_3 is a constant that depends on the reaction stage and on the kinetic model.

Using the same assumptions as used in the derivation of Equation 7, it has been shown [1] that the maximum reaction rate, in good approximation, occurred at a fixed stage of transformation. Hence, special cases for Equation 7 and 9 are obtained by substituting the temperature at maximum reaction rate, T_m , for T_f .

The derivation of Equation 5, 8 and 9 depends on the assumption that it is possible to define a state variable that fully determines the fraction transformed, α (see for instance [1]). However, as mentioned in the introduction, x_{end} generally depends on the temperature and this means that α not only depends on the microstructural state (amount of new phase formed) but also directly on the temperature. Hence, a state variable that fully determines α does not exist and application of Equations 5, 8 and 9 will lead to errors in the determination of E_A . These deviations will be analysed in the next section.

2.2. Reaction kinetics for the case of a T-dependent equilibrium state

We have concluded that when x_{end} varies with temperature it is not possible to unambiguously define α . Therefore we will no longer use the fraction transformed to define the stage of the reaction. Further, it will not be possible to use the 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 a fraction transformed, α . As α will now depend on both $x(t)$ and T the general form of the reaction rate equation should instead read

$$\frac{d\xi}{dt} = k(T)f'(\xi, T) \quad (11)$$

with

$$\xi = \frac{x(t)}{x_{\text{max}}} \quad (12)$$

where x_{max} is a constant representing the maximum amount of material that can transform, i.e. the maximum value that $x(T, t)$ can attain for the range of temperatures in which the transformation occurs. For example, in a binary alloy A–B in which precipitation of element B from the A-rich matrix phase occurs, $x(t)$ can be chosen as the amount of element A precipitated in the course of the reaction, and x_{max} is the final amount that precipitates at the temperature at which the solubility of B in the A-rich matrix phase is lowest.

For the kinetic model term $f'(\xi, T)$ it is required that in the case that x_{end} is constant Equations 1 and 11 are equivalent. This can be achieved by defining a generalized form of $f'(\xi, T)$

$$f'(\xi, T) = (1 - \alpha')^{p_1} (1 - \xi)^{p_2} \left[\ln \frac{1}{(1 - \alpha')} \right]^{q_1} \left[\ln \frac{1}{(1 - \xi)} \right]^{q_2} \quad (13)$$

where $p_1, p_2, q_1, q_2 \geq 0, p_1 + p_2 = p, q_1 + q_2 = q$, and

$$\alpha' = x(t)/x_{\text{eq}}(T) \quad (14)$$

in which $x_{\text{eq}}(T)$ is the maximum amount that can transform at a given temperature, i.e.

$$x_{\text{eq}}(T) = \lim_{t \rightarrow \infty} x(t, T)$$

The variation of the reaction rate with temperature can be obtained from Equations 11–14 in the following way. Assume that $d\xi/dT$ can be approximated by an expression in which the temperature dependence is represented solely by an exponential term, while the dependence on ξ is represented by a separate function $H(\xi)$

$$\left(\frac{d\xi}{dt} \right)_{1^{\text{st order}}} = A_2 k'(T) H(\xi) \quad (15)$$

where $k'(T) = k_0 \exp(-E_{\text{app}}/k_B)$ and A_2 is a constant. In order for this approximation to be correct in first-order around a certain characteristic transformation temperature, T_{ch} , it is required that

$$\left(\frac{d\xi}{dt} \right)_{1^{\text{st order}}}(T_{\text{ch}}) = \frac{d\xi}{dt}(T_{\text{ch}}) \quad (16a)$$

and

$$\frac{d}{dT} \left(\frac{d\xi}{dt} \right)_{1^{\text{st order}}}(T_{\text{ch}}) = \frac{d}{dT} \frac{d\xi}{dt}(T_{\text{ch}}) \quad (16b)$$

Combination of Equation 11, 12, 15 and 16 results in

$$E_{\text{app}} = E_A + k_B T_{\text{ch}}^2 \frac{\partial f'}{\partial T}(T_{\text{ch}}) \frac{1}{f'(T_{\text{ch}})} \quad (17)$$

Hence, the apparent activation energy obtained from an isoconversion method deviates from E_A and the deviation is given by the last term in Equation 17. For evaluation of Equation 17 the correct definition of T_{ch} needs to be obtained. For the case of isothermal experiments, evidently $T_{\text{ch}} = T_i$. In fact, for isothermal studies the apparent activation energy obtained from Equation 5 can be evaluated directly using Equation 5 and 11

$$\begin{aligned} E_{\text{app}} &= k_B \frac{\partial \ln(d\xi/dt)^{-1}}{\partial(1/T)}(T_i) = -k_B \frac{\partial \ln k(T)}{\partial(1/T)}(T_i) \\ &\quad - k_B \frac{\partial \ln f'(\xi, T)}{\partial(1/T)}(T_i) \\ &= E_A + k_B T_i^2 \frac{\partial f'}{\partial T}(T_i) \frac{1}{f'(T_i)} \end{aligned} \quad (18)$$

Comparison of Equations 17 and 18 confirms that for isothermal studies $T_{\text{ch}} = T_i$. For non-isothermal studies at constant heating rates, T_{ch} must be a characteristic temperature intermediate between the start of the transformation and T_f (T_f is the temperature at which a certain fixed amount of matter, x_f , has been transformed). The difference between T_{ch} and T_f is expected to depend on the parameters p_1, p_2, q_1 and q_2 . A reasonable approximation for T_{ch} would be the

temperature at which half of x_f has been transformed. (This has been attempted and reasonable results were obtained.) However, a better estimate of T_{ch} can be obtained by the following reasoning. Consider what would happen in the limit of apparent activation energies being calculated at the largest value of ξ possible, ξ_{max} , given a certain heating rate. For this stage of the transformation, a characteristic previous stage of the transformation that to a high degree determined the progress of the reaction is the stage at maximum transformation rate, ξ_{mtr} , i.e.

$$\left[\frac{\xi(T_{ch})}{\xi(T_f)} \right]_{end} = \frac{\xi_{mtr}}{\xi_{max}} \quad (19)$$

By assuming that $\xi(T_{ch})/\xi(T_f)$ is constant during the reaction one finds

$$\xi(T_{ch}) = \frac{\xi_{mtr}}{\xi_{max}} \xi(T_f) \quad (20)$$

Thus Equation 20 defines T_{ch} . For most solid state reactions ξ_{mtr}/ξ_{max} is about 0.5 to 0.7 [15].

Equation 18 shows that the apparent activation energy depends on the reaction model through the term $1/f' \partial f / \partial T$. To perform this derivation both f' and $\partial x_{eq}(T) / \partial T$ need to be known. To obtain these one could perform an isothermal experiment in the temperature range of interest to fit p and q using Equation 4 and subsequently perform more experiments in that temperature range to obtain $x_{eq}(T)$. However, generally this long winded approach can be avoided as in many cases a good estimate of $x_{eq}(T)$ can be made on the basis of thermodynamic data. For instance, for precipitation reactions $x_{eq}(T)$ can generally be obtained in the following way. For these types of reaction, $x_{eq}(T)$ is determined by the solubility of an alloying element in the matrix. The equilibrium solubility, $c_{eq}(T)$, of alloying elements in a matrix can often be described using the regular solution model, which results in

$$c_{eq}(T) = c_{\infty} \exp\left(-\frac{\Delta H_{sol}}{k_B T}\right) \quad (21)$$

where c_{∞} is a constant (the solubility extrapolated to $T = \infty$) and ΔH_{sol} is the enthalpy of solution of the alloying element concerned in the matrix phase. Equation 21 describes the solubility of elements in several binary Al-based alloys accurately [16, 17] and also holds for metastable solubilities in various alloys [17, 18]. Using Equations 11–14 and 21 $1/f' \partial f / \partial T$ can be evaluated and the solution for Equation 17 is

$$E_{app} = E_A + k_B T_{ch}^2 \left[-p_1 + q_1 \left[\ln \frac{1}{(1-\alpha')} \right]^{-1} \right] \times \frac{\alpha'^2}{\xi} \frac{1}{1-\alpha'} \frac{\partial c_{eq}}{\partial T} \quad (22)$$

It was found that for an Al–1 at % Si alloy the DSC curves could be described well with $q_1 = 0$. This simplifies the evaluation of Equation 17 and after

rearranging one finds

$$E_{app} = E_A - \Delta H_{sol} p_1 \xi(T_{ch}) \left[\left[\frac{x_{max}}{c_{eq}(T_{ch})} - 1 \right] \times \left[1 - \frac{c_{eq}(T_{ch})}{x_{max}} - \xi(T_{ch}) \right] \right]^{-1} = E_A - \Delta H_{sol} p_1 \lambda_1 [c_{eq}(T_{ch}) \xi(T_{ch}) x_{max}] \quad (23)$$

where

$$\lambda_1 = \xi(T_{ch}) \left[\left[\frac{x_{max}}{c_{eq}(T_{ch})} - 1 \right] \left[1 - \frac{c_{eq}(T_{ch})}{x_{max}} - \xi(T_{ch}) \right] \right]^{-1} \quad (24)$$

Hence, according to Equation 23 the true activation energy can be obtained from an extrapolation of E_{app} against λ_1 .

It should be stressed that the above expressions for E_{app} are only valid for stages of the reaction occurring at fixed ξ and are not valid for fixed α or α' . It is possible to reason in a qualitative manner what effect a variation in x_{eq} will have on apparent activation energies obtained from stages at constant fractions of transformed material, α , using a Kissinger-like analysis. Providing there is a driving force for the transformation in a certain temperature range, a stage that occurs at a constant α will always be observed for any finite heating rate. If during heating eventually a temperature, T_m , is reached at which $x_{eq} = 0$, it is clear that T_f will always be lower than T_m (for precipitation reactions in aluminium alloys T_m is the solvus temperature). Hence, on increasing the heating rate (consider for instance continuously doubling the heating rate) a T_f will always be found, and T_f will increase with heating rate, but T_f will always be lower than T_m . Thus, isoconversion methods will yield apparent activation energies that increase with increasing T_f , and, when T_f approaches T_m , E_{app} will tend towards infinity (this follows from Equations 8 or 9). With similar reasoning it can be shown that also E_{app} calculated from the stage at maximum reaction rate, i.e. the peak of a DSC effect, will tend to infinity when the temperature of this stage, T_p , approaches T_m .

3. Experimental procedure

DSC experiments were performed on a conventionally cast Al–1 at % Si alloy. Chemical analysis showed the following composition: 1.0 at % Si, 0.002 at % Cu, 0.003 at % Fe, balance Al. DSC specimens were machined from the homogenized castings, solution treated for 2 h at 575 °C inside the DSC apparatus and cooled inside the DSC apparatus. Subsequently, the temperature was cycled between room temperature and 575 °C. For the heating stage of the cycle the heating rates were varied between 1.25 and 80 °C min⁻¹. During the cooling, no heat was supplied by the heating elements and the cooling was determined by the heat loss to the environment. The cooling for each experiment was identical and nearly

exponential: the cooling rate on passing 490 °C was 22 K min⁻¹ and on passing 275 °C it was 6.5 °C min⁻¹ (see also [18]). The total cooling time was 200 min. The DSC apparatus used was a Dupont type 910; experimental and calibration procedures are described elsewhere [8, 19].

4. Results and discussion

It has been shown elsewhere [8] that Equations 11–14 combined with Equation 21 can describe the DSC curves obtained from slowly cooled Al–1 at % Si very well. In this previous work the parameters $p = 1.5$ and $m = 1.45$ were used (for calculation of m in Al–Si see also Refs [20, 21]), while the solubility of Si in Al was obtained from the known phase diagram of Al–Si (see e.g. [20]). The parameters k_0 , E_A (0.97 eV) and p_2 ($\neq 0$) were obtained by fitting of the experimental curves. The curves thus obtained are presented in Fig. 1. Experimental complications, like noise, baseline stability, reproducibility of cooling before the DSC experiment, limit the accuracy of E_{app} determinations from two consecutive heating rates to about 5%. This is not sufficiently accurate to evaluate Equation 23 critically. Hence the computer generated curves, which are an accurate representation of experiments on Al–1 at % Si will be used to check the validity of the equations presented in the previous section.

To obtain activation energies for each heating rate, the temperature at which a certain fixed amount transformed is obtained is calculated. For this several values of ξ between 0.01 and 0.64 were used. In addition also the temperature at the maximum transformation rate was evaluated. The apparent activation energies were obtained for two consecutive heating rates β_1 and β_2 , using three different isoconversion methods: the generalized Kissinger method. (Equation 8), the Ozawa method (see [3]) and the method derived by the present author (Equation 9). As shown before [5] the latter is the more accurate method, and thus only this method is used in the present section. Results obtained with the Kissinger analysis and the Ozawa analysis add no new insights to the theory presented in Section 2.2, but they do confirm that the accuracy of the isoconversion methods decrease in the following order: Equation 9, generalized Kissinger

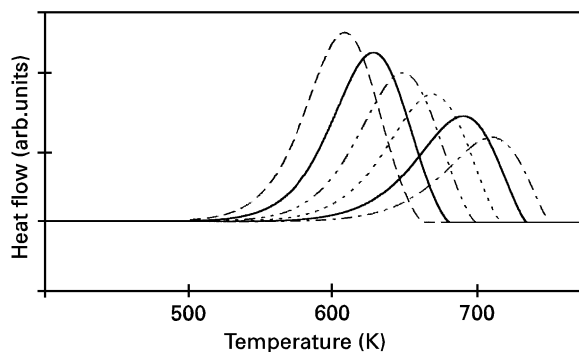


Figure 1 Six computer generated DSC curves of precipitation in Al–1 at % Si (heating rates 2.5, 5, 10, 20, 40 and 80 K min⁻¹). They fit closely to experimental curves (see [8]).

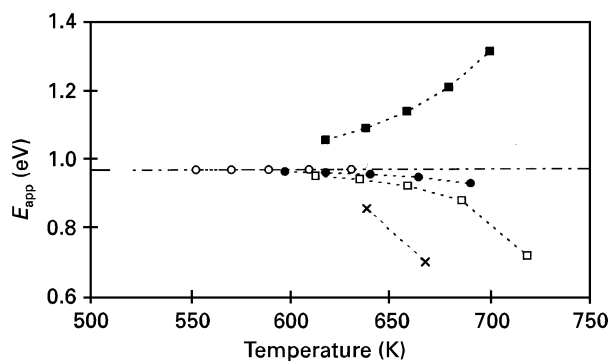


Figure 2 Apparent activation energies obtained from the method developed by the present author (Equation 9) for the computer generated curves (Fig. 1) for $\xi = 0.022$ (○), 0.21 (●), 0.37 (□) and 0.64 (×) and for the maximum reaction rate (■). Heating rates used range from 2.5 to 80 K min⁻¹.

method (Equation 8), Ozawa method. These results will be dealt with separately in the appendix.

In Fig. 2 the apparent activation energies obtained with Equation 9 are plotted as a function of the temperature T_f [T_f is taken to be the average of $T_f(\beta_1)$ and $T_f(\beta_2)$]. This figure shows that E_{app} decreases with increasing T_f and also decreases with increasing ξ . For low T and ξ , the values obtained appear in good approximation to converge to the true activation energy 0.97 eV. Also in the same figure the apparent activation energies obtained from the peak of the DSC effect, i.e. the temperature at maximum reaction rate, are plotted. As expected (see last paragraph of Section 2.2) these E_{app} values increase with T_f .

Next the applicability of the extrapolation method presented in Equation 23 is tested. For this we first obtain ξ_{mtr}/ξ_{max} needed in Equation 20. It can be expected that ξ_{mtr}/ξ_{max} varies with heating rate and for the lower range of heating rates (2.5–20 K min⁻¹), which are the most important ones in determining the slope in subsequent Figs 3 and 4, ξ_{mtr}/ξ_{max} increases with heating rate from 0.56 to 0.6. To limit the complexity of the calculations, ξ_{mtr}/ξ_{max} is assumed to be constant and approximated as 0.58. (Note that this simplifying assumption will cause the plots in subsequent Figs 3 and 6 to be slightly bent.)

In Fig. 3 the apparent activation energy obtained with Equation 9 is plotted versus the extrapolation function, λ_1 . It is observed that, in correspondence with Equation 23, the plot is in good approximation a straight line. The value of E_A resulting from the extrapolation is 0.9709 eV, which is equal to the value one finds in the range of $T = 500$ –560 K for the case $c_{eq} = \text{constant}$. Hence, the small difference with the true activation energy 0.97 eV is entirely due to the extremely small inaccuracy (0.1%) that occurs when Equation 9 is used (see also Ref. [5]). The slope of the line in Fig. 3 in the range $0 < \lambda_1 < 0.06$ is -0.79 ± 0.02 eV. For Al–Si, $\Delta H_{sol} = 0.52$ eV [8] and thus according to Equation 23 the slope should equal $-p_1 \times \Delta H_{sol} = -0.78$ eV. Hence, also the slope is predicted very accurately.

Finally, the method is applied to actual DSC data obtained for the Al–1 at % Si alloy (for experimental

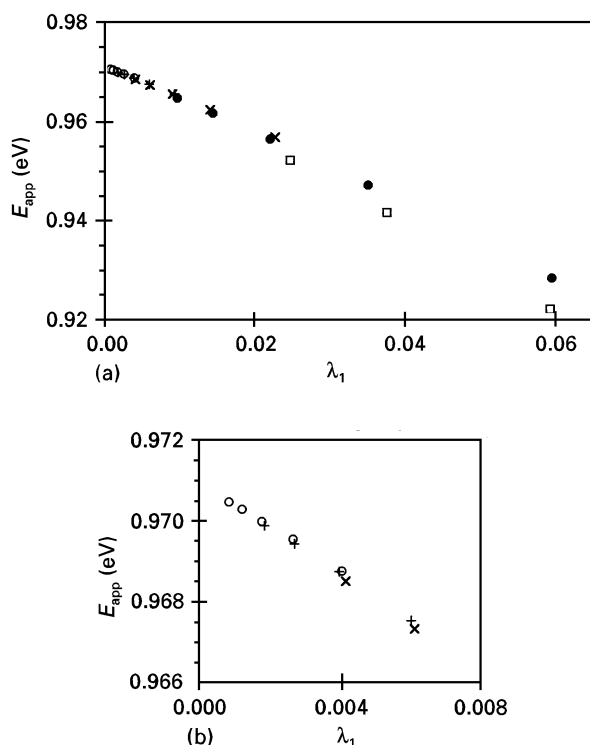


Figure 3(a, b) Apparent activation energies obtained from Equation 9 for the computer generated curves (Fig. 1) versus the extrapolation function, λ_1 , for $\xi = 0.039$ (○), 0.068 (+), 0.12 (×), 0.21 (●) and 0.37 (□). Heating rates used range from 2.5 to 80 K min⁻¹.

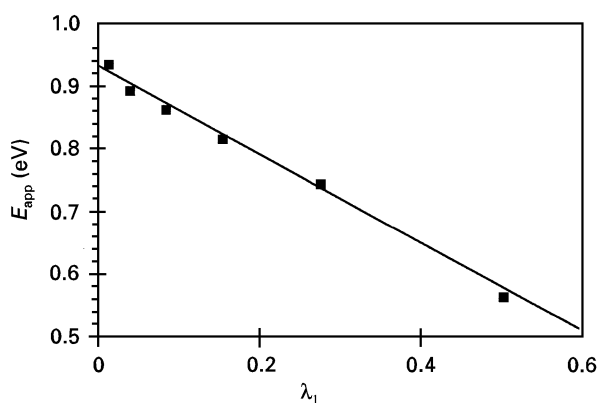


Figure 4 Apparent activation energies obtained using Equation 9 for the Al-1 at % Si alloy versus extrapolation function, λ_1 for various ξ . Heating rates used were 20 and 40 K min⁻¹.

DSC curves, see Ref. [8]). Results are presented in Fig. 4, where E_{app} calculated with Equation 9 using heating rates of 20 and 40 K min⁻¹ is plotted as a function of λ_1 . In accordance with the theory presented, the plot is a straight line. The abscissa (0.93 ± 0.02 eV) calculated from the fitted straight line corresponds reasonably well with the true activation energy of the reaction. It should be noted that systematic errors in E_{app} calculations up to about 5% can be introduced due to instabilities of the DSC baseline and other experimental inaccuracies, and hence the observed deviation of the abscissa in Fig. 5 from the true activation energy may well be due to this. In correspondence with this, at lower heating rates the accuracy appears to degrade (results not presented). As in Fig. 3 the slope of the fitted straight

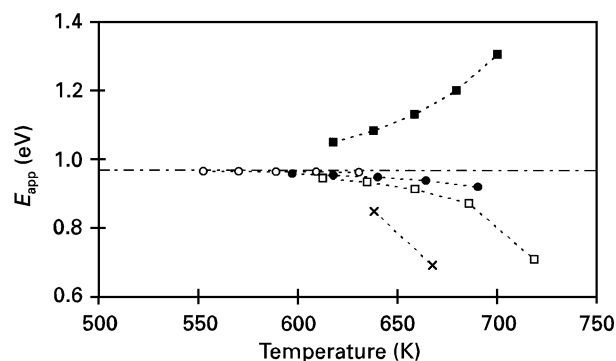


Figure 5 Apparent activation energies obtained from the Kissinger method (Equation 8) for the computer generated curves for $\xi = 0.022$ (○), 0.21 (●), 0.37 (□) and 0.64 (×) and for the maximum reaction rate (■). Heating rates used range from 2.5 to 80 K min⁻¹.

line in Fig. 4 (0.72 eV) corresponds well with the predictions.

In concluding this section a few remarks on the practical applicability of the theory presented in the previous section are in order. The popularity of isoconversion methods like the (generalized) Kissinger method (Eq. 8), the Ozawa method, or the one described by Equation 9 are largely due to the relative ease of their application. But if the equilibrium state depends on the temperature, these isoconversion methods are no longer valid and the more complex Equation 17 describes the variation of E_{app} with the temperature and stage of the reaction. It has been shown that under certain conditions Equation 17 can be evaluated and Equations 22 and 23 can be used as an extrapolation method to obtain the true activation energy. This procedure is somewhat cumbersome, but Figs 2, 3 and 4 show that it is imperative to check whether E_{app} varies with the extrapolation function, λ_1 ; depending on the choice for the amount transformed, apparent activation can deviate by up to 30% from the true activation energy. If no correction was made according to the extrapolation method (Equation 22) the activation energies obtained by an isoconversion method would be too low, and incorrect conclusions concerning the thermally activated process could result. Hence, it is advised that if for a thermally activated reaction x_{eq} is found to vary with the heating rate or isothermal ageing temperature, an analysis of the apparent activation energies along the lines of the description in the previous section should always be made.

5. Conclusions

When the equilibrium state of the reaction depends on the temperature, apparent activation energies calculated using isoconversion methods vary with temperature and fraction transformed even though the true activation energy of the thermally activated process is constant. For DSC experiments on Al-1 at % Si the apparent activation energy can deviate by up to 30% from the true activation energy of the reaction. Expressions that describe the influence of the reaction

parameters (p_1 , p_2 , q_1 and q_2) and the equilibrium state on the apparent activation energy are derived. A new method of extrapolating activation energies is introduced that allows the determination of the true activation energy for precipitation in alloys with a known solubility. Verification of this extrapolation method shows a good correspondence between experiment and calculations. It is advised that if for a thermally activated reaction the maximum amount transformed is found to vary with the heating rate or isothermal ageing temperature, always an analysis of the apparent activation energies along the lines of the description in this paper should be made.

Appendix

Comparison with the Kissinger and Ozawa methods

Fig. 5 is a plot similar to Fig. 2, but now the apparent activation energies are obtained using the Kissinger method and the generalized Kissinger method. The general features are similar to the ones in Fig. 2, but the calculated activation energies are on average about 0.3% smaller. A similar plot to Figs 2 and 5 was constructed for apparent activation energies calculated with Ozawa's method (results not presented). It was observed that E_{app} obtained from Ozawa's method is generally larger than 0.97 eV. For this method, in the range of heating rates studied, no convergence to the true activation energy is observed for low T and ξ .

Fig. 6 is a plot similar to the extrapolation in Fig. 3, but now the apparent activation energies are obtained with the generalized Kissinger method. Also in Fig. 6 the plot is in good approximation a straight line. The value of E_A resulting from the extrapolation is about 0.967 eV, i.e. very close to the true activation energy. The slope of the line in Fig. 6 in the range $0 < \lambda_1 < 0.06$ is identical to the one in Fig. 3. Hence, when the Kissinger analysis is used, the theory in Section 2.2 also predicts the slope of the line very accurately.

The same extrapolation procedure applied for E_{app} values calculated with Ozawa's method does not yield a straight line (results not presented). This is due to the relatively large temperature-dependent deviations from the real activation energy that result from an Ozawa analysis (see [5, 22]). Most of the E_{app} values for low λ are around 1.015 eV. Hence, the correspondence with the true value (0.97 eV) is an order of magnitude worse than results obtained using Kissinger's method. Also other researchers [23, 24] have pointed out that Kissinger's method is generally much more accurate than Ozawa's method. This may be surprising as some researchers (see e.g. [3]) have stated that the approximation of $p(y)$ used for the derivation of Ozawa's analysis is more accurate than the one in Equation 7. However, it has been shown elsewhere [5] that the approximation of $p(y)$ used in the derivation of the generalized Kissinger method is the more appropriate one and that the method in Equation 9 is even more accurate than Kissinger's method.

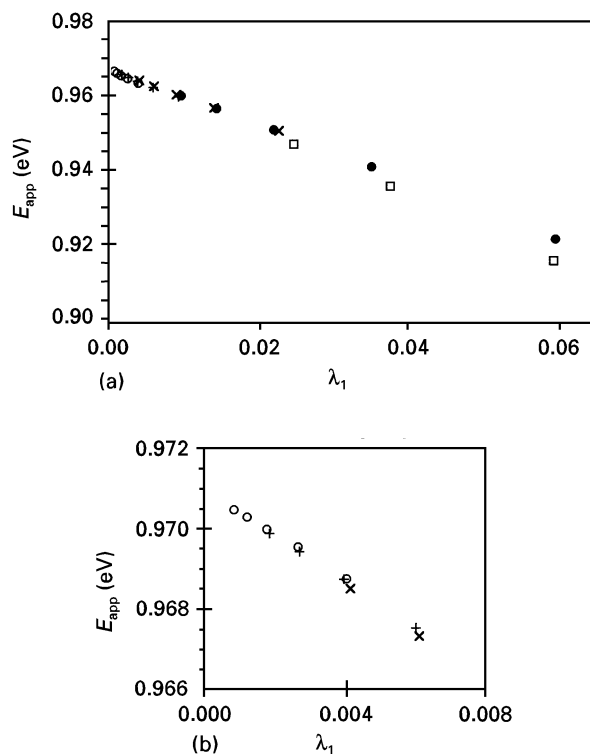


Figure 6 Apparent activation energies obtained from the Kissinger method for the computer generated curves (Fig. 1) versus the extrapolation function, λ_1 , for $\xi = 0.039$ (\circ), 0.068 ($+$), 0.12 (\times), 0.21 (\bullet) and 0.37 (\square). Heating rates used range from 2.5 to 80 K min⁻¹.

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