

In celebration of the 60th birthday of Dr. Andrew K. Galwey

THE INFLUENCE OF HEAT TRANSFER ON REDUCED-TIME PLOTS

F. W. Wilburn and J. H. Sharp

Department of Engineering Materials, University of Sheffield, Mappin Street, Sheffield, S1 4DU, UK

Abstract

A theoretical approach has been used to show that, except for certain types of reaction mechanism, the ease with which it is possible to distinguish the form of the reaction mechanism by the reduced-time plot method depends particularly on the rate of transfer of heat into the sample. The original reduced-time plots [1] were calculated from model equations which assume that the sample is, from the outset, at a fixed temperature and remains under isothermal conditions throughout the reaction. The variations produced in the appearance of reduced-time plots when the sample is programmed to rise to a given fixed temperature through various temperature schedules have been investigated. It is shown that even relatively rapid temperature rises can produce distortion of the reduced-time plots for various reaction equations. If the reaction mechanism is known, however, fairly accurate values of the activation energy for the reaction can be determined, even when the furnace used has relatively poor heat-transfer characteristics.

Keywords: activation energy, heat transfer, kinetics, reaction mechanism, reduced-time plots

Introduction

The associated techniques of TG and DTG are often used to determine kinetic parameters, namely the pre-exponential factor and the activation energy of a given reaction. However, to determine these parameters it is necessary initially to be able to determine the kinetic mechanism of the reaction which is occurring. The classical method is to carry out an experiment under isothermal conditions (e.g. to follow the change in mass with respect to time at constant temperature). From the results, a reduced-time plot, of fraction reacted, x , against $t/t_{0.5}$, where $t_{0.5}$ is the time taken to reach a fraction reacted of 0.5, can be drawn. This reduced-time plot can then be compared with a calculated set of reduced-time plots for many different reaction mechanisms in order to deter-

mine the most probable type of mechanism being followed by the reaction under study, as suggested by Sharp *et al.* [1].

Sometimes it is difficult to determine the specific equation from this technique, for some reduced time plots of experimental data do not follow precisely any of the curves given in reference [1]. These differences have been attributed to various causes, particularly that the reaction does not follow any of the model reactions under consideration, or that there is an 'induction' period prior to the main reaction. There is, however, an alternative explanation for many such deviations. The curves produced in reference [1] were generated from model equations, no account being taken of either the initial heating of the sample or the temperature variations which can occur within the sample during the reaction.

Practical considerations

In a practical experiment the sample has, in principle, to be heated up to the isothermal temperature infinitely quickly, which is, of course, impossible to achieve and difficult to approach. The time taken to reach the isothermal temperature is dependent on the furnace design and the size of the sample. If this time is relatively long, some degree of reaction will inevitably have taken place before the isothermal temperature is reached, thus distorting the shape of the resulting reduced-time plot. Once equilibrium has been established, and if no reaction has occurred in the sample, there will be a small but constant temperature difference between the measuring thermocouple and the sample, sufficient for some heat to flow to overcome heat losses. However, when an endothermic reaction is occurring within the sample, more heat must be supplied to sustain the reaction and so this temperature difference will increase, and the sample temperature will be lower than that of the measuring thermocouple. Furthermore the magnitude of this increase is dependent on the reaction rate, so that, as the rate of reaction varies, so does this temperature gradient. Thus the temperature of the sample will not be isothermal throughout the reaction. This temperature gradient will be dependent on the heat transfer characteristics of the space between the heat source and sample, as well as the conductivity of the sample. The space between the source of heat and sample will of necessity be a gaseous space, which is usually (except for helium) a poor conductor of heat.

For exothermic reactions, heat is given out from the sample as the reaction proceeds so that the temperature of the sample will be higher than that of the measuring thermocouple and will still vary with the reaction rate. It is also difficult to measure the actual sample temperature in a TG apparatus since the temperature measurement has, of necessity, to be located outside the sample. Theoretical calculations for endothermic reactions, using a heat-transfer model

set up some years ago [2], would suggest that the sample temperature is some 1 to 2 degrees (variable) lower than the temperature of the measuring thermocouple whilst an endothermic reaction is proceeding.

It is interesting to evaluate how k , the rate constant, varies with temperature. It is usually assumed that

$$k = A \cdot e^{-E/RT} \quad (1)$$

where A is the pre-exponential constant

E is the activation energy of the reaction

R is the gas constant

T is Kelvin temperature

Using this equation with values of A and E of 10^9 s^{-1} and $176.4 \text{ kJ} \cdot \text{mol}^{-1}$ respectively, Table 1 gives calculated values of k over a temperature range of 445–455°C. Thus a change of $\pm 1^\circ\text{C}$ in temperature at 450°C gives a $\pm 4\%$ change in the k value, whilst a change of $\pm 2^\circ\text{C}$ produces a $\pm 9\%$ change in the value of k . Such variations in temperature are common, even in 'isothermal' experiments.

Table 1 Variation of k with temperature

Temperature/ $^\circ\text{C}$	k/s^{-1}
445	1.9852×10^{-4}
446	2.0676×10^{-4}
447	2.1532×10^{-4}
448	2.2421×10^{-4}
449	2.3344×10^{-4}
450	2.4302×10^{-4}
451	2.5297×10^{-4}
452	2.6329×10^{-4}
453	2.7401×10^{-4}
454	2.8513×10^{-4}
455	2.9667×10^{-4}

Generation of TG curves when the sample temperature approaches equilibrium in an exponential manner

The types of equation used to describe solid state reactions are difficult to solve analytically, and are usually of the form:

$$g(x) = k \cdot t \quad (\text{constant temperature})$$

where x has values 0 to 1, $g(x)$ is the function representing the particular reaction and t is the time.

Differentiating:

$$g'(x) \cdot dx = k \cdot dt$$

where $g'(x)$ is the first differential of $g(x)$ and is often designated $1/f(x)$.

$$dx/dt = \frac{k}{g'(x)} = k \cdot f(x)$$

The rate constant k can be replaced by Eq. (1)

Thus

$$dx/dt = f(x) \cdot A \cdot e^{-E/RT}$$

This type of differential equation is difficult to solve analytically, particularly if the function $f(x)$ is non-linear. For such equations, finite difference techniques are used when the equation is transformed into the following form:

$$dx = f(x) \cdot A \cdot e^{-E/RT} \cdot dt \quad (2)$$

where dx is an incremental amount of x generated over a small time step dt . Relatively meaningful results can be obtained if care is taken in the choice of the time step. Initially x is given the value 0, unless such a value will produce a large value of dx . For some reaction equations, e.g. $D_2(x)$, $f(x) = 1/\ln(1-x)$, if initially $x = 0$ then $f(x) = \text{infinity}$, giving an infinite value for dx . In such situations the initial value of x is given a small value .00001. The time step, dt , is set to, say 0.1 s, and dx is calculated using these values. (If the temperature is constant, then the exponential function is constant.) The calculated value, dx , is added to x and this new value of x is used to calculate another new value of dx , with dt again equal to 0.1 s. The total time t is the sum of all the dt 's. This process is repeated until x reaches a value of 1. The plotted of x vs. time produces

a curve of mass-loss vs. time, such as that normally plot in a kinetic investigation carried out under isothermal conditions. If, however, the temperature varies during the reaction and the equation relating temperature with time is known, then this equation for T can replace the constant T in Eq. (2) to produce the temperature regime during the calculations. If the temperature rises exponentially this can be represented by:

$$T = T_i e^{-t/CR} + T_f(1 - e^{-t/CR}) \quad (3)$$

where T is the temperature (K) at any time t_a during the calculations (t_a is the sum of dt up to the measuring point), T_i and T_f are the initial and final temperatures and CR is the time constant, i.e. the time taken for the temperature to rise to 63% of its final value.

By using T from Eq. (3), in place of T in Eq. (2), the final x and dx/dt plots are those in which the sample temperature varies in a similar manner to that often experienced in a practical situation. By altering the time constant, CR, between short and long times, the exponential temperature rise to the 'isothermal' temperature can be varied. To obtain reduced-time plots from x vs. t plots, the method given by Sharp *et al.* [1] is used.

The influence of variation of temperature within the sample

The theory given above treats the whole sample as if its temperature were uniform, and assumes that the absorption of heat during the reaction does not affect the temperature of the sample. The results quoted here also assume that the whole sample is at a uniform temperature, so that the results given only illustrate the influence of poor transfer of heat into the sample.

Results

Three sets of calculations were carried out, using one example from each of the three different groups of reaction Eqs (1, 3). Two different conditions were considered, one where the heat transfer into the sample was high (low CR value of 1 s) representative of a modern miniature TG apparatus. In the other condition, the heat-transfer into the sample was low, representative of apparatus in which relatively large samples are used or in which heat has to pass through a ceramic (e.g. quartz) tube and a gaseous space before reaching the sample (high CR value of 30 s). Calculations were carried out under these conditions for the Avrami-Erofeev equation with $m = 2$,

$$A_2(x) = \{-\ln(1-x)\}^{1/2} = k \cdot t$$

the two-dimensional diffusion equation

$$D_2(x) = (1-x)\ln(1-x) + x = k \cdot t$$

and the contracting-area equation

$$R_2(x) = 1 - (1-x)^{1/2} = k \cdot t$$

These were chosen as being representative of each of the three main groups of reaction types listed in [1] and [3]. Reduced-time plots were constructed and compared graphically with the equivalent reduced-time plot from reference [1].

The results for the Avrami equation are shown in Fig. 1. The curve for the reduced-time plot without heat-transfer (i.e. as calculated by Sharp *et al.*[1]) and that for the high heat-transfer case, are superimposed (Fig. 1(a)), there being a slight deviation at higher $t/t_{0.5}$ values. The curve for the low heat transfer case deviates from these two latter curves (Fig. 1(b)). However, despite the difference between the curves, it is still possible to identify the reaction type, as the curve shape is not distorted.

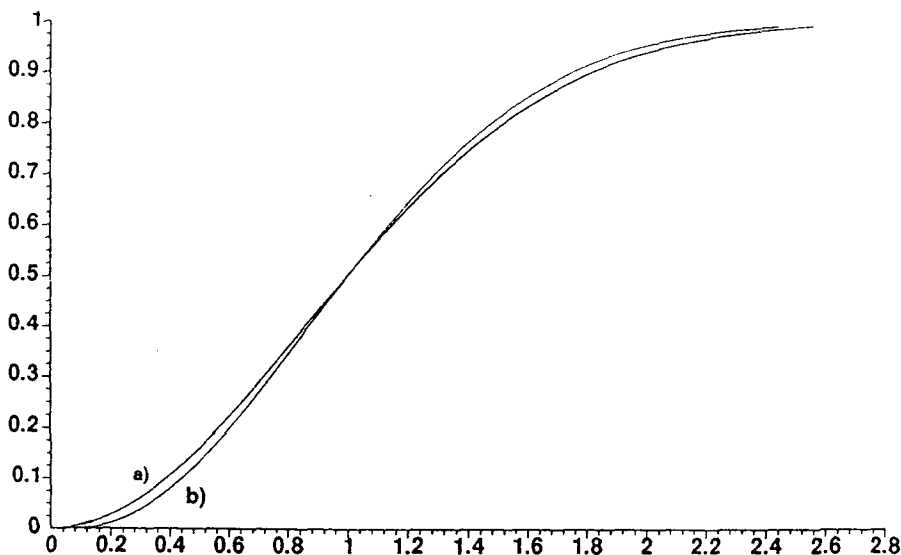


Fig. 1 Reduced-time plots for reaction A2; x-axis caption: $t/t_{0.5}$; y-axis caption: fraction reacted

Figure 2 shows similar curves for the two-dimensional diffusion equation under similar conditions. The curve for the high heat-transfer case follows closely that for the no heat-transfer case (Fig. 2(a)), although some deviation is

just evident. The curve for the low heat-transfer case (Fig. 2(b)) differs significantly from the two previously mentioned and exhibits an 'induction' period at the commencement. The distortion of shape is extensive, making it difficult to decide that such a curve represents two-dimensional diffusion, particularly with the apparent initial 'induction' period, caused by the distorting effect of poor heat-transfer. Despite this, it is interesting to measure k from the slope of the curve (Fig. 3) obtained when using the results from the low heat-transfer calculations for the diffusion equation (D2). Ignoring the initial non-linear portion, the measured value of k from the slope of the linear portion of the curve was $2.38 \times 10^{-4} \text{ s}^{-1}$ compared with the value of $2.43 \times 10^{-4} \text{ s}^{-1}$ calculated, when using the value of A and E quoted above, from Eq. 1. This represents only a 2% error.

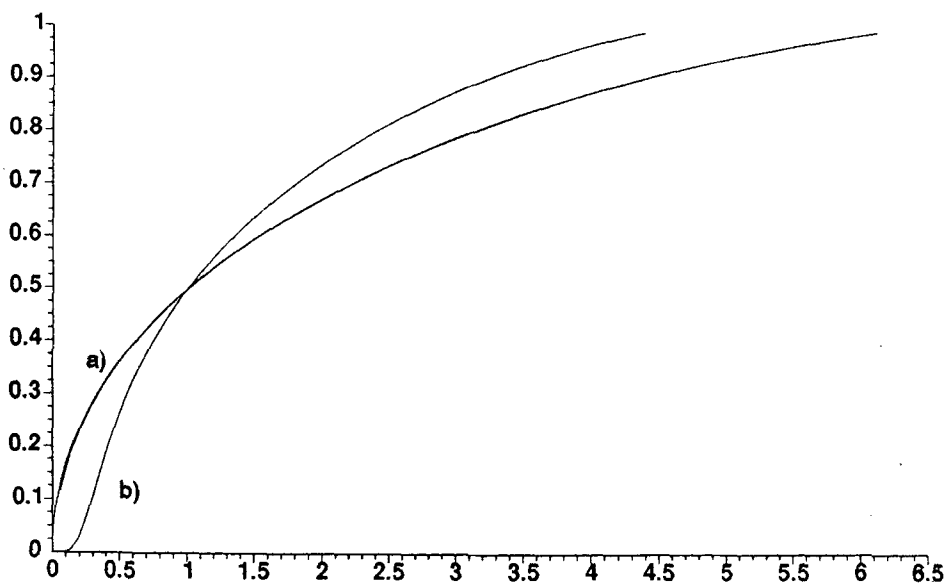


Fig. 2 Reduced-time plots for reaction D2; x-axis caption: $t/t_{0.5}$; y-axis caption: fraction reacted

Similar results are illustrated in Fig. 4 for the contracting-area (R2) mechanism. Only very slight deviation is apparent in the high heat-transfer case (Fig. 4(a)) but considerable distortion is evident in the low heat-transfer case (Fig. 4(b)). The distortion of the curve is so bad, clearly suggesting an apparent 'induction' period, that it is doubtful whether the type or reaction would be recognised from such a curve.

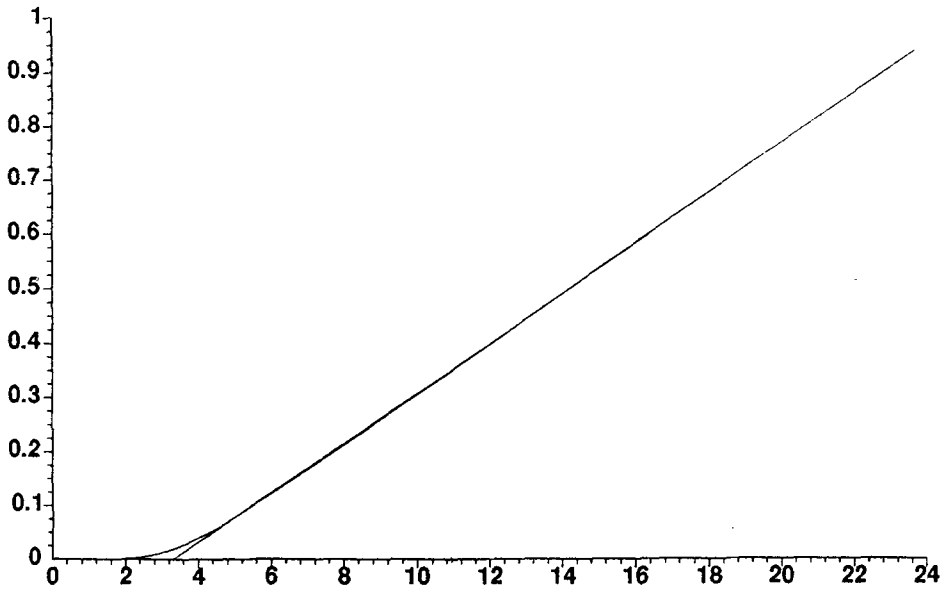


Fig. 3 Isothermal mass loss curve for D2 in low conductivity system; x-axis caption: $t(\text{mins})$; y-axis caption: fraction reacted

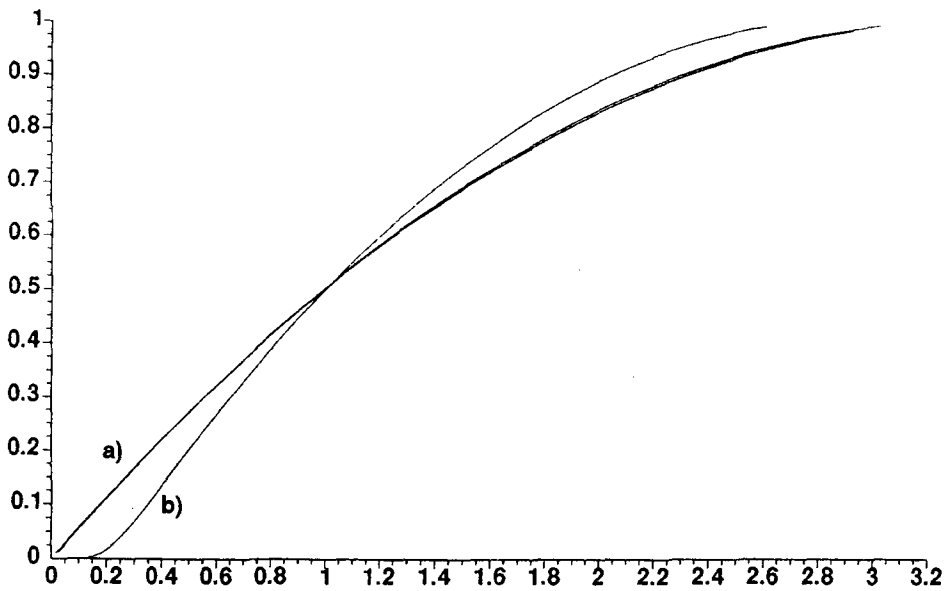


Fig. 4 Reduced-time plots for reaction R2; x-axis caption: $t/t_{0.5}$; y-axis caption: fraction reacted

Heat transfer

The heat transfer characteristics of a furnace may be tested by inserting an inert sample at ambient temperature into the furnace which has been held at a controlled higher temperature for some time. A plot of 'sample' temperature (that of the thermocouple under or near the sample) versus time, from that time at which the sample is placed in the furnace, will produce an exponential curve which gradually approaches the final isothermal temperature. The time taken to reach 63% (the time-constant) of the isothermal temperature should be less than about 20 s, if the reduced-time plots are not to be distorted for reaction models D2 and R2. Longer times can be tolerated for reaction model A2. It should be remembered, however, that the temperature of the sample will probably take longer to reach the isothermal temperature than does the measuring thermocouple, especially when an endothermic reaction takes place.

It has been shown by Brown [4] that the thermal conductivity of lightly packed powders is generally an order of magnitude lower than that of a bulk sample of the material. This comparatively low sample conductivity means that heat transfer into the sample is slow. This cannot easily be observed, but will affect the results, as suggested above, when using a standard TG apparatus where the temperature is measured close to, but not within, the sample.

Conclusions

This work has shown that, as long as the mathematical equation of the reaction is known, then reliable activation energy data can be derived from isothermal temperature curves in a thermobalance. However, if the transfer of heat from the furnace to the sample and within the sample is poor, as indicated by a long time-constant, then the determination of the reaction mechanism using the reduced-time plot technique can be difficult.

References

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Zusammenfassung — Mit Hilfe einer theoretischen Näherung wurde gezeigt, daß — mit Ausnahme einiger Typen von Reaktionsmechanismen — die Leichtigkeit, mit der die Formen des Reaktionsmechanismus durch die reduzierte Zeit-Plot-Methode voneinander unterschieden werden können, besonders von der Geschwindigkeit abhängt, mit der der Probe Wärme übertragen wird. Die ursprünglichen reduzierten Zeit-Plot-Darstellungen [1] wurden anhand von

Modellgleichungen unter der Annahme berechnet, daß die Probe von Anfang an eine feste Temperatur hat und über die gesamte Reaktion hinweg unter isothermen Bedingungen verbleibt. Die Variationen im Erscheinungsbild der reduzierten Zeit-Plots, wenn die Probe über verschiedene Temperaturprogramme auf eine bestimmte Temperatur gebracht wird, wurden untersucht. Es wurde gezeigt, daß für verschiedene Reaktionsgleichungen gerade schnelle Temperatursteigerungen Verzerrungen der reduzierten Zeit-Plots verursachen können. Ist der Reaktionsmechanismus irgendwie bekannt, kann man sehr genaue Werte für die Aktivierungsenergie der Reaktion erhalten, besonders dann, wenn der verwendete Ofen eine relativ schwache Wärmetransfer-Charakteristik hat.