Thermochimica Acta, 78 (1984) 93–100
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA. REACTION RATE DETERMINATION

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(Received 3 February 1984)

ABSTRACT

The relation between the slope of the thermogravimetric curves and the reaction rate is analyzed assuming that the variables in the kinetic equations are separable. The reaction rate may be obtained from either the slope

$$\frac{d\alpha}{dt} = A\exp(-E/RT)f(\alpha)$$

or from

$$\frac{d\alpha}{dt} = A\exp(-E/RT')f(\alpha)\left[1 + E/RT'^2(T - T_0)\right]$$

where

$$T' = \frac{T}{1 + RT/E\ln\left[1 + E(T - T_0)/RT'^2\right]}$$

These relationships were tested against theoretical data and found to be satisfactory.

INTRODUCTION

Determination of the kinetic behaviour of a solid decomposition under non-isothermal conditions is a complex task, due to the multiple steps occurring during the transformation and the lack of knowledge on their relative importance in this type of experiment, etc. This requires data interpretation methods capable of defining the difference between cases where the kinetic behaviour is amenable to a description based on a very simplified model and those requiring a more complex one [1].

The amount of work involved to decide between conflicting models is

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reduced if the models are compared in their differential form. To do this we need reaction rate data at various compositions and temperatures. From the non-isothermal α–t curves the rate may be obtained by derivation. The problem arises when these rates are to be correlated to $\mathrm{d}\alpha/\mathrm{d}t$ values from a non-isothermal test.

A literature search shows an evolving controversy on the actual relationship between both quantities. Some authors [2–4] favour the relation $r = \mathrm{d}\alpha/\mathrm{d}t$ while others [5–7] take $\mathrm{d}\alpha/\mathrm{d}t = (\mathrm{d}\alpha/\mathrm{d}t)_T + \beta(\mathrm{d}\alpha/\mathrm{d}T)_t$. Logical attempts are made to justify either one. Our objective is to solve this controversy.

PROCEDURES TO CALCULATE THE REACTION RATE

The rate of a chemical reaction in a closed, isothermal and uniform composition system is defined as the variation of the reaction extent with time, referred to the chosen extensive quantity of the system. Assuming the coefficients of the selected component in the stoichiometric reaction to be the unit and the initial number of moles as the extensive quantity, the kinetics of a chemical change fitting a model of separable variables is expressed in terms of the transformed fraction as

$$r = \frac{\mathrm{d}\alpha}{\mathrm{d}t} = A \exp\left(-\frac{E}{RT}\right)\mathrm{f}(\alpha) \tag{1}$$

If the reaction conditions are non-isothermal and the time–temperature relation, usually linear, is known, then the α–t relationship is obtained on integration

$$\int_0^\alpha \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \int_0^t A \exp\left(-\frac{E}{RT}\right)\mathrm{d}t \tag{2}$$

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

The variation of α as a function of the variables (t, T) and the operating parameter (β), may by expressed in the three following ways.

(1) $\alpha = \mathrm{NIF}(t, \beta)$

$$\int_0^\alpha \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \int_0^t A \exp\left[-\frac{E}{R(T_0 + \beta t)}\right]\mathrm{d}t \tag{4}$$

(2) $\alpha = \mathrm{NIF}(T, \beta)$

$$\int_0^\alpha \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \int_{T_0}^T A \exp\left(-\frac{E}{RT}\right)\frac{\mathrm{d}T}{\beta} \tag{5}$$

(3) $\alpha = \mathrm{NIF}(t, T)$ eqns. (2) and (3)

Where NIF is the non-isothermal function. The reaction rate may be obtained from any of these three relations.

The derivative of eqn. (4) with respect to time gives

$$\frac{d\alpha}{dt} = A \exp\left[-\frac{E}{R(T_0+\beta t)}\right] f(\alpha) \tag{6}$$

Thus, the slope at any point (α, t) on a curve obtained from a non-isothermal experiment carried out at a heating rate β corresponds to the reaction rate at $T = T_0 + \beta t$.

The correlation between the reaction rate in isothermal and non-isothermal experiments can be visualized from Fig. 1. To obtain this figure a KEKAM equation ($n = 2$) has been assumed. The isothermals (T parameter) have been obtained by integrating the kinetic equation. The non-isothermals (β parameter) have been obtained by applying Simpson's rule to eqn. (4). The time and the corresponding temperature (eqn. 3) at two heating rates are plotted on the abscissae.

By derivating eqn. (5) with respect to temperature we get

$$\frac{d\alpha}{dT} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \frac{1}{\beta} \tag{7}$$

That is, the reaction rate at temperature T, is obtained by multiplying the derivative of the α–T curve at the point T by the heating rate. Visualization of this equality can be achieved through a figure similar to Fig. 1.

The time derivative of eqn. (2) gives

$$\frac{1}{f(\alpha)} \frac{d\alpha}{dt} = \frac{d}{dt}\left[\int_0^t A \exp\left(-\frac{E}{RT}\right) dt\right]_T + \frac{d}{dT}\left[\int_0^t A \exp\left(-\frac{E}{RT}\right) dt\right]_t \frac{dT}{dt} \tag{8}$$

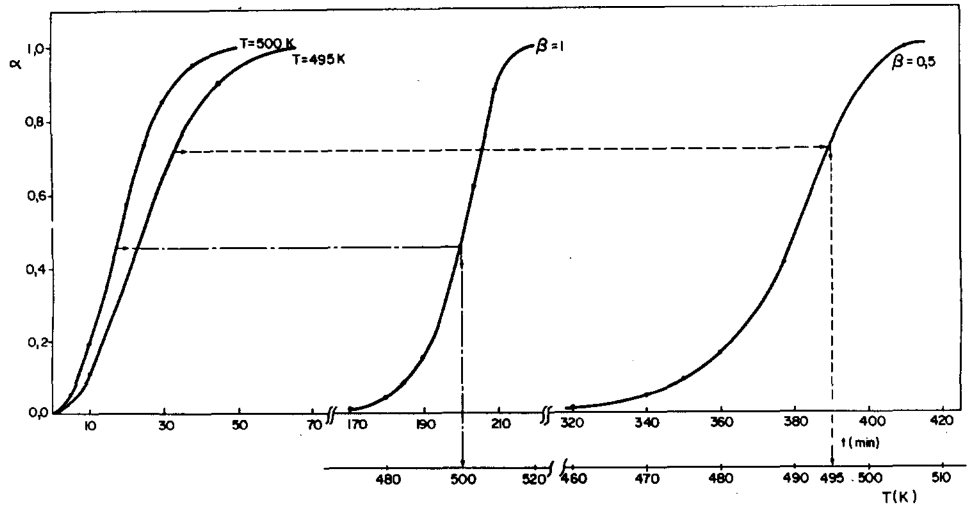

Fig. 1. Relation between reaction rate in isothermal and non-isothermal curves.

The meaning of each term is as follows. The term $\mathrm{d}\alpha/\mathrm{d}t$ is the time derivative of the curve $\alpha = \mathrm{NIF}(t, T)$ in the β plane. This derivative is equal to $\mathrm{d}\alpha/\mathrm{d}t$ from the curve $\alpha = \mathrm{NIF}(t, \beta)$ and, therefore, the rate of reaction at T. The term $\mathrm{d}/\mathrm{d}t[\int_0^t A \exp(-E/RT)\mathrm{d}t]_T$ is the time derivative of the curve $\alpha = \mathrm{NIF}(t, T)$ on the plane T, that is $(\mathrm{d}\alpha/\mathrm{d}t)_T$. This term is not the reaction rate at temperature T corresponding to the point where the derivative is obtained.

To calculate the derivative of the integral we would have to find the derivative of the curve obtained by the intersection of the non-isothermal curves with the plane T.

This curve equation is identical to that corresponding to an isothermal experiment at an equivalent temperature (T'). The relationship between T' and the temperature of the intersecting plane is [1]

$$A \exp\left(-\frac{E}{RT'}\right) = \frac{\int_{T_0}^{T} A \exp(-E/RT)\mathrm{d}T}{T - T_0} \tag{9}$$

By derivation of eqn. (9) with consideration of eqn. (3)

$$\frac{\mathrm{d}}{\mathrm{d}t}\left[A \exp\left(-\frac{E}{RT'}\right)\beta t\right]_T = \frac{\mathrm{d}}{\mathrm{d}t}\left[\int_0^t A \exp\left(-\frac{E}{RT}\right)\beta \mathrm{d}t\right]_T \tag{10}$$

$$A \exp\left(-\frac{E}{RT'}\right) = \frac{\mathrm{d}}{\mathrm{d}t}\left[\int_0^t A \exp\left(-\frac{E}{RT}\right)\mathrm{d}t\right]_T \tag{11}$$

The term $\mathrm{d}/\mathrm{d}T[\int_0^t A \exp(-E/RT)\mathrm{d}t]_t(\mathrm{d}T/\mathrm{d}t)\mathrm{f}(\alpha)$ is the temperature derivation of the curve $\alpha = \mathrm{NIF}(t, T)$ on the t plane, that is $(\mathrm{d}\alpha/\mathrm{d}T)_t \mathrm{d}T/\mathrm{d}t$. Its calculation as a function of the equivalent temperature can be performed by the derivation of eqn. (9)

$$\frac{\mathrm{d}}{\mathrm{d}T}\left[A \exp\left(-\frac{E}{RT'}\right)\beta t\right]_t = \frac{\mathrm{d}}{\mathrm{d}T}\left[\int_0^t A \exp\left(-\frac{E}{RT}\right)\beta \mathrm{d}t\right]_t \tag{12}$$

$$\frac{E}{RT'^2} A \exp\left(-\frac{E}{RT'}\right)\beta t = \frac{\mathrm{d}}{\mathrm{d}T}\left[\int_0^t A \exp\left(-\frac{E}{RT}\right)\beta \mathrm{d}t\right]_t \tag{13}$$

The mutually relative location of the planes where these derivations are carried out is represented in Fig. 2. To obtain this figure the same kinetic equation and the same calculation technique was used as for Fig. 1.

Substituting eqns. (11) and (13) into eqn. (8) gives

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A \exp\left(-\frac{E}{RT'}\right)\left(1 + \frac{E}{RT'^2}\beta t\right)\mathrm{f}(\alpha) \tag{14}$$

That is

$$r_T = r_{T'}\left[1 + \frac{E}{RT'^2}(T - T_0)\right] \tag{15}$$

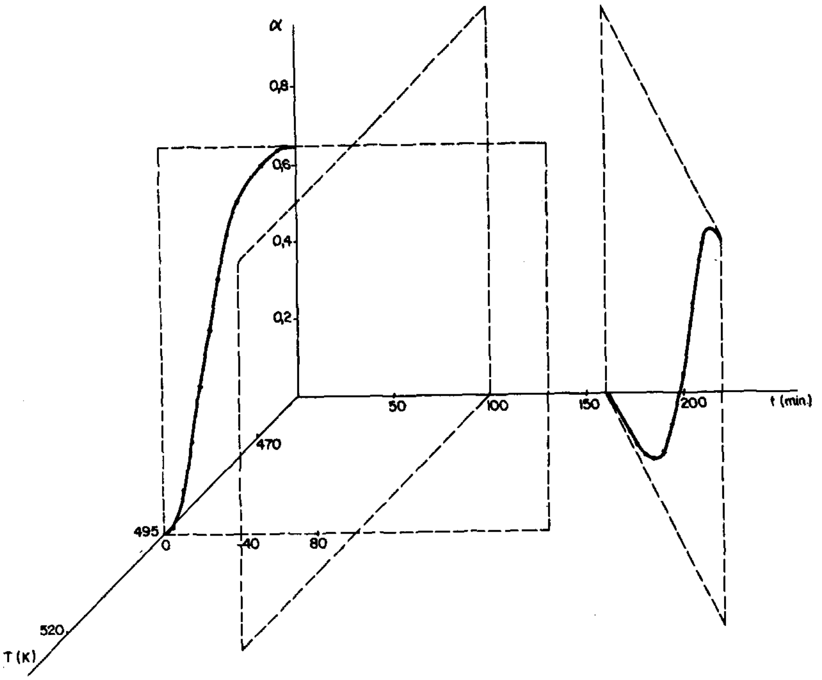

Fig. 2. Three-dimensional representation of isothermal and non-isothermal ($\beta = 1°\text{C min}^{-1}$) curves and derivation planes.

To obtain the relation between T and T' we proceed as follows. Equating eqns. (6) and (14)

$$A \exp\left(-\frac{E}{RT}\right) = A \exp\left(-\frac{E}{RT'}\right)\left[1 + \frac{E}{RT'^2}(T - T_0)\right] \tag{16}$$

From eqn. (16)

$$T' = \frac{T}{1 + \frac{RT}{E} \ln\left[1 + \frac{E(T - T_0)}{RT'^2}\right]} \tag{17}$$

and using eqns. (15) and (17)

$$T' = \frac{T}{1 + T(T - T_0)/(r_T/r_{T'} - 1)T'^2 \ln\frac{r_T}{r_{T'}}} \tag{18}$$

If the reaction occurs under isothermal conditions the time development of α is given by

$$\int_0^\alpha \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = A \exp\left(-\frac{E}{RT}\right)\int_0^t \mathrm{d}t \tag{19}$$

Coupling various isothermal tests each described by eqn. (19) we obtain the hypothetical variation of α with time and temperature by the relation

$\alpha = \mathrm{IF}(t, T)$ (eqn. 19)

Where IF is the isothermal function. Assuming by analogy with a non-isothermal experiment that a temperature–time relation obeys eqn. (3), then this relation may be given as

$$\alpha = \mathrm{IF}(t, \beta); \int_0^\alpha \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = A \exp\left[- \frac{E}{R(T_0 + \beta t)} \right] \int_0^t \mathrm{d}t \tag{20}$$

$$\alpha = \mathrm{IF}(T, \beta); \int_0^\alpha \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = A \exp\left(- \frac{E}{RT} \right) \int_{T_0}^T \frac{\mathrm{d}T}{\beta} \tag{21}$$

By combining the time derivative of eqn. (19) with eqn. (3)

$$\frac{1}{\mathrm{f}(\alpha)} \frac{\mathrm{d}\alpha}{\mathrm{d}t} = A \exp\left(- \frac{E}{RT} \right) + \frac{E}{RT^2} A \exp\left(- \frac{E}{RT} \right) t\beta \tag{22}$$

or

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = r_T \left(1 + \frac{E}{RT^2} \beta t \right) \tag{23}$$

Derivation of eqn. (20) gives

$$\frac{1}{\mathrm{f}(\alpha)} \frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{E\beta}{R(T_0 + \beta t)^2} A \exp\left(- \frac{E}{RT} \right) t + A \exp\left[- \frac{E}{R(T_0 + \beta t)} \right] \tag{24}$$

identical to eqn. (23).

The temperature derivate of eqn. (21) gives

$$\frac{1}{\mathrm{f}(\alpha)} \frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{E}{RT^2} A \exp\left(- \frac{E}{RT} \right) \frac{(T - T_0)}{\beta} + A \exp\left(- \frac{E}{RT} \right) \frac{1}{\beta} \tag{25}$$

From this and eqn. (3) we may obtain eqn. (23).

In other words eqn. (23) would allow determination of the reaction rate r_T, if $\mathrm{d}\alpha/\mathrm{d}t$ was determined on a curve drawn by hypothetical sequence (IF) of isothermal reactions. Evidently this (IF) curve is not obtained in non-isothermal tests but the NIF curve. Consequently the reaction rate could be determined from non-isothermal tests by using eqns. (6), (7) or (14).

PROCEDURES TESTING

To test the validity of the suggested procedures to calculate reaction rates we have selected the following kinetic equation

$$r = K2(1 - \alpha)[-\ln(1 - \alpha)]^{1/2} \tag{26}$$

where $K = A\ \exp(-E/RT)$; $A = 6.10^{11}$ min^{-1} and $E = 30$ kcal mol^{-1}.

Integration of eqn. (5) applying Simpson's rule ($T_0 = 300$ K, $\Delta T = 1$ K) to the right-hand side gives the $(\alpha - T)$ values in Table 1 for six heating rates.

From the $\alpha - T$ values and eqn. (3) the values for the derivative $(\mathrm{d}\alpha/\mathrm{d}t)$ at six different points for each β value have been obtained. Taking the temperature and the corresponding transformed fraction at each point the reaction rate (r_T) is calculated using eqn. (26). As an example, the reaction rates and the derivative values for a heating rate ($\beta = 2$) are gathered in Table 2. (This is a testing of eqns. 6 and 7.)

The $\mathrm{d}\alpha/\mathrm{d}t$ values are similar to the r_T values at corresponding points. This is true for any heating rate.

To test the validity of eqns. (15) and (17) and the meaning of $r_{T'}$, Table 3 has been prepared in the following way.

From data in Table 1 for a given T_i, and keeping in mind eqn. (3), the isothermal curves generated by intersection of the non-isothermal curves with the T_i plane are drawn. To draw these curves the same number of α–T points as heating rates are available. It is on the isothermal curves that the derivatives are obtained.

TABLE 1

Conversion and temperature at different heating rates (°C min^{-1})

T (K)	α					
	$\beta = 0.5$	1	2	5	10	20
460	0.009	0.002				
470	0.040	0.010	0.003			
475	0.080	0.021	0.005			
480	0.154	0.041	0.010	0.001		
485	0.283	0.080	0.021			
490	0.479	0.150	0.040	0.006	0.002	
495	0.717	0.271	0.076		0.003	
500	0.910	0.453	0.150	0.024	0.006	0.002
505	0.989	0.679	0.248			
510	1	0.880	0.411	0.081	0.021	0.005
515		0.980	0.623			
520		0.999	0.831	0.247	0.068	0.018
525			0.960	0.400		
530			0.997	0.598	0.204	0.055
535			1	0.800	0.305	
540				0.940	0.504	0.161
545				0.992	0.702	
550				1.0	0.874	0.404
555					0.970	0.585
560					0.997	0.775
565					1.0	0.916
570						0.983
575						0.999

TABLE 2

Values of the derivatives and reaction rates ($\beta = 2$)

T (K)	α	Derivative (min^{-1})	r_T (min^{-1})
490	0.040	0.011	0.010
500	0.150	0.030	0.032
510	0.411	0.073	0.072
515	0.623	0.084	0.083
520	0.831	0.068	0.066
525	0.960	0.026	0.028

TABLE 3

Values of the derivatives and reaction rates for isothermal and non-isothermal reactions ($T = 500$ K, $T' = 458.6$ K)

t (min)	α	$\frac{d\alpha}{dt}$ (min^{-1})[a]	$r_{T'}$ (min^{-1})[b]	r_T (min^{-1})[c]	r_T (min^{-1})[d]	r_T (min^{-1})[e]
400	0.910	7.69×10^{-4}	8.43×10^{-4}	0.012	0.013	0.013
200	0.453	3.33×10^{-3}	2.57×10^{-3}	0.051	0.039	0.039
100	0.150	2.44×10^{-3}	2.07×10^{-3}	0.037	0.032	0.032
40	0.024	1.16×10^{-3}	9.19×10^{-4}	0.018	0.014	0.014

[a] Derivatives from isothermal curves.

[b] $r_{T'}$ from (19).

[c] r_T from eqn. (15). $r_{T'}$ from isothermal curves, T' from eqn. (17).

[d] r_T from eqn. (19).

[e] r_T from eqn. (15). $r_{T'}$ from eqn. (19), T' from eqn. (17).

For each T_i, T_i' is calculated using eqn. (17) and r_T through eqn. (26); e.g., Table 3 shows the derivatives (column 1) and $r_{T'}$ values (column 2) for a given temperature ($T = 500$, $T' = 458.6$). The following column shows r_T values calculated from eqn. (15); where $r_{T'}$ is the derivative value from the isothermal curves and T' is calculated from eqn. (17).

Finally, r_T values calculated from eqn. (26) are gathered in column 4 while in column 5 are the r_T values calculated from eqn. (15), where $r_{T'}$ is calculated from eqn. (26) and T' from eqn. (17).

A good agreement is observed among the values in the equivalent columns of Table 3.

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