Thermochimica Acta, 32 (1979) 205–211

DETERMINATION OF REACTION KINETICS BASED ON A PART OF A DIFFERENTIAL THERMAL ANALYSIS OR THERMOGRAVIMETRIC CURVE

Ž. D. ŽIVKOVIĆ*
Faculty of Mining and Metallurgy in Bor, University of Beograd, 19210 Bor (Yugoslavia)
B. DOBOVIŠEK
Faculty of Natural Science and Technology, University of Ljubljana, 61000 Ljubljana (Yugoslavia)

(Received 3 October 1978)

ABSTRACT

A method is suggested for the kinetic consideration of a differential thermal analysis (DTA) or thermogravimetric (TG) curve which is based on a relation for the first-order reaction rate and Arrhenius's equation.

The suggested method was tested on several different systems and during these tests it was established that, by using a part of a TG or DTA curve up to maximum reaction rate, one can obtain satisfactory results.

INTRODUCTION

There are numerous methods for the determination of reaction kinetics based on thermogravimetric (TG) or differential thermal analysis (DTA) results, which are based on the determination of kinetic parameters using one[1–4] or several curves obtained with different heating rates[5].

Kinetic studies based on one DTA or TG curve are of special interest because they make it possible to derive very quickly, the necessary kinetic parameters. These are in good agreement with results obtained in classic isothermal studies[6].

The method due to Borchardt and Daniels[1] for the kinetic consideration of a DTA curve is well known. In defining this method, the starting point was a large number of parameters that showed great influence and a complex relation was obtained which, as such, has little practical value. After that, a large number relations were determined, especially for application to heterogeneous systems, until one was obtained which did have a practical value[7].

In recent literature[8, 9] for the kinetic processing of DTA results, other methods

---

[*] To whom correspondence should be addressed.

have been reported which use quite complex relations and for the solution of which current computer technique is used.

In this area, the method used by Dobovišek and Sever[10] for isothermal DTA in the oxidation of carbon should be pointed out. The derivation of DTA for other systems (carbonates, hydroxides, sulphides etc.) under isothermal conditions is very difficult to achieve and therefore this method has not yet found a wider application.

Using the idea of Chatterjee[2], which was proved in considering TG results, and the results of Dobovišek and Sever[10] for isothermal DTA, a method is defined for the determination of the reaction kinetics from a part of a DTA or TG curve which characterises a starting point of the process.

KINETIC METHOD FOR THE DETERMINATION OF REACTION KINETICS BASED ON A PART OF A DTA OR TG CURVE

Thermal decomposition processes of solid components belong to the group of first-order reactions ($n = 1$).

If the initial concentration of reactants is a moles and, after a time t, x moles of starting materials react, the concentration of the starting materials after a time t will be $(a - x)$ moles. For a first-order reaction, the expression

$$\ln\left(\frac{a}{a-x}\right) = kt \tag{1}$$

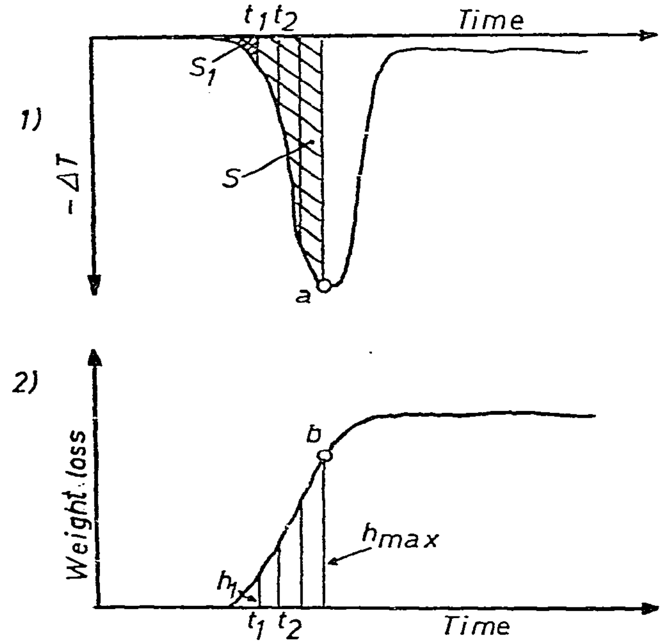

Fig. 1. Determination of reaction kinetics based on a part of the DTA or TG curve. (1) For the case of DTA curve; (2) for the case of TG curve.

is valid where k is the rate constant of the reaction. If k is expressed as an Arrhenius equation, then

$$k = A\mathrm{e}^{-E/RT} \tag{2}$$

where E is the activation energy, A the frequency factor, R the universal gas constant and T the absolute temperature.

By substituting eqn. (2) into eqn. (1) and rearranging the logarithmic base, the following expression is obtained.

$$\log\left\{\frac{\ln[a/(a-x)]}{t}\right\} = \log A - \frac{E}{2.303\ RT} \tag{3}$$

If $\log\{\ln[a/(a - x)]/t\}$ is plotted against $1/T$, a straight line is obtained from the slope of which it is possible to determine the value of the activation energy, E.

Equation (3) may be applied to DTA or TG curves. For DTA curves, the quantity of reacted substance is proportional to the area under the peak, and for TG curves it is proportional to the height of the slope from the base line (Fig. 1).

If the process is observed up to maximum rate, these are points a and b on the DTA and TG curves in Fig. 1, and eqn. (3), adjusted for these conditions, may be written

$$\log\left\{\frac{\ln[S/(S-S_t)]}{t}\right\} = \log A - \frac{E}{2.303\ RT} \tag{4}$$

for the DTA curve and

$$\log\left\{\frac{\ln[h_{\max}/(h_{\max}-h_t)]}{t}\right\} = \log A - \frac{E}{2.303\ RT} \tag{5}$$

for the TG curve where S is the area under the DTA peak up to the maximum reaction rate, S_t the area under the DTA peak after time t, $h_{\max}$ the height of the TG curve up to maximum reaction rate and h_t the height of the TG curve after time t.

If eqn. (3) should be applied to a complete DTA or TG curve, then the quantity S in eqn. (4) would represent the total area of the DTA peak and $h_{\max}$ in eqn. (5) would be the maximum height of the TG curve at the end of the process.

EXPERIMENTAL CHECK OF THE SUGGESTED METHOD

An experimental check of the application of eqns. (4) and (5) was carried out on samples of magnesite and calcite with mean particle diameters of 20 and 18 μm, respectively, with a concurrent check by processing the same results by the method of Borchardt and Daniels[1] for the case of the DTA curve, and that of Chatterjee[2] in the case of the TG curve. The relationships obtained for eqns. (4) and (5) are shown in Figs. 2 and 3.

The results show that there exists a linear relationship in all cases. By the least squares method, slopes of the most probable curves were determined, which made it

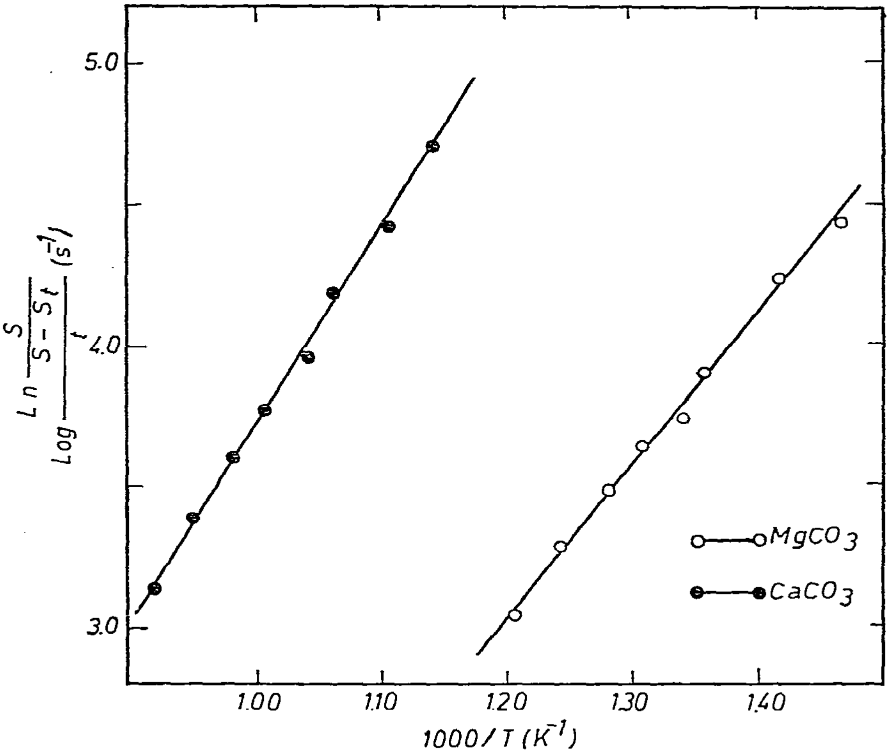

Fig. 2. Arrhenius diagrams for $MgCO_3$ and $CaCO_3$ obtained from eqn. (4).

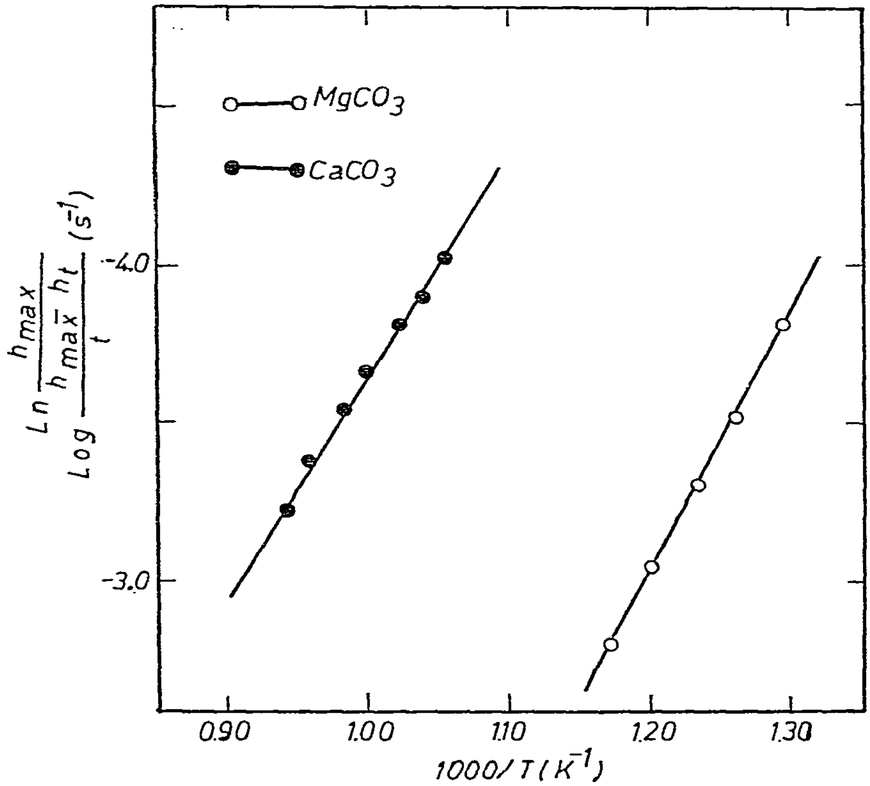

Fig. 3. Arrhenius diagrams for $MgCO_3$ and $CaCO_3$ obtained from eqn. (5).

TABLE 1

VALUES OF THE ACTIVATION ENERGY FOR THE THERMAL DECOMPOSITION OF $MgCO_3$ AND $CaCO_3$ OBTAINED BY DIFFERENT METHODS

Reaction	*Activation energy (kJ mole^{-1})*			
	DTA		*TG*	
	Part of the curve, eqn. (4)	*Borchardt and Daniels*	*Part of the curve, eqn. (5)*	*Chatterjee*
$MgCO_3 = MgO + CO_2$	106	111	127	188
$CaCO_3 = CaO + CO_2$	126	130	114	206

TABLE 2

VALUES OF THE ACTIVATION ENERGY FOR THE THERMAL DECOMPOSITION OF SOLIDS OBTAINED BY DIFFERENT METHODS

Reaction	*Activation energy (kJ mole^{-1})*			
	DTA		*TG*	
	Part of the curve to max. rate, eqn. (4)	*Borchardt and Daniels*	*Part of the curve to max. rate, eqn. (5)*	*Chatterjee*
$CuCO_3Cu(OH)_2 = 2CuO + CO_2 + H_2O$	101	110	48	71
$Ca(OH)_2 = CaO + H_2O$	182	164	117	142
$Al(OH)_3 = AlOOH + H_2O$	46		$T < 530$ K, 1.09 $T > 530$ K, 82	$T < 526$ K, 15 $T > 526$ K, 116
$2\,AlOOH = Al_2O_3 + H_2O$	186		$T < 750$ K, 6.16 $T > 750$ K, 88	$T < 700$ K, 0.20 $T > 700$ K, 92
$3\,PbCO_3 = 2\,PbO \cdot PbCO_3 + 2\,CO_2$	87	113	123	118
$2\,PbO \cdot PbCO_3 = 3\,PbO + CO_2$	298	245	245	235
$3\,(PbCO_3)_2Pb(OH)_2 = 3\,(PbO)_2PbCO_3 + 3\,CO_2 + 3\,H_2O$	82	90	136	157
$3\,(PbO)_2PbCO_3 = 9\,PbO + CO_2$	250	232	206	208

possible to calculate the corresponding values for the activation energy. The results obtained, together with those obtained by using other methods, are shown in Table 1. From these, it is evident that the values obtained for the activation energy of the processes studied, from a part of a DTA and TG curve (up to the maximum rate of reaction) and those obtained by methods reported in the literature, show very good

TABLE 3

VALUES OF THE ACTIVATION ENERGY FOR THE THERMAL DECOMPOSITION OF SOLIDS OBTAINED FROM A PART OR THE WHOLE OF THE DTA AND TG CURVES BY EQNS. (4) AND (5)

Reaction	*Activation energy (kJ mole^{-1})*			
	DTA eqn. (4)		*TG eqn. (5)*	
	Part of curve to max. rate	*Complete curve*	*Part of curve to max. rate*	*Complete curve*
$MgCO_3 = MgO + CO_2$	106	79	127	103
$CaCO_3 = CaO + CO_2$	126	92	114	92
$Ca(OH)_2 = CaO + H_2O$	182	161	117	86
$3\ PbCO_3 = 2\ PbO \cdot PbCO_3 + 2\ CO_2$	87	61	123	96
$2\ PbO \cdot PbCO_3 = 3\ PbO + CO_2$	298	240	245	201
$3\ (PbCO_3)_2Pb(OH)_2 =$ $3\ (PbO)_2PbCO_3 + 3\ CO_2 + 3\ H_2O$	82	58	136	102
$3\ (PbO)_2PbCO_3 = 9\ PbO + CO_2$	250	231	206	139

agreement. It may be observed that the values of the activation energy obtained by Chatterjee's method are slightly higher than those based on the thermogravimetric results for both $MgCO_3$ and $CaCO_3$.

By application of the proposed method to the determination of the reaction kinetics for other systems, it was established, in the same way as for $MgCO_3$ and $CaCO_3$, that the values determined for the activation energy of the systems studied were in good agreement with the corresponding values obtained by methods widely quoted in the literature. The results obtained are shown in Table 2.

Equations (4) and (5) may also be applied to complete DTA and TG curves, as already pointed out, and not only up to the maximum rate of the processes studied. In this case, the area S in eqn. (4) represents the total area of the DTA peak and $h_{\max}$ in eqn. (5) the maximum height at the end of the process.

The results obtained by processing the curves for several different systems by both methods (a part of the curve up to the maximum rate of the reaction and the complete curve) are shown in Table 3.

The results presented in Table 3 show that, for both DTA and TG curves, the values obtained from the complete curve are 20–30 kJ mole^{-1} lower than those obtained by considering the process up to the maximum reaction rate. This is probably due to the greater influence of diffusion resistance after the maximum reaction rate has been reached.

It was observed that, for those processes where the DTA peaks are extremely elongated, i.e. the duration of which is very short, very high values of the activation energy are obtained and that scattering of the points in the Arrhenius diagrams is very marked. This shows that the suggested method could not be applied with satisfactory accuracy to those DTA peaks which are relatively narrow, because in splitting up the process into time intervals, an error is made in the determination of the areas under the curves after a certain process duration.

Considering the relatively good agreement between the results obtained by considering processes up to the maximum rate of the reaction with those obtained by other methods, the suggested method may be recommended for this type of determination.

REFERENCES

1 H. J. Borchardt and F. Daniels, *J. Am. Ceram. Soc.*, 79 (1957) 41.
2 P. K. Chatterjee, *J. Polym. Sci. Part A*, 3 (1965) 4253.
3 E. S. Freeman and B. Carrol, *J. Phys. Chem.*, 62 (1958) 394.
4 V. Šatava, *Thermochim. Acta*, 2 (1971) 423.
5 H. E. Kissinger, *Anal. Chem.*, 29 (1957) 1702.
6 Ž. D. Živković, *Rud. Metal. Zb.*, 4 (1977) 359.
7 H. J. Borchardt, *J. Inorg. Nucl. Chem.*, 12 (1960) 252.
8 R. Altorfer, *Thermochim. Acta*, 24 (1978) 17.
9 P. Holba, M. Nevriva and J. Šestak, *Thermochim. Acta*, 23 (1978) 223.
10 B. Dobovišek and L. Sever, *Rud. Metal. Zb.*, 3 (1957) 253.