*Thermochimica Acta,* 157 (1990) 89–93
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

# COMPUTER SIMULATION OF THERMOGRAVIMETRIC CURVES FOR CARBONATE DECOMPOSITION IN CARBON DIOXIDE ATMOSPHERES

H.J. HURST

*CSIRO Division of Fuel Technology, Lucas Heights Research Laboratories, Private Mail Bag 7, Menai, NSW 2234 (Australia)*

(Received 10 May 1989)

## ABSTRACT

Thermogravimetric curves have been calculated by numerical predictor–corrector methods using a first order equation including a pressure term allowing for chemisorption of carbon dioxide at the reaction interface. The results simulate the observed experimental behaviour and demonstrate the compensation effect over a narrow pressure range.

## INTRODUCTION

The application of computer solutions using numerical predictor–corrector methods to model the thermal decomposition of solids [1–4] is now increasingly applied to the analysis of thermogravimetric (TG) curves and their derivatives (DTG). This note shows that the approach can be extended to model carbonate decomposition in carbon dioxide atmospheres.

## MODEL

In a number of studies of carbonate decomposition in carbon dioxide atmospheres [5–7], Criado analysed the TG curves using the first order expression

$$\frac{\mathrm{d}x}{\mathrm{d}T} = (1-\alpha)\frac{A'}{H}\mathrm{e}^{-E'/RT} \tag{1}$$

to obtain values of the parameters $A'$ and $E'$ in the Arrhenius equation, and qualitatively observed that the behaviour may be explained by the modified expression

$$\frac{\mathrm{d}x}{\mathrm{d}T} = (1-\alpha)\frac{A}{H}\ \mathrm{e}^{-E/RT}\frac{1}{1+aP} \tag{2}$$

0040-6031/90/$03.50

where the pressure dependent term arises from a Langmuir treatment of adsorption at the reaction surface. The term $a$ is given by

$$a = a_0 \, e^{E_1/RT} \tag{3}$$

As the pressure of carbon dioxide increases, the reaction rate given by eqn. (2) decreases, and the TG curves move to higher temperatures. In addition, the apparent activation energy $E'$ given by eqn. (1) varies from $E$ when $aP \ll 1$ to $E + E_1$ when $aP \gg 1$.

One such example is the thermal decomposition of cadmium carbonate [6], where the apparent activation energy increases rapidly from 80 kJ mol$^{-1}$ at zero pressure to ca. 280 kJ mol$^{-1}$ at 10 kPa of carbon dioxide. The DTG curves show that the maximum mass loss rate shifts to a higher temperature with increasing pressure, and reaches a maximum value.

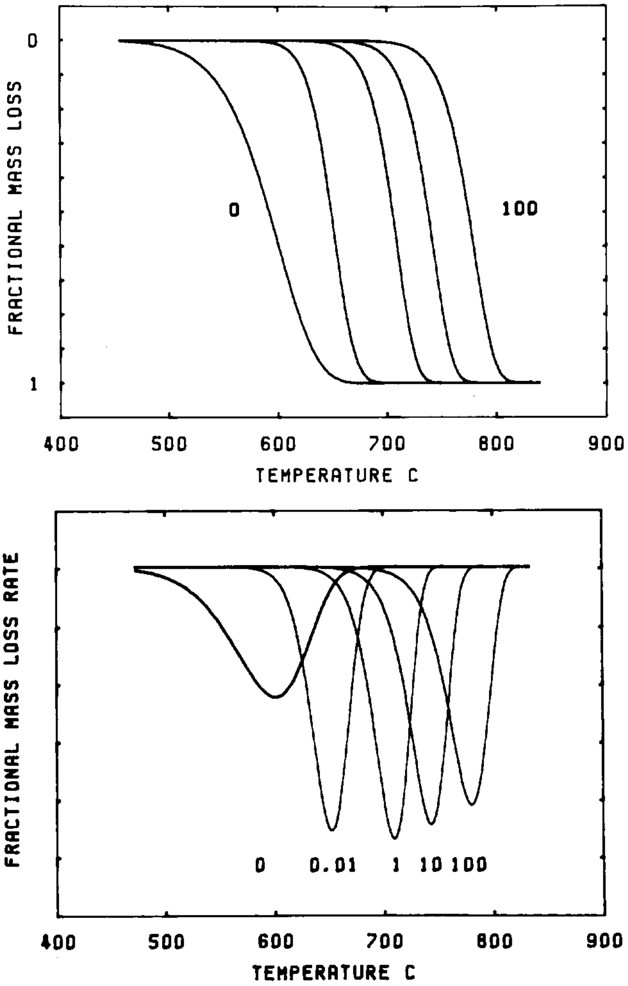

Fig. 1. Variation of calculated TG and DTG curves with pressure.

## RESULTS

Computer solutions of eqn. (2) have been found by predictor–corrector methods using the following parameters: $A = 7.0 \times 10^8$ min$^{-1}$; $H = 10.0$ C min$^{-1}$; $E = 85$ kJ mol$^{-1}$; $a_0 = 1.0 \times 10^{-14}$ kPa$^{-1}$; $E_1 = 200$ kJ mol$^{-1}$; $P = 0$–$100$ kPa.

The results for the calculated TG and DTG curves are shown in Fig. 1. It can be seen that they simulate both the experimental behaviour of sharpening the TG curves and the shift to higher temperatures with increasing pressure, and the variation of the DTG curves with temperature, with the maximum near 700 °C.

Apparent activation energies $E'$ and pre-exponential constants $A'$ were obtained by comparing TG curves calculated from eqn. (1) with those calculated from eqn. (2) using the above parameters displayed on a VDU screen. Because of the interdependence of $A'$ and $E'$, there is a range of values giving visual fits with the calculated TG curve, so the best $A'$ and $E'$ values were selected by matching their maximum rate loss with the calculated DTG curves. A plot of the apparent activation energy against carbon dioxide pressure (Fig. 2) shows the effect of varying the parameter $a_0$. The curve with $a_0 = 10^{-14}$ demonstrates the rapid change of $E'$ from 85 to 285 kJ mol$^{-1}$ with pressure that was observed by Criado. It is not claimed that the chosen parameters apply to cadmium carbonate, and fine tuning of the $aP$ term will affect the position of the TG curves, but it is apparent that the model successfully simulates the observed experimental behaviour.

Figure 3 shows a plot of log $A'$ against $E'$ for values of the apparent pre-exponential constant and activation energy. It is clear that the initial

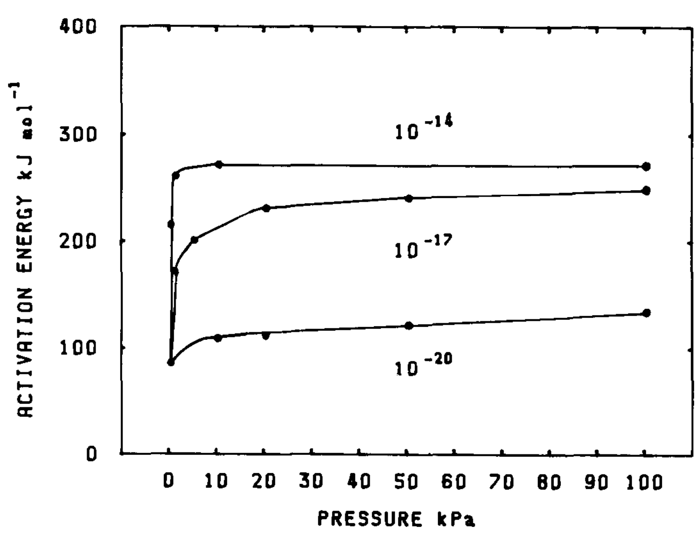

Fig. 2. Variation of apparent first order activation energy with pressure for values of $a_0$.

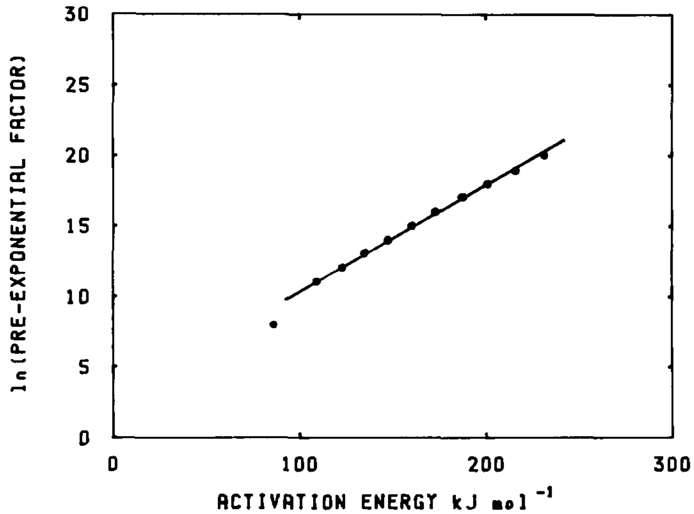

Fig. 3. Compensation effect plot.

TABLE 1

Interdependence of Arrhenius parameters

| $E'$ | $A'$ | $E'$ | $A'$ | $E'$ | $A'$ | $\Delta \log A/\Delta E$ |
|---|---|---|---|---|---|---|
| 120 | $10^{12}$ | 109 | $10^{11}$ | 98 | $10^{10}$ | 0.09 |
| 242 | $10^{21}$ | 230 | $10^{20}$ | 217 | $10^{19}$ | 0.08 |

part of the curve, with carbon dioxide pressures in the range 1–10 kPa, follows the linear expression

$$\log A' = 3.0 + 0.074\ E'$$

known as the compensation effect. This topic has been recently reviewed [8] and various reasons advanced for such behaviour. In this case, the relationship probably arises from fitting an incorrect model to the data and from the interdependence of the $A'$ and $E'$ values. This is demonstrated in Table 1, which gives the values of $A'$ and $E'$ pairs that give superimposable TG curves for the limits of the compensation effect plot.

It is noticeable that the value of the ratio $\Delta \log A/\Delta E$ does not alter greatly, and is close to the value of the slope of the compensation plot.

## CONCLUSIONS

The model successfully predicts the observed behaviour of the thermal decomposition of cadmium carbonates in carbon dioxide atmospheres. Verification of the model requires firstly accurate experimental data, because of the large effects caused by small changes in pressure, and secondly analysis of these data by non-linear least-squares techniques.

The increases in speed and memory size of minicomputers mean that experimental data may be rapidly compared with calculations based on models for different mechanisms for the rate determining process. The ultimate goal of obtaining useful kinetic parameters from the analysis of non-isothermal experiments may then be possible.

## ACKNOWLEDGEMENT

The author wishes to thank W.I. Stuart for his assistance.

## REFERENCES

1 I.C. Hoare and W.I. Stuart, Thermochim. Acta, 113 (1987) 53.
2 W.I. Stuart and J.H. Levy, Proc. 14th Conf. of the North American Thermal Analysis Society, San Francisco, CA, September 15–18, 1985.
3 I.C. Hoare and W.I. Stuart, Proc. 15th Conf. of the North American Thermal Analysis Society, Cincinnati, OH, September 21–24, 1986.
4 I.C. Hoare, H.J. Hurst, W.I. Stuart and T.J. White, J. Chem. Soc., Faraday Trans. 1, 84 (1987) 3071.
5 J.M. Criado, F. Gonzalez and M. Gonzalez, J. Therm. Anal., 24 (1982) 59.
6 J.M. Criado, M. Gonzalez and M. Macias, Thermochim. Acta, 113 (1987) 31.
7 J.M. Criado, M. Gonzalez and M. Macias, Thermochim. Acta, 113 (1987) 39.
8 G. Pokol and G. Varhegyi, CRC Crit. Rev. Anal. Chem., 19 (1988) 65.