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The effect of the CO_2 pressure on the thermal decomposition kinetics of calcium carbonate

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Abstract

The influence of the pressure of carbon dioxide on the thermal decomposition kinetics of calcium carbonate is studied. It is shown that it is possible to obtain meaningful and reliable kinetic parameters from isothermal and non-isothermal data provided that the pressure correction term is included in the kinetic equation.

Keywords: Calcium carbonate; Carbon dioxide; Decomposition; Kinetics; Pressure

1. Introduction

The thermal decomposition kinetics of calcium carbonate has been studied intensively by a large number of authors over many years. Thus, one might assume that this reversible decomposition process could be considered as a textbook case for kinetic studies. However, a more detailed inspection of published papers shows that there are many different values given for the activation energy and different mechanisms are given for the decomposition process. A statistical survey of the published values for the activation energy has been carried out [1].

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This scatter in the kinetic data has led some authors to conclude that it is impossible to characterize a reversible solid state decomposition by one value of the activation energy and that the kinetic mechanism varies under different experimental conditions [1]. This statement is interesting when considered together with the conclusion of a paper published ten years earlier [2] "... when reversible reactions of thermal decomposition of solids are concerned, an abrupt sharpening of TDA or DTG diagrams because of the pressure would be expected without assuming any change of the reacton mechanism."

This problem was recently analysed and discussed in a comprehensive paper by Reading et al. [3], in which the authors successfully applied the constant rate thermal analysis (CRTA) method developed by Rouquerol [4] which has significant advantages for solid state decomposition studies [5]. The aim of the present paper is to show that conventional thermal analysis experiments also yield correct values of the kinetic parameters when the partial pressure of carbon dioxide is controlled precisely.

2. Theory

The course of the solid state thermal decomposition processes is usually described by the equation

$$(\mathrm{d}\alpha/\mathrm{d}t) = k(T)f(\alpha) \tag{1}$$

where α is the degree of conversion, n is the reaction order, $k(T)$ is the Arrhenius rate constant and $f(\alpha)$ is an algebraic function depending on the reaction mechanism. It was shown by several authors [3,6-8] that for the reversible decomposition of calcium carbonate the rate constant can be expressed as

$$k(T) = A\exp(-\Delta E/RT)(1 - p/p^*) \tag{2}$$

where A is the pre-exponential factor, E is the activation energy, p is the partial pressure of CO_2 and p^* is the equilibrium pressure of CO_2. The temperature dependence of the equilibrium pressure can be expressed by [2,9]

$$p^*/\mathrm{kPa} = 1.87 \times 10^9 \exp(-19697/T) \tag{3}$$

Thus, combining Eqs. (1)-(3) we obtain the kinetic equation for the decomposition of calcium carbonate

$$(\mathrm{d}\alpha/\mathrm{d}t) = A\exp(-\Delta E/RT)f(\alpha)(1 - p/p^*) \tag{4}$$

If the thermal decomposition is carried out in an isothermal manner, $k(T)$ is a constant, and from Eq. (4) one obtains after integration

$$g(\alpha) = \int \frac{\mathrm{d}\alpha}{f(\alpha)} = k(T)t \tag{5}$$

The functions $f(\alpha)$ and $g(\alpha)$ corresponding to the kinetic models most commonly used in the literature for describing solid state reactions are summarized in Table 1.

Table 1
Algebraic expressions for $f(\alpha)$ and $g(\alpha)$ functions for the most common mechanisms operating in solid state reactions

Mechanism		$f(\alpha)$	$g(\alpha)$
Phase boundary controlled reaction (contracting area)	R2	$(1-\alpha)^{1/2}$	$2[1-(1-\alpha)^{1/2}]$
Phase boundary controlled reaction (contracting volume)	R3	$(1-\alpha)^{1/3}$	$3[1-(1-\alpha)^{1/3}]$
Unimolecular decay	F1	$(1-\alpha)$	$-\ln(1-\alpha)$
Random nucleation and growth of nuclei (Avrami-Erofeev)	Am	$m(1-\alpha)[-\ln(1-\alpha)]^{1-1/m}$	$[-\ln(1-\alpha)]^{1/m}$
Two-dimensional diffusion	D2	$1/[-\ln(1-\alpha)]$	$(1-\alpha)\ln(1-\alpha)+\alpha$
Three-dimensional diffusion. Jander equation	D3	$\dfrac{3(1-\alpha)^{2/3}}{2[1-(1-\alpha)^{1/3}]}$	$[1-(1-\alpha)^{1/3}]^2$
Three-dimensional diffusion. Ginstlein-Brounshtein equation	D4	$\dfrac{3}{2[(1-\alpha)^{-1/3}-1]}$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$

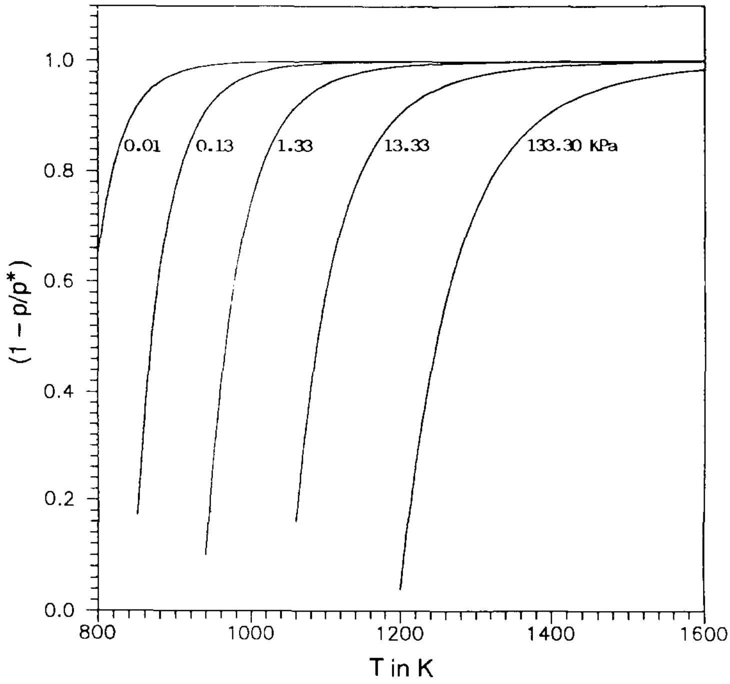

Fig. 1. The temperature dependence of the pressure correction term at different partial pressure of CO_2.

Fig. 1 shows the temperature dependences of the pressure correction term $(1 - p/p^*)$ at different pressures of carbon dioxide. One can deduce from these dependences and Eq. (4) that the reaction rate decreases with increasing partial pressure of CO_2 and, therefore, the corresponding DTA or DTG curves move to higher temperatures. However, the DTA and DTG peaks become narrower and sharper with increasing CO_2 pressure. This effect can lead to the erroneous conclusion that the decomposition mechanism changes during the course of the process. It is clear that these effects have an important influence on the value of the activation energy calculated from DTA or DTG data. If the pressure term $(1 - p/p^*)$ is neglected, the calculated value of the activation energy is overestimated, particularily at low temperature and high pressure.

This explains the well-known fact that the decomposition of calcium carbonate in vacuum leads to reasonable values of E [10,11] and decomposition under an uncontrolled atmosphere of CO_2 gives completely misleading values [12,13] for the activation energy.

3. Experimental

Analytical grade calcium carbonate (D'Hemio, A.R.) and 99.9% carbon dioxide (Coromina, S.A.) were used for the experiments. A Cahn electrobalance, model RG (sensitivity 0.2 μg) equipped with a derivation adapter Mark II was used. This instrument permits the simultaneous recording of both TG and DTG curves at pressures ranging from 1.33×10^{-5} kPa to about 25 kPa. All samples weighed about 25 mg. Non-isothermal experiments were performed at a heating rate of 12 K $\min^{-1}$ and CO_2 pressure of 1.3, 2.7, 12.0 and 20.0 kPa.

The isothermal runs were carried out by heating the sample at the desired temperature under a CO_2 pressure of 1 bar in order to prevent the thermal decomposition of $CaCO_3$. Once the steady state temperature was reached the CO_2 pressure was quickly decreased to the value selected for recording the $\alpha - T$ plot.

4. Results and discussion

Fig. 2 shows the thermogravimetric diagrams of calcium carbonate decomposition under different pressures of CO_2 and a heating rate of 12 K $\min^{-1}$. It is evident that the TG curves shift to higher temperatures with increasing pressure of carbon dioxide.

It is well known that for a reliable kinetic analysis of a single curve a kinetic model should be supposed a priori. Then it is possible to calculate reliable values for the activation energy and pre-exponential factor. In this analysis we will suppose that the decomposition of $CaCO_3$ can be described by the reaction order kinetics R3 (contracting volume, i.e. $f(\alpha) = (1 - \alpha)^{2/3}$ and $g(\alpha) = 3[1 - (1 - \alpha)^{1/3}]$), according to previous results [14] obtained for the kinetic analysis, under high vacuum, of the same sample of $CaCO_3$ used here. Then Eq. (4) can be written as

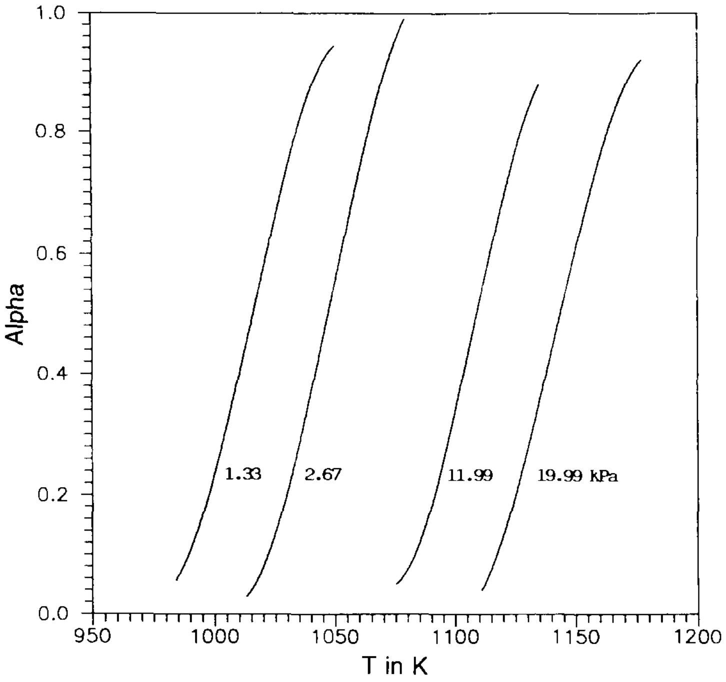

Fig. 2. Thermogravimetric curves corresponding to the thermal decomposition of calcium carbonate at different partial pressures of carbon dioxide: heating rate, 12 K min^{-1}.

$$Y = \ln \frac{(\mathrm{d}\alpha/\mathrm{d}t)(1-\alpha)^{-2/3}}{(1-p/p^*)} = \ln A - E/RT \tag{6}$$

From the intercept and slope of the Y vs. $1/T$ dependence, both the pre-exponential factor and activation energy can be determined. These dependences are shown in Fig. 3 for the experimental data plotted in Fig. 1. The calculated values of the kinetic parameters are summarized in Table 2.

Fig. 4 shows the isothermal traces of calcium carbonate decomposition under a pressure of 19.995 kPa of CO_2. The values of the activation energy and the pre-exponential factor calculated from the values of $k(T)$ determined from data in Fig. 4 by means of Eq. (5) are also included in Table 2. It is seen that if the $(1 - p/p^*)$

Table 2
The kinetic parameters of calcium carbonate decomposition at different pressures of CO_2

Method	p/kPa	E/kJ mol^{-1}	$\ln(A/\mathrm{min}^{-1})$
Non-isothermal	1.3	187	21.2
	2.7	196	21.6
	12.0	188	18.8
	20.0	195	19.7
Isothermal	20.0	187	21.7

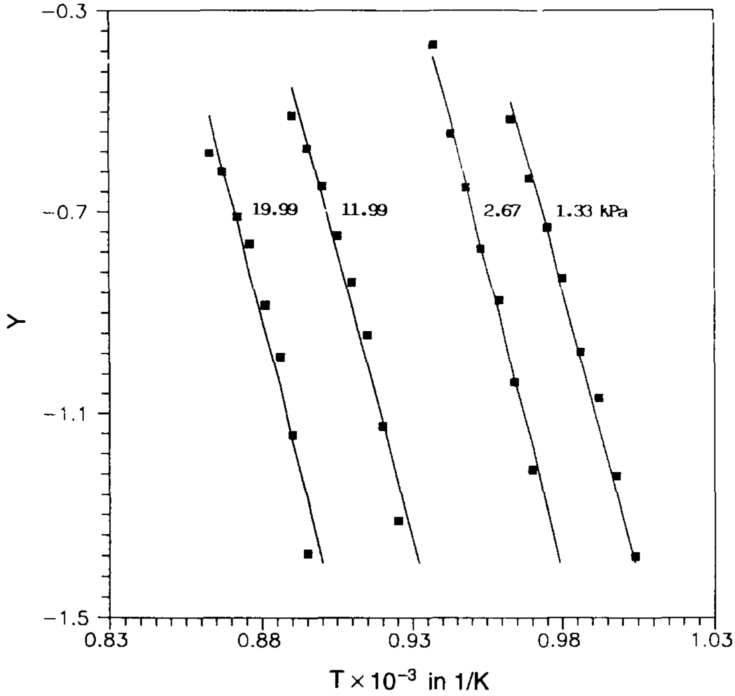

Fig. 3. Determination of kinetic parameters from experimental data shown in Fig. 2.

correction term is applied a good agreement between the values of the activation energy obtained for both isothermal and non-isothermal methods is achieved. The slight variation in E is within 5% and is usually expected in experiments of this type. The variation in the ln A value is not too surprising as this would be very sensitive to errors in the intercept of the Y vs. $1/T$ plot which do occur. The mean value of the activation energy (191 ± 5 kJ mol^{-1}) is lower than the 210 kJ mol^{-1} published by Reading et al. [15]. The difference can be explained as a consequence of thermal lag due to the relatively high heating rate (12 K min^{-1}) used for the measurement. The integral non-isothermal method has not been used because it is not possible to select the lower integration limit T_0 without a prior knowledge of the kinetic parameters.

All these results clearly support the applicability of the Arrhenius model in thermal analysis and indicate that it is very important to control the pressure of gaseous products in reversible decomposition reactions. If this effect is taken into account it is possible to obtain correct kinetic parameters even from non-isothermal data.

Acknowledgements

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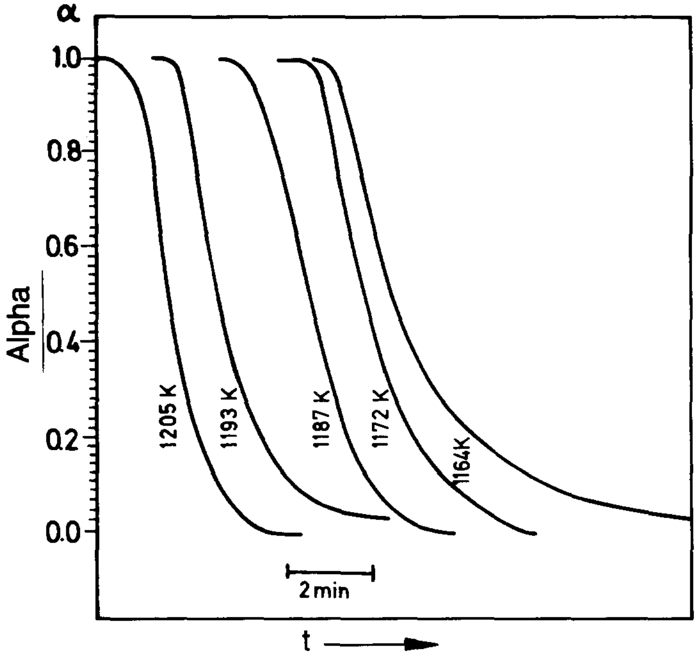

Fig. 4. Isothermal curves for the thermal decomposition of calcium carbonate.

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