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Thermochimica Acta 392–393 (2002) 135–145

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Comparison of dolomite decomposition kinetics with related carbonates and the effect of procedural variables on its kinetic parameters

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Received 18 November 2000; accepted 10 May 2001

Abstract

The three naturally occurring available carbonates in northwest Ohio are magnesite, calcite and dolomite. Dolomite is a double carbonate containing calcium and magnesium carbonate in equimolar concentrations. All three carbonates decompose via a single stage process in an atmosphere of nitrogen. The thermal behavior and the kinetics of decomposition were studied using the Arrhenius equation applied to solid-state reactions. It was found that calcite and dolomite supposedly decompose via a zero order mechanism while magnesite decomposes via a first order process. The energy of activation for the decomposition of magnesite, calcite and dolomite were 226.34, 192.50 and 175.05 kJ/mol, respectively. Similarly the ln A-values for magnesite, calcite and dolomite decomposition were 30.70, 20.73 and 18.76, respectively. Finally, the effect of procedural variables on the kinetic parameters of dolomite decomposition was investigated. The three procedural variables studied included flow rate, heating rate and sample size. The kinetic parameters and mechanism remain unaffected by a change in these variables.

Keywords: Calcite; Dolomite; Magnesite; Kinetics and procedural variables

1. Introduction

Naturally occurring dolomite [$CaMg(CO_3)_2$] is a double salt of calcium and magnesium carbonate. Limestone exists in two forms calcite and dolomite. The thermal decomposition of dolomite has been widely studied. The decomposition of dolomite in an inert nitrogen (N_2) atmosphere occurs in a single step and can be depicted by the following reaction:

$$CaMg(CO_3)_2 \rightarrow CaO + MgO + 2CO_2 \quad (1)$$

The decomposition of magnesite and calcite in an inert N_2 atmosphere can be represented as follows:

$$MgCO_3 \rightarrow MgO + CO_2 \quad (2)$$

$$CaCO_3 \rightarrow CaO + CO_2 \quad (3)$$

The kinetics for the thermal decomposition of dolomite in a vacuum has been studied by various authors [1,2]. Criado and Ortega [2] performed the kinetic studies using two different techniques, i.e. TG and constant rate thermal analysis (CRTA). They conclude that a close agreement between the kinetic parameters from the two methods allows an excellent way for determining the exact reaction mechanism. They identified the reaction mechanism as a first order

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PII: S0040-6031(02)00094-1

process (F1). The energy of activation (E) and pre-exponential factor values by TG and CRTA (in brackets) were 149.6 (146.3) kJ/mol and 5.6×10^6 (1.3×10^6) min^{-1}, respectively. The earlier study by Britton et al. [1] reported higher E-values in the range of 206.5–232.4 kJ/mol. The authors [2] state that the kinetic study by Britton et. al. used a sample mass of 400 mg and a starting vacuum of 0.01 mbar. These experimental conditions lead to a modified reaction process and a higher value for E due to mass and heat transfer phenomena. The objective of our study was to assess dolomite decomposition kinetics in a N_2 atmosphere. Our aim was to evaluate whether kinetic parameters are influenced by the procedural variables used in the kinetic study. The method used to compute the kinetic parameters is described below.

The computation of the kinetic parameters was based on the use of the Arrhenius equation applied to solid-state reactions. To obtain the kinetic parameters, a combination of equations is used which include the following:

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{4}$$

$$\ln k = \ln A - \frac{E}{RT} \tag{5}$$

Alpha (α) is the fraction reacted, $d\alpha/dt$ the rate of the reaction and $f(\alpha)$ the mathematical expression in α. Eq. (5) is the Arrhenius equation written in the log form, where k is the specific rate constant, A the pre-exponential term, E the energy of activation, R the universal gas constant and T the temperature in Kelvin. The use of the Arrhenius equation for calculating the kinetic parameters in all solid-state reactions has been the subject of debate [3–7]. However, if the Arrhenius hypothesis is accepted, then kinetic analysis of rising temperature data can be accomplished by the method described here. Sestak and Berggren [8] summarized many equations relating the rate of solid-state reactions to α. The mathematical models for the reaction mechanisms are given in Table 1.

Combining Eqs. (4) and (5) give

$$\ln\left[\frac{d\alpha/dt}{f(\alpha)}\right] = \ln A - \frac{E}{RT} \tag{6}$$

Alpha at a particular time or temperature was calculated from the weight of the sample at time or temperature t (w_t) and the initial (w_i) and final weight (w_f), using the equation

Table 1
The mathematical models for the reaction mechanisms

Type	$f(\alpha)$
Order equation	
Zero order	1
First order (F1)	$1-\alpha$
Second order (F2)	$(1-\alpha)^2$
Geometric	
Contracting area (R2)	$2(1-\alpha)^{1/2}$
Contracting volume (R3)	$3(1-\alpha)^{2/3}$
Sigmoid curve	
Avrami–Erofeev (A1.5)	$1.5(1-\alpha)(-\ln(1-\alpha))^{1/3}$
Avrami–Erofeev (A2)	$2(1-\alpha)(-\ln(1-\alpha))^{1/2}$
Avrami–Erofeev (A3)	$3(1-\alpha)(-\ln(1-\alpha))^{2/3}$
Avrami–Erofeev (A4)	$4(1-\alpha)(-\ln(1-\alpha))^{3/4}$
Prout–Tompkins (B1)	$\alpha(1-\alpha)$
Diffusion	
1D diffusion (D1)	$1/2\alpha$
2D diffusion (D2)	$-(\ln(1-\alpha))^{-1}$
3D diffusion (D3)	$1.5(1-(1-\alpha)^{1/3})^{-1}(1-\alpha))^{2/3}$
Ginstling–Brounshtein (D4)	$1.5(1-(1-\alpha)^{1/3})^{-1}$
Power law, $m > 1$ (P1)	$m(\alpha)^{(m-1)/m}$

$$\alpha = \frac{w_i - w_t}{w_i - w_f} \tag{7}$$

The differential form of Eq. (7) gives

$$\frac{d\alpha}{dt} = -\frac{dw_t/dt}{w_i - w_f} \tag{8}$$

The function (dw_t/dt) can be obtained directly from the differential thermogravimetry (DTG) plot, and the rate of the reaction can be calculated using Eq. (8). This value of $d\alpha/dt$ obtained from Eq. (8) is substituted into Eq. (6) and finally a plot of $\ln[(d\alpha/dt)/f(\alpha)]$ versus $1/T$ is constructed. This plot is directly analogous to the Arrhenius plot. Using a spreadsheet, different values of $f(\alpha)$ from Table 1 can be tested. The form of $f(\alpha)$ that gives the best straight line is selected and the mechanism corresponding to this value of $f(\alpha)$ is assigned as the mechanism for the reaction. The best straight line is chosen based on the R-squared value and the random distribution of points about the straight line. The slope of this particular plot yields the energy of activation while the y-intercept provides the pre-exponential factor (A-value) for the reaction.

2. Materials and methods

2.1. Materials

The material studied was James River White Rock Dolomite. This sample was ground for 3 h using a ceramic ball mill equipped with a General Electric AC motor. The following set of US standard sieves was used for size classification, namely the 20, 40, 60, 80 100, 120, 140, 170, 200, 230, 250, 300 and 325 mesh sieves. A Rotap Sieve Shaker was used to hasten the size classification process. The period of operation for this equipment was 1.5 h. The fraction retained on the 200-mesh sieve was used for this study. Calcium carbonate was obtained from Fisher Scientific (Lot # 966502). Thermogravimetic studies were done on a pure magnesite sample obtained from a natural source.

Table 2
The program design employed for studying the effect of individual procedural variables on the kinetics of dolomite decomposition in nitrogen

Variable studied	Flow rate (ml/min)	Heating rate (°C/min)	Sample size (mg)
Heating rate	50	5	14–20
	50	10	14–20
	50	20	14–20
	50	25	14–20
Flow rate	25	10	14–20
	50	10	14–20
	100	10	14–20
Sample size	50	10	14.6
	50	10	23.0
	50	10	40.1
	50	10	57.5

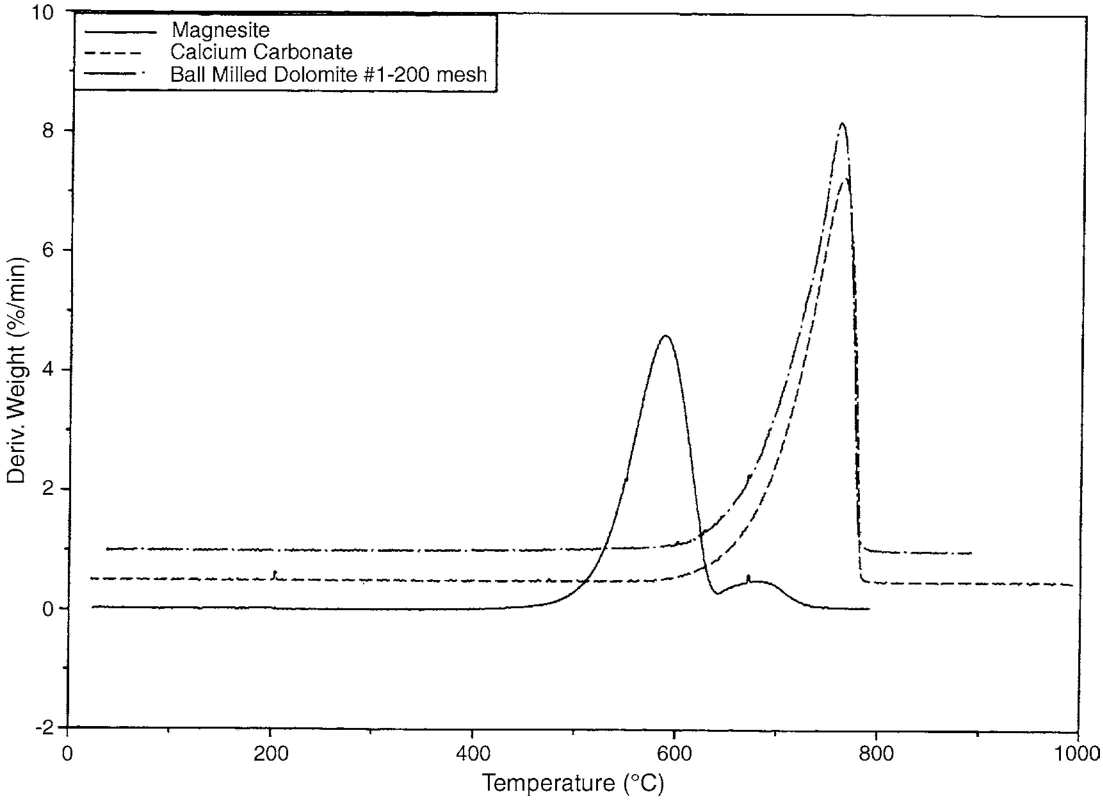

Fig. 1. Thermal decomposition of magnesite, calcium carbonate and dolomite in an atmosphere of nitrogen (flow rate 50 ml/min at a heating rate of 10 °C/min).

2.2. Equipment

The SDT 2960 simultaneous thermogravimetric analysis and differential thermal analysis (TGA-DTA) from TA Instruments, with Universal Analysis for Windows 95/NT Ver. 2.3 C, was used to examine the thermal decomposition of dolomite. An electronic flow meter from J & W Scientific, model ADM 1000, was used to regulate the flow of purge gas through the sample. Statistical analysis was performed using the SAS System for Windows (Release 6.12 TS Level 0020) loaded on a PC computer with Windows NT (Ver. 4.0) operating system.

2.3. Procedure

For comparing the decomposition behavior of the three carbonates, the samples were heated at a steady rate of 10 °C/min with the flow rate of the purge gas being maintained at 50 ml/min. Additionally, a TG run on magnesite was performed in an atmosphere of carbon dioxide (flow rate 50 ml/min and heating rate of 10 °C/min). The effect of three procedural variables on the kinetic parameters of dolomite decomposition was evaluated. While studying one variable, the other two variables were kept constant. The program design for the 11 TG runs is illustrated in Table 2.

3. Results and discussion

3.1. Comparison of the decomposition kinetics for the three carbonates

The DTG plots for the thermal decomposition of the three carbonates is depicted in Fig. 1. Magnesite decomposition in nitrogen shows an additional peak on the DTG plot. From the temperature at which the

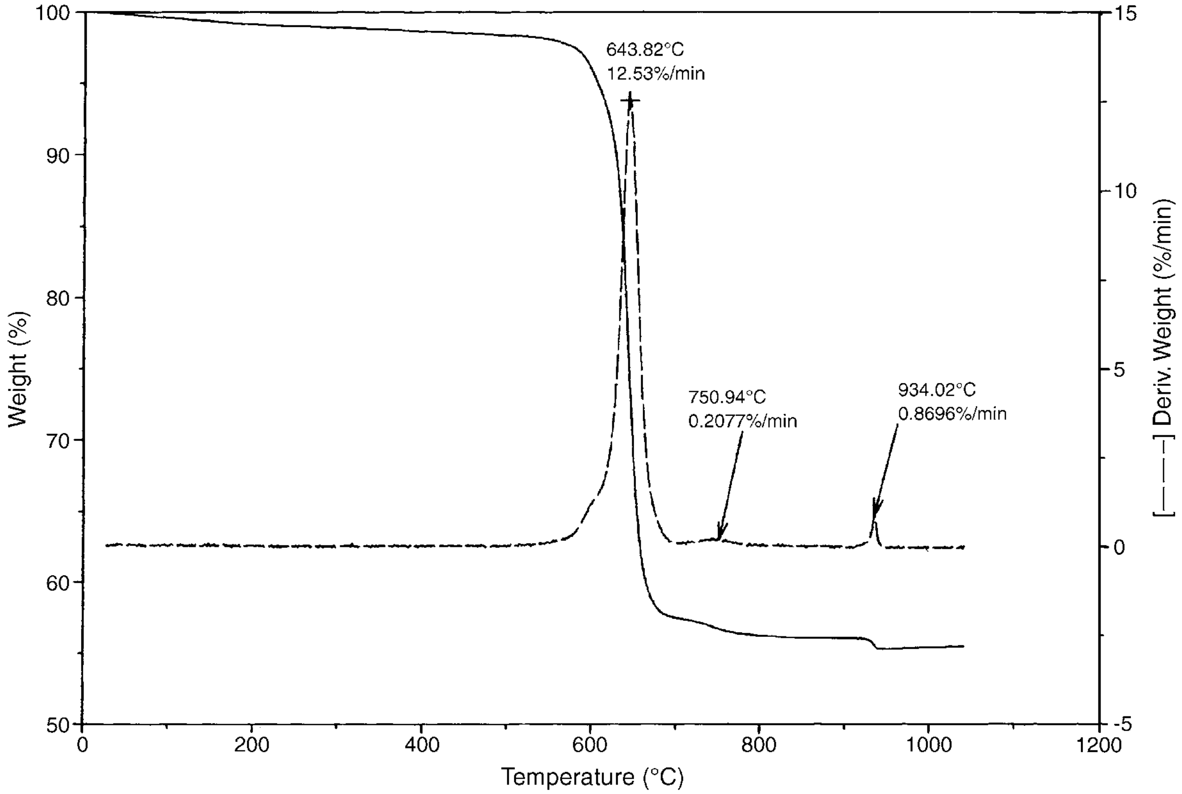

Fig. 2. TG/DTG plot of magnesite decomposition in an atmosphere of carbon dioxide. Sample indicates presence of dolomite, which appears as two separate peaks (marked by arrows) on the DTG plot.

Table 3
The spreadsheet calculations for computing the kinetic parameters for dolomite decomposition

Temperature (°C)	Weight (%)	Derivative weight (%/min)	dα/dt	ln k (min^{-1})	1/T (K)
646	97.60	0.599	0.013	−4.356	0.001088
648	97.47	0.640	0.014	−4.289	0.001086
650	97.34	0.667	0.014	−4.249	0.001083
652	97.20	0.708	0.015	−4.190	0.001081
654	97.05	0.741	0.016	−4.144	0.001079
656	96.90	0.806	0.017	−4.059	0.001076
658	96.73	0.853	0.018	−4.003	0.001074
660	96.55	0.906	0.019	−3.943	0.001072
662	96.37	0.945	0.020	−3.900	0.001069
664	96.17	0.992	0.021	−3.852	0.001067
666	95.96	1.055	0.023	−3.790	0.001065
668	95.75	1.112	0.024	−3.737	0.001063
670	95.51	1.208	0.026	−3.655	0.001060
672	95.25	1.273	0.027	−3.602	0.001058
674	95.00	1.311	0.028	−3.573	0.001056
676	94.73	1.373	0.029	−3.527	0.001054
678	94.44	1.456	0.031	−3.468	0.001051
680	94.14	1.534	0.033	−3.416	0.001049
682	93.82	1.605	0.034	−3.370	0.001047
684	93.48	1.687	0.036	−3.321	0.001045
686	93.13	1.782	0.038	−3.266	0.001043
688	92.76	1.898	0.041	−3.203	0.001040
690	92.37	1.971	0.042	−3.165	0.001038
692	91.96	2.064	0.044	−3.119	0.001036
694	91.53	2.184	0.047	−3.062	0.001034
696	91.07	2.256	0.048	−3.030	0.001032
698	90.60	2.357	0.050	−2.986	0.001030
700	90.11	2.455	0.053	−2.945	0.001028
702	89.60	2.565	0.055	−2.902	0.001025
704	89.07	2.694	0.058	−2.853	0.001023
706	88.51	2.792	0.060	−2.817	0.001021
708	87.93	2.917	0.062	−2.773	0.001019
710	87.32	3.073	0.066	−2.721	0.001017
712	86.68	3.180	0.068	−2.687	0.001015
714	86.02	3.306	0.071	−2.648	0.001013
716	85.33	3.430	0.073	−2.611	0.001011
718	84.62	3.575	0.077	−2.570	0.001009
720	83.88	3.693	0.079	−2.537	0.001007
722	83.11	3.837	0.082	−2.499	0.001005
724	82.31	4.002	0.086	−2.457	0.001003
726	81.48	4.146	0.089	−2.421	0.001001
728	80.62	4.282	0.092	−2.389	0.000999
730	79.73	4.411	0.094	−2.359	0.000997
732	78.81	4.553	0.098	−2.328	0.000995
734	77.86	4.729	0.101	−2.290	0.000993
736	76.88	4.894	0.105	−2.256	0.000991
738	75.86	5.048	0.108	−2.225	0.000989
740	74.81	5.248	0.112	−2.186	0.000987
742	73.72	5.437	0.116	−2.150	0.000985
744	72.58	5.647	0.121	−2.112	0.000983
746	71.39	5.910	0.127	−2.067	0.000981
748	70.15	6.122	0.131	−2.032	0.000979
750	68.87	6.383	0.137	−1.990	0.000977
752	67.53	6.609	0.142	−1.955	0.000975

peak was observed it was suspected that this impurity is dolomite. It is known that dolomite decomposition is dependent on the partial pressure of carbon dioxide [9]. At high partial pressure, the reaction occurs via a 2-stage process. However, as the pressure is decreased the process separating the two peaks gradually diminishes leading to a single peak [9]. It is thought that the TG run for magnesite in a nitrogen atmosphere had low partial pressure and hence the dolomite impurity decomposed via a single stage process. To confirm the presence of a dolomite impurity in the magnesite sample, an additional run was performed in CO_2 (Fig. 2). It was anticipated that if this impurity were truly dolomite then the high partial pressure of carbon dioxide (~1 atm) would cause dolomite decomposition to occur via a 2-step process. This expectation was realized in our experimental results (Fig. 2) where the 2-stage process, apart from the magnesite decomposition peak, is visibly evident.

It was found that calcite and dolomite supposedly decompose via a zero order mechanism, while magnesite decomposes via a first order process. The energy of activation for the decomposition of magnesite, calcite and dolomite were 226.34, 192.50 and 175.05 kJ/mol, respectively. Similarly the ln A-value for magnesite, calcite and dolomite decomposition works out to be 30.70, 20.73 and 18.76. Dolomite decomposition is used as an example to demonstrate the method of calculating the kinetic parameters. The spreadsheet calculations are depicted in Table 3, while the linear regression plot for this sample is illustrated in Fig. 3.

3.2. Effect of procedural variables on the shape of the DTG curves

Compared to the TG, the DTG plots are more sensitive to weight changes in the sample and hence will be used to study the effect of procedural variables on the shape of the curves. The aim in using the purge gas (N_2) is to ensure an inert environment around the sample. The purge gas ensures that

(i) There is no reaction with the product gas and the gaseous environment;
(ii) The product gas is removed as fast as possible from the decomposing sample.

It is expected that the flow rate of the purge gas should not effect the decomposition reaction and hence will not affect the shape of the DTG curves. Our observations confirm this fact and are depicted in Fig. 4.

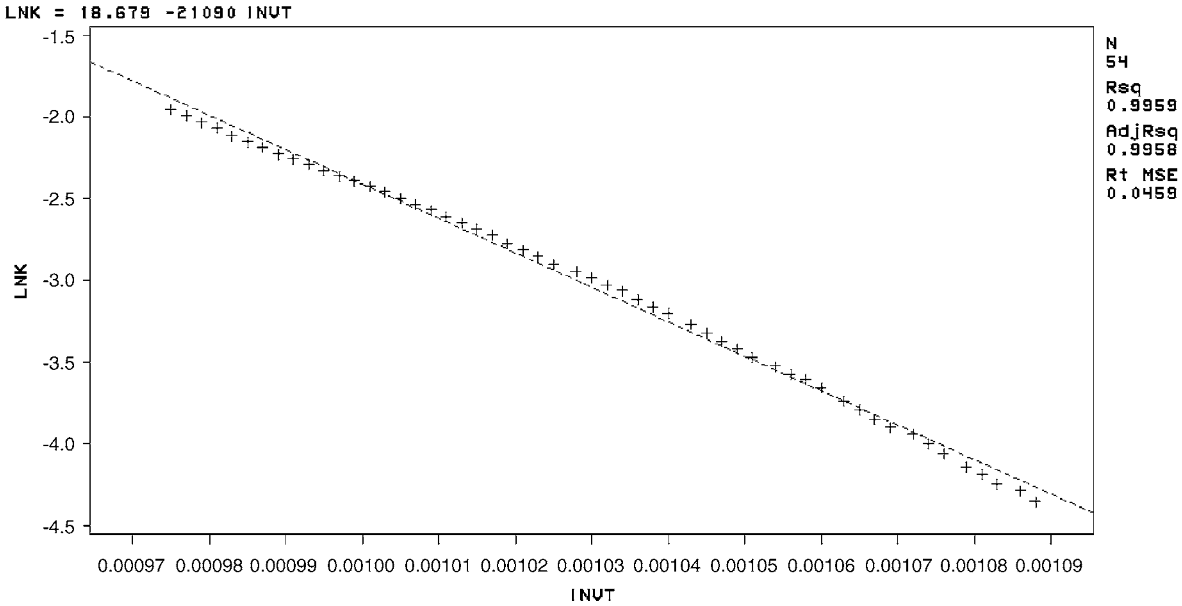

Fig. 3. The Arrhenius plot for dolomite decomposition (sample size 14.6 mg) using an $f(\alpha)$-value of one which corresponds to a zero order mechanism. The linear regression provides the R^2-value and the equation for the linear model.

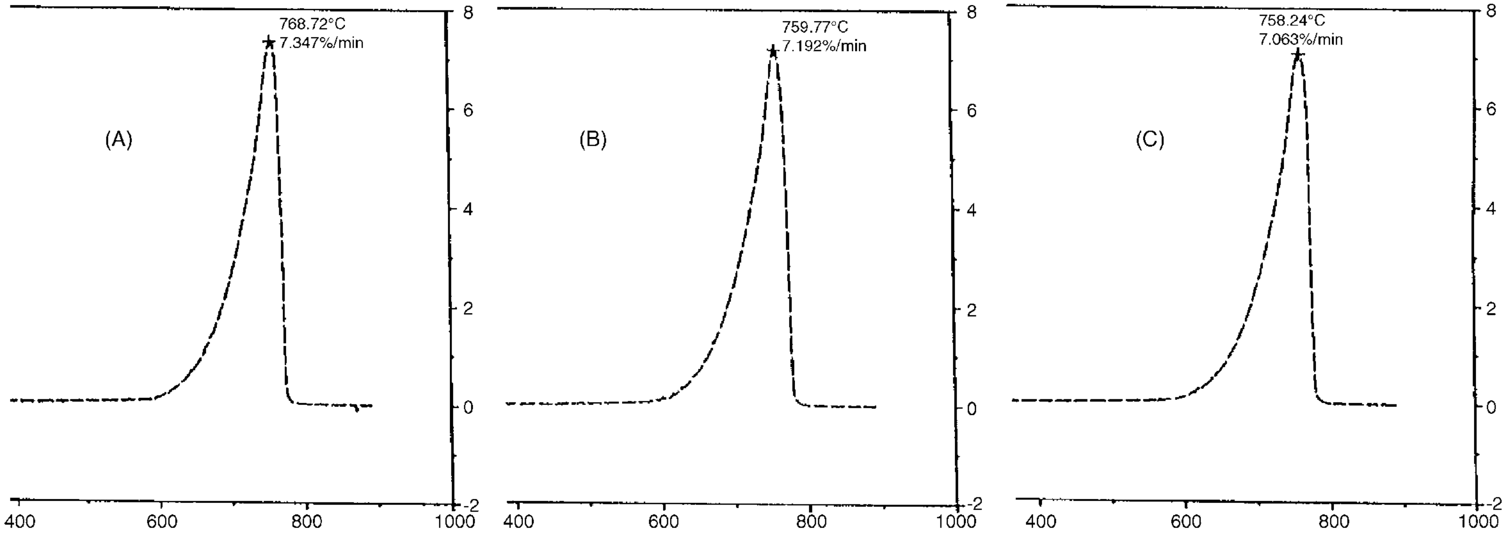

Fig. 4. The DTG plots (temperature plotted as the abscissa and derivative weight (%/min) as the ordinate) employed for studying the impact of the flow rate on dolomite decomposition in N_2. The three flow rates studied were 25, 50 and 100 ml/min which are represented by A, B and C, respectively.

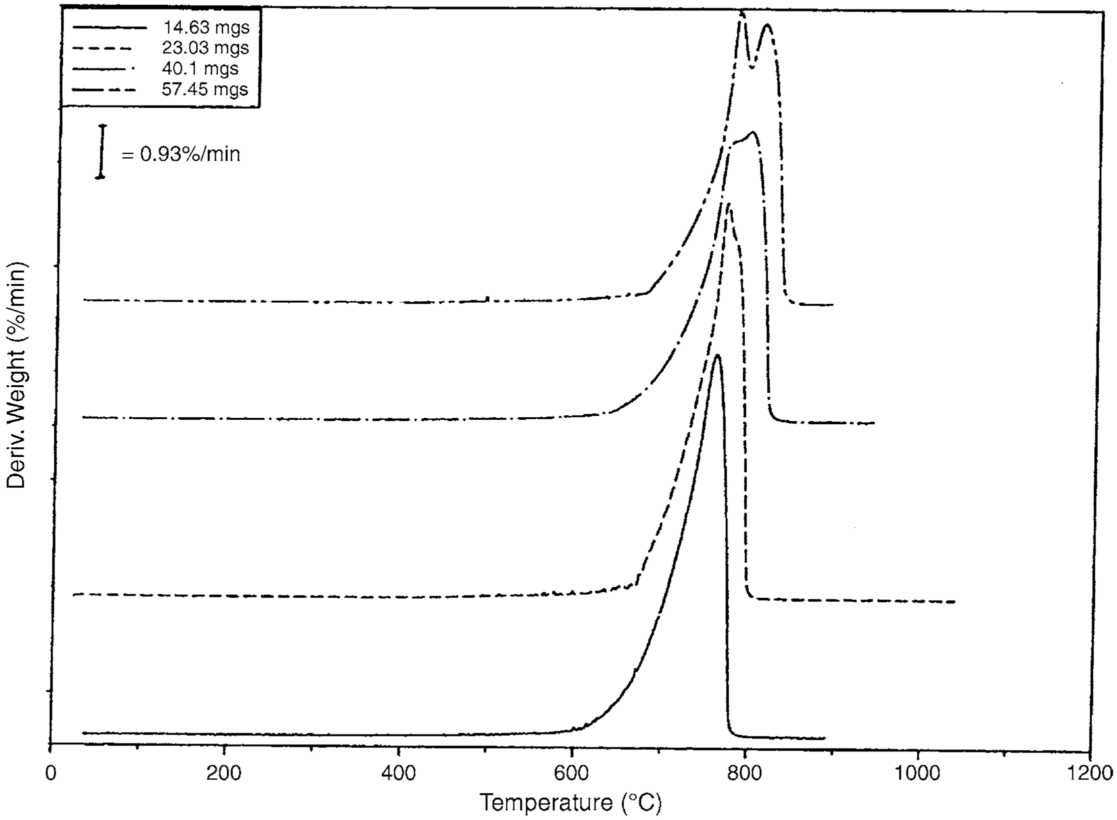

Fig. 5. The DTG plots employed for studying the impact of the sample size on dolomite decomposition in N_2. The four sample sizes studied were 14.63, 23.03, 40.10 and 57.45 mg.

From Fig. 5, it can be observed that the DTG peaks become broader and the peak temperature increases with sample size. The sample mass controls the amount of evolved volatile product and thus has an effect on the decomposition temperature. It would be expected that with an increase in sample mass the time required for the reaction would increase, thus leading to broad peaks.

The important factor to be considered here is the existence of temperature gradients. Two types of temperature gradients exist. The first is between the sample crucible, which is placed in the center of the furnace tube, and the furnace wall. The second temperature gradient exists within the sample. These gradients affect the transfer of heat between the sample and furnace and influence the temperatures at which the mass changes occur. The magnitude of these gradients increase with an increase in sample mass and, in general, it can be stated that for an endothermic reaction like dolomite decomposition the larger the sample weight the higher is the temperature range at which the reaction is observed [10]. Moreover, the peaks tend to split into two with an increase in sample size, this is explained on the basis of the self-generated atmosphere of the volatile product. The pressure of the generated product gas causes the peaks to separate.

Using a theoretical model [11], it can be shown that both the peak temperature and height for the typical DTG curve increases with a corresponding increase in the heating rate. This is observed in Fig. 6. Thus, for the two procedural variables heating rate and sample size, the shape of the curves alter with a change in these variables. It therefore becomes important to study the effect of these variables on the kinetic parameters of dolomite decomposition.

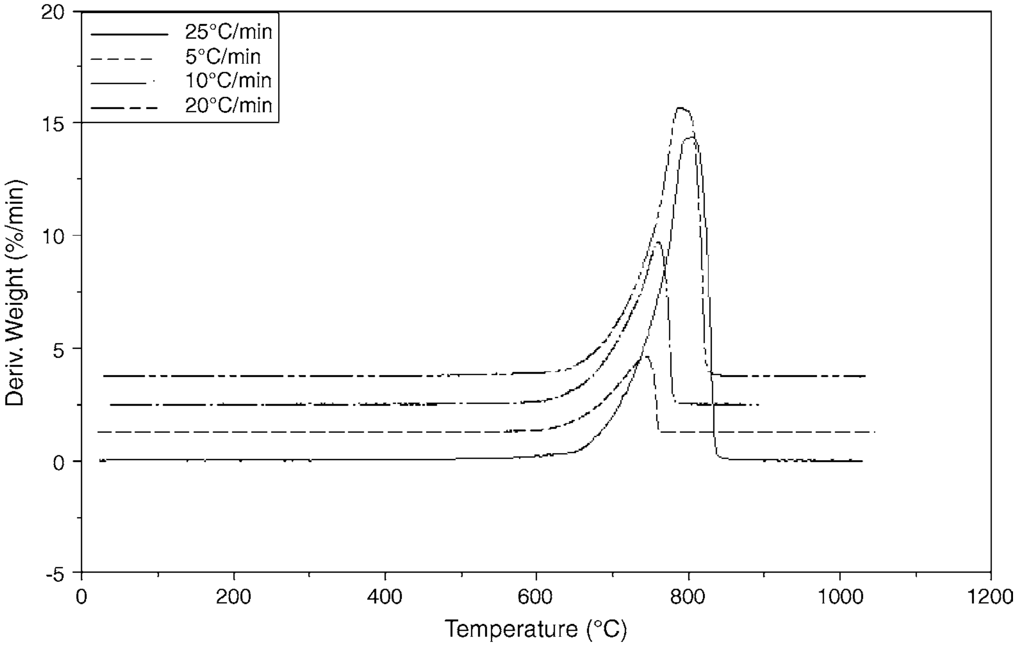

Fig. 6. The DTG plots employed for studying the impact of the heating rate on dolomite decomposition in nitrogen. The four heating rates studied were 5, 10, 20 and 25 °C/min.

3.3. Study of the procedural variables

For all the experiments the DTG curve shows a very specific pattern. The curve rises at a steady rate, reaches the peak and is finally followed by a sharp fall. This behavior is typical of a zero order mechanism. Moreover, when an $f(\alpha)$-value of one is tested it produces a straight line on the Arrhenius plot. This confirms the fact that dolomite follows a zero order mechanism. Dolomite exhibits a zero order mechanism for all the procedural variables tested. The results are illustrated in Table 4.

Table 4
The effect of procedural variables on the kinetic parameters of dolomite decomposition in nitrogen

Variable	Change in variable	R^2	Energy of activation obtained from the slope					Pre-exponential term 'A' obtained from the y-intercept				
			E (kJ/mol)	Mean	S.D.	95% lower CI	95% upper CI	ln A	Mean	S.D.	95% lower CI	95% upper CI
Heating rate	5	0.9939	182.66					19.36				
	10	0.9959	173.21					18.45				
	20	0.9981	183.41	181.18	5.44	172.52	189.83	19.55	19.28	0.58	18.36	20.21
	25	0.9980	185.42					19.77				
Flow rate	25	0.9966	177.19					19.02				
	50	0.9964	170.78	175.44	4.08	165.31	185.58	18.16	18.75	0.51	17.47	20.03
	100	0.9981	178.36					19.08				
Sample size	14.6	0.9959	175.05					18.68				
	23.0	0.9904	197.60					21.01				
	40.1	0.9987	183.30	190.80	14.38	167.91	213.68	18.91	20.01	1.42	17.75	22.27
	57.5	0.9944	207.23					21.45				

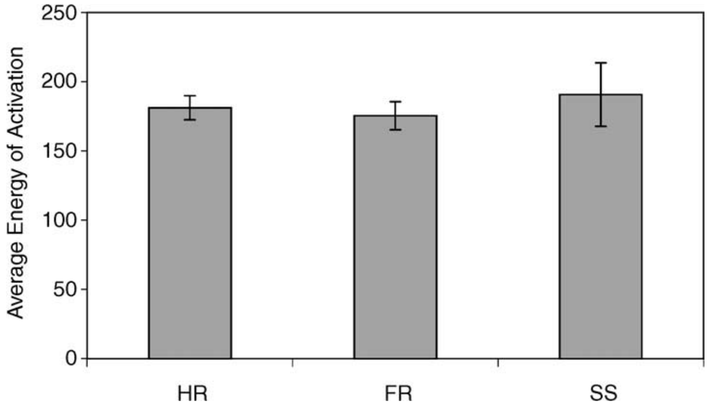

Fig. 7. The 95% confidence interval of the mean for the three groups of procedural variables, heating rate (HR), flow rate (FR) and sample size (SS). Depicted here is the mean of the energy of activation in kJ/mol.

For each regression analysis the R^2-value was greater than 0.99 and the p-value was always 0.0001. These p-values relate to the null hypothesis that the linear model does not explain the variation in data. The significance level was set at 0.05. It can be concluded that the null hypothesis is false and the linear model does explain the variation in data and that dolomite follows zero order kinetics irrespective of the procedural variables used.

The E and $\ln A$-values for the three different procedural variables were classified as three different groups and the statistical parameters, mean standard deviations and 95% confidence limits, were calculated for the E and $\ln A$-values using the SAS software (Table 4). Figs. 7 and 8 illustrate the 95% confidence interval of the mean for the three groups. Fig. 7 relates to the energy of activation while Fig. 8 deals with the pre-exponential term ‘A’.

The E and $\ln A$-values for the three different procedural variables were classified as three different groups. The kinetic parameters for the various procedural variables were compared using a completely randomized analysis of variance (ANOVA) test. The procedure tests the null hypothesis that the means of the three groups are not significantly different statistically. The p-values for the E and $\ln A$-values were found to be 0.1622 and 0.2837, respectively. The significance level was set at 0.05 and was compared with the p-values obtained. It can be concluded that the null hypothesis is true and the kinetic parameters

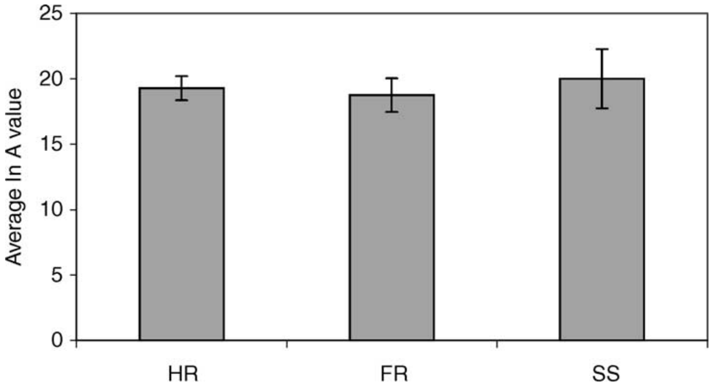

Fig. 8. The 95% confidence interval of the mean for the three groups of procedural variables, heating rate (HR), flow rate (FR) and sample size (SS). Depicted here is the mean of the second kinetic parameter $\ln A$, where A is the pre-exponential term.

remain unaffected even upon change in the procedural variables.

4. Conclusions

1. Calcite and dolomite supposedly decompose via a zero order mechanism while magnesite decomposes via a first order process. Magnesite shows the presence of an impurity, which was confirmed to be dolomite.
2. The energy of activation for the decomposition of magnesite, calcite and dolomite was 226.34, 192.50 and 175.05 kJ/mol, respectively. Additionally, the $\ln A$-value for magnesite, calcite and dolomite decomposition were estimated to be 30.70, 20.73 and 18.76, respectively.
3. The procedural variables can affect the shape of the curves. An increase in the heating rate causes an increase in the peak temperature, and an increase in the peak height.
4. An increase in sample weight causes the peak to broaden and finally the peaks tend to split because of the backpressure of the volatile product formed upon decomposition. However, the flow rate of the purge gas has no effect on the shape of the DTG curves.
5. Dolomite decomposition follows a zero order mechanism and its kinetic parameters (E and $\ln A$) remain unaffected even upon alterations in the procedural variables. This is confirmed by the ANOVA test.

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