

KINETICS OF THERMAL DECOMPOSITION OF MCO_3 TO MO (M = Ca, Sr AND Ba)

*Nobuyoshi Koga and Haruhiko Tanaka**

LABORATORY OF CHEMISTRY, FACULTY OF SCHOOL EDUCATION,
HIROSHIMA UNIVERSITY, SHINONOME, MINAMI-KU, HIROSHIMA, 734, JAPAN

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The kinetics of the thermal decompositions of CaCO_3 , SrCO_3 and BaCO_3 into their oxides were studied by thermogravimetry at constant and linearly increasing temperatures. The kinetics of the isothermal decompositions of calcium and strontium carbonates were described by the law $R_n = 1 - (1 - \alpha)^{1/n}$, where $n = 1.8$ and 1.2 , respectively. The kinetics of the non-isothermal decompositions of the two carbonates, analysed by the Ozawa and Coats–Redfern methods, were in keeping with the isothermal kinetics. “True” kinetic compensation laws were established for each decomposition of the two carbonates, including the data under both isothermal and non-isothermal conditions.

As concerns the decompositions of BaCO_3 , however, there was some difference between the kinetic features relating the isothermal and non-isothermal conditions. A “true” kinetic compensation law was not established in this case.

As concerns a given thermal decomposition of a solid, it is well known that the kinetic model and parameters derived from thermal analysis are dependent on the measuring and sample conditions. If both the kinetic model and the parameters derived from thermal analysis differ under various experimental conditions, we may find that these changes are due to a variation in the decomposition mechanism, which is sometimes encountered in higher-temperature decompositions [1]. In such a case there is a possibility that physical changes, e.g. sintering, occur at a given reaction fraction during the solid decomposition process under certain conditions [2]. On the other hand, if only the kinetic parameters are different, this seems to be due to a “kinetic compensation effect” [1, 3–10]. Therefore, a systematic analysis should be performed, in order to understand the kinetics of solid decompositions, including detection of variations in the decomposition model and kinetic parameters in thermal analyses under various experimental conditions.

The kinetics of thermal decomposition of alkaline earth carbonates are of great interest, particularly as regards comparison of the kinetic features [11–21]. It is

* Author for correspondence.

worth-while to reexamine such kinetics extensively, because the influence of the experimental conditions on these decomposition kinetics does not seem to have been fully and systematically clarified.

The present paper deals with an investigation of the kinetics of thermal decomposition of the carbonates of calcium, strontium and barium to their oxides by means of TG at various heating rates, as well isothermal mass-change measurements. The results are discussed on the basis of our data alone, since comparison with the results of other workers does not seem to be realistic due to the different experimental conditions.

Experimental

The three anhydrous carbonates were obtained by decomposing 10.0 mg of the hydrated oxalates, which were prepared as described earlier [1], using a Rigaku Thermoflex TG-DSC (8085E1) apparatus. TG measurements were carried out on the decompositions of these carbonates to their oxides in a flow of nitrogen gas at a rate of 30 ml/min, at various heating rates. Mathematical analyses were performed by the integral methods of Coats-Redfern [22, 23] and Ozawa [24-26], in the decomposition fraction range 0.1-0.9.

Isothermal mass-change traces were also recorded for their decompositions under the same measuring conditions as in the dynamic runs. All the carbonates were identified by means of IR and TG.

Results and discussion

Isothermal analysis

For the isothermal decompositions of the solids, the kinetic equation

$$F(\alpha) = kt \quad (1)$$

was assumed, where $F(\alpha)$ is a function depending on the mechanism of thermal decomposition, α is the fraction of decomposition at time t , and k is the rate constant. The most appropriate $F(\alpha)$ can be estimated to some extent by plotting it against t ; the correct $F(\alpha)$ should give a straight line with slope k .

In this study we examined twelve models of $F(\alpha)$, as listed elsewhere [27]. It follows that the three carbonates decompose according to either a phase boundary-controlled reaction law R_n or an Avrami-Erofeyev law A_m . Figure 1 shows plots of various $F(\alpha)$ against t for the thermal decomposition of CaCO_3 to CaO , as an example.

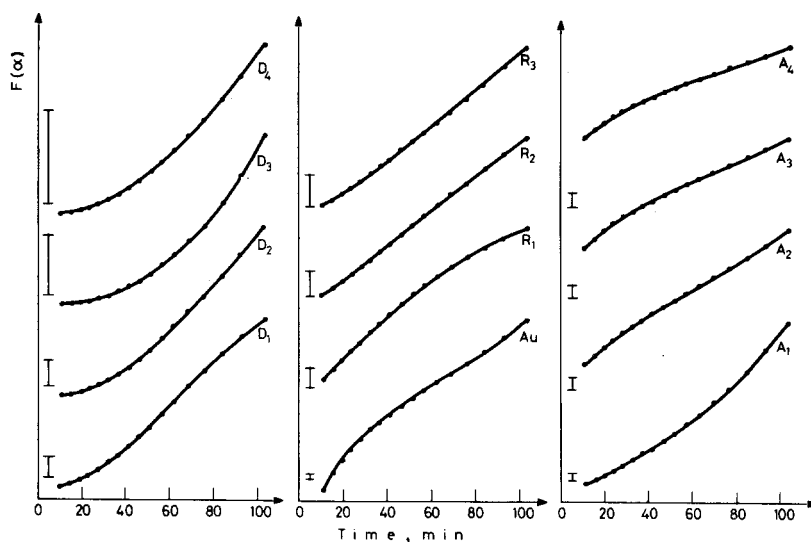


Fig. 1 Typical $F(\alpha)$ vs. t plots for the isothermal decomposition of CaCO_3 to CaO at a temperature of 616.8°C . Each vertical segment refers to an ordinate scale of 0.1

The most appropriate values of n and m , which give the highest correlation coefficients γ for linear regression analysis of the $F(\alpha)$ vs. t plot, were assessed by "scanning" the n and m values via two possible functions $R_n = 1 - (1 - \alpha)^{1/n}$ and $A_m = [-(1 - \alpha)]^{1/m}$, respectively [28]. Table 1 lists the functions of R_n and A_m which gave the highest values of γ , together with the activation energy E and pre-exponential factor A derived from the Arrhenius plot. The non-integral values of n and m imply deviation from the theoretical decomposition models [29, 30]. We see from Table 1 that the kinetic model cannot be singled out from the isothermal analysis alone, because the linearity of the $F(\alpha)$ vs. t plots and the kinetic parameters derived from the Arrhenius plot are nearly equal, irrespective of the kinetic law assumed [31].

Table 1 Appropriate $F(\alpha)$ and kinetic parameters for the isothermal decomposition of MCO_3 to MO

M	Temp. range, $^\circ\text{C}$	$F(\alpha)$	E , kJ/mol	$\log A$, 1/s
Ca	608.8–627.6	$R_{1.8 \pm 0.1}$	237 ± 10	10.1 ± 0.4
		$A_{1.8 \pm 0.1}$	238 ± 10	10.3 ± 0.4
Sr	773.4–806.5	$R_{1.2 \pm 0.1}$	203 ± 7	5.9 ± 1.4
		$A_{2.8 \pm 0.1}$	204 ± 7	6.0 ± 1.4
Ba	906.2–946.1	$R_{1.5 \pm 0.1}$	329 ± 8	10.4 ± 0.4
		$A_{2.0 \pm 0.1}$	339 ± 8	10.6 ± 0.4

Dynamic analysis

Typical TG traces for the non-isothermal decompositions of the three carbonates into their oxides are given in Fig. 2.

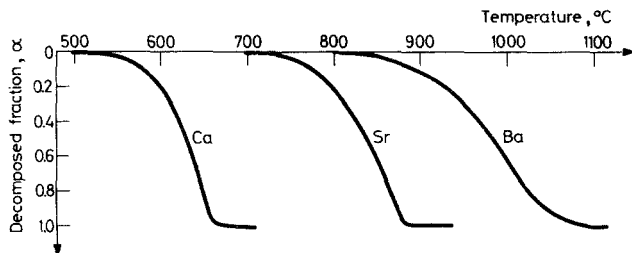


Fig. 2 Typical TG traces for the dynamic decompositions of CaCO_3 , SrCO_3 and BaCO_3 to their oxides at heating rates of 1.32, 1.30 and 1.22 $^\circ\text{C}/\text{min}$, respectively

The kinetic parameters can be derived for the decomposition at a given heating rate, using a modified Coats–Redfern equation [22, 23]:

$$\ln [F(\alpha)/T^2] = \ln (AR/aE)[1 - (2RT/E)] - (E/R)(1/T) \quad (2)$$

where T is the absolute temperature, R is the gas constant, and a is the heating rate. If the correct $F(\alpha)$ is used, a plot of $\ln [F(\alpha)/T^2]$ vs. $1/T$ should give a straight line, from which the values of E and A can be derived.

In Tables 2 and 3, the kinetic parameters derived from the Coats–Redfern plot, in terms of the most appropriate $F(\alpha)$ determined isothermally, are listed for the non-isothermal decompositions of calcium and strontium carbonates, respectively. We see from Tables 2 and 3 that the linearities of the Coats–Redfern's plots are higher for R_n laws than for A_m laws.

Table 2 The kinetic parameters derived from Coats & Redfern's plot for the dynamic decomposition of CaCO_3 to CaO

Heating rate, $^\circ\text{C}/\text{min}$	$F(\alpha)$					
	$R_{1.8}$			$A_{1.8}$		
	E , kJ/mol	$\log A$, 1/s	$-\gamma^*$	E , kJ/mol	$\log A$, 1/s	$-\gamma^*$
1.32	220	9.16	0.9991	139	4.68	0.9980
2.39	198	7.84	0.9968	124	3.89	0.9966
4.78	195	7.59	0.9986	122	3.81	0.9969

* Correlation coefficient of the linear regression analysis.

Table 3 The kinetic parameters derived from Coats & Redfern's plot for the dynamic decomposition of SrCO₃ to SrO

Heating rate, °C/min	$F(\alpha)$					
	$R_{1,2}$			$A_{2,8}$		
	E , kJ/mol	$\log A$, 1/s	$-\gamma^*$	E , kJ/mol	$\log A$, 1/s	$-\gamma^*$
0.78	297	10.5	0.9969	140	3.01	0.9969
1.30	207	6.04	0.9976	94.1	0.784	0.9971
2.38	239	7.57	0.9998	109	1.63	0.9893
4.67	222	6.77	0.9995	100	1.35	0.9888

* Correlation coefficient of linear regression analysis.

The effect of the heating rate on the non-isothermal decomposition of barium carbonate into the oxide is tabulated for all model functions except A_u in Table 4. Table 4 indicates that the non-isothermal decomposition of barium carbonate is regulated by the diffusion of gaseous product and/or the random nucleation of the solid product and its subsequent growth.

We see from Fig. 2 that the decomposition temperature ranges of the three carbonates are rather wide. The wider the decomposition temperature range becomes, the less accurate the Coats-Redfern method is. It is therefore of interest to derive the kinetic parameters by using the Ozawa method, since TG traces at various heating rates are available here.

According to Ozawa [24-26], the generalized time θ is introduced as

$$\theta = \int_0^t \exp(-E/RT) dt = (E/aR)p(E/RT) \quad (3)$$

where p is the function expressed by Doyle [32]. In Eq. (3), the p function can be approximated as follows:

$$p(x) : \exp(-x)/x^2 \quad (4)$$

We then obtain the following equation:

$$\ln(a/T^2) = (-E/R)(1/T) + \ln(R/\theta E) \quad (5)$$

Equation (5) shows that the values of E and θ can be obtained by plotting $\ln(a/T^2)$ vs. $1/T$ for a given α . As an example, Fig. 3 shows the $\ln(a/T^2)$ vs. $1/T$ plot for the non-isothermal decomposition of CaCO₃ to CaO. Figure 4 shows the α vs. θ plot, which is called the "experimental master curve", for the same decomposition [24]. The mean values of E , in the α range 0.1-0.9, derived from $\ln(a/T^2)$ vs. $1/T$ plots for the non-isothermal decompositions of the three carbonates, are listed in Table 5.

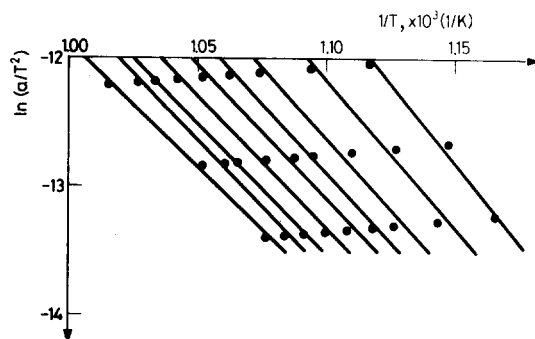


Fig. 3 $\ln(\alpha/T^2)$ vs. $1/T$ plots for the dynamic decomposition of CaCO_3 to CaO

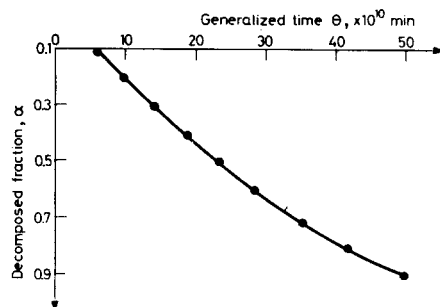


Fig. 4 Plot of α vs. θ for the dynamic decomposition of CaCO_3 to CaO

Table 5 Appropriate $F(\alpha)$ and the kinetic parameters derived from Ozawa's method for the dynamic decomposition of MCO_3 to MO

M	Heating rate, °C/min	$F(\alpha)$	E , kJ/mol	$\log A$, 1/s	$-r^*$
Ca	1.32-4.78	$R_{1.6}$	173 ± 3	6.4 ± 3.8	0.9997
Sr	0.78-4.67	$R_{1.3}$	218 ± 5	6.5 ± 3.9	0.9997
Ba	0.63-4.91	$A_{1.3}$	220 ± 4	5.5 ± 2.7	0.9998

* Correlation coefficient of the linear regression analysis for the $F(\alpha) - \theta$ plot.

For the analysis of the "experimental master curve", the equation

$$F(\alpha) = A\theta \quad (6)$$

is used, which is derived from Eqs (1) and (3) and the Arrhenius equation. In the $F(\alpha)$ vs. θ plots, the correct $F(\alpha)$ should give a straight line with slope A . Table 5 lists the $F(\alpha)$ which gave the highest values of r of linear regression analysis, together with the values of E and $\log A$. For the thermal decompositions of calcium,

strontium and barium carbonates, the plots of the most appropriate $F(\alpha)$ against θ are given in Figs 5, 6 and 7, respectively. We see from the results estimated from the Ozawa method that the thermal decomposition of calcium and strontium carbonates are governed by an R_n law and that of barium carbonate by an A_m law. Application of the Avrami–Erofev equation to non-isothermal analysis is not

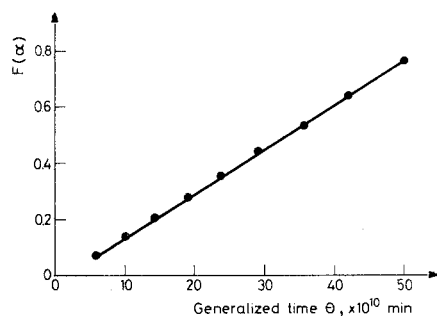


Fig. 5 Plot of $R_{1.6}$ vs. θ for the dynamic decomposition of CaCO_3 to CaO

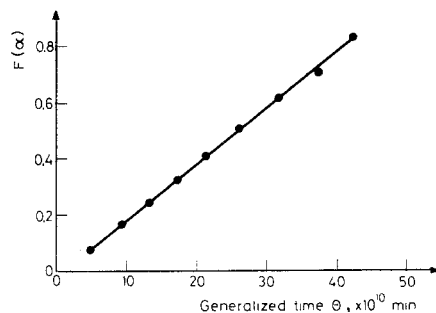


Fig. 6 Plot of $R_{1.3}$ vs. θ for the dynamic decomposition of SrCO_3 to SrO

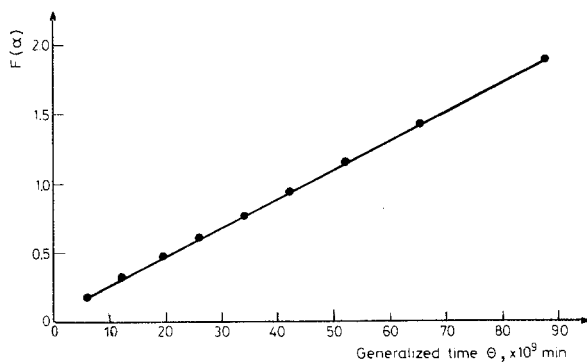


Fig. 7 Plot of $A_{1.3}$ vs. θ for the dynamic decomposition of BaCO_3 to BaO

generally correct: the A_m model assessed from non-isothermal analysis has no physical meaning [33] if it is different from that obtained isothermally. We assume that A_m law assessed non-isothermally can have a physical meaning only when it corresponds with the isothermal kinetic law.

Comparison between isothermal and non-isothermal analyses

We see from Tables 1 and 5 that the $R_{1.8}$ and $R_{1.2}$ decomposition laws derived isothermally are in good agreement with the $R_{1.6}$ and $R_{1.3}$ laws derived from the Ozawa method for the thermal decompositions of calcium and strontium carbonates, respectively. The Coats–Redfern plots also suggest a phase boundary-controlled reaction, as seen from Tables 2 and 3. Here, the $R_{1.8}$ and $R_{1.2}$ laws can be interpreted in terms of a combination of the R_1 and R_2 laws [29, 30]. The close agreement of the kinetic laws indicates that the decomposition law does not differ between the isothermal and dynamic decompositions. On the other hand, the kinetic parameters differ depending on the measuring conditions, which seems to be explained by a kinetic compensation effect. Figure 8 shows the compensation plot using the kinetic parameters derived from the isothermal, Coats–Redfern and Ozawa analyses in terms of the $R_{1.8}$ and $R_{1.2}$ laws for the thermal decompositions of calcium and strontium carbonates, respectively. These compensation parameters a and b are listed in Table 6, assuming the compensation equation $\log A = a + bE$.

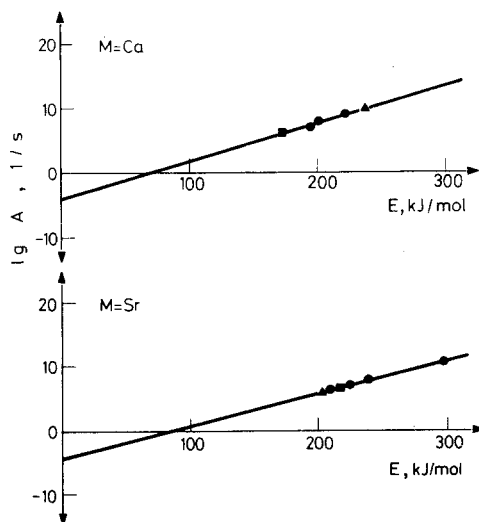


Fig. 8 Compensation plots for the thermal decomposition of MCO_3 to MO in terms of the equation, $\log A = a + bE$. \blacktriangle , \bullet and \blacksquare are the points according to the kinetic parameters derived from isothermally, Coats & Redfern's and Ozawa's methods, respectively

Table 6 "True" kinetic compensation parameters*¹ for the thermal decomposition of MCO₃ to MO

M	$F(\alpha)$	$-a, 1/s$	$b, \text{mol/kJ} \cdot s$	γ^{*2}
Ca	$R_{1.8}$	4.079 ± 0.085	0.05987 ± 0.00040	0.9996
Sr	$R_{1.2}$	4.130 ± 0.042	0.04917 ± 0.00018	0.9998

*¹ For the equation, $\log A = a + bE$.

*² Correlation coefficient of the linear regression analysis for the $\log A - E$ plot.

We have suggested that the "true" compensation laws are established if we use the correct kinetic models [1]. This suggestion seems valid for calcium and strontium carbonates too, as the kinetic parameters derived isothermally fit the compensation line for non-isothermal analyses.

As concerns the decomposition of barium carbonate, neither the isothermal $R_{1.5}$ decomposition law nor A_2 agrees with the dynamic $A_{1.3}$ decomposition law derived from the Ozawa method, as seen from Tables 1 and 5. We assume here, as described above, that the $A_{1.3}$ law has no physical meaning, because it does not correspond with the $A_{2.0}$ law assessed isothermally. Moreover, the highest value of r from the linear regression analysis for the Coats-Redfern plot results from a diffusion-controlled law (see Table 4). The above discrepancy may arise from the fact that the solid product becomes coagulated, probably due to sintering during the dynamic decomposition [1]. It seems that the degree of participation of sintering in the decomposition process increases at higher heating rates. In such a case it is rather meaningless to discuss the establishment of the "true" kinetic compensation effect.

Conclusion

The isothermal decompositions of calcium and strontium carbonates are regulated by $R_{1.8}$ and $R_{1.2}$ phase boundary-controlled reaction laws, respectively. The kinetic parameters estimated from both isothermal and dynamic measurements show a "true" compensation relation [1]. This establishment implies that the kinetic laws estimated from conventional isothermal analysis are correct and also appropriate for the corresponding dynamic decompositions. As concerns the decomposition of barium carbonate, however, there was some difference between the kinetic features under isothermal and non-isothermal conditions.

It proved that the Ozawa method is excellent for analysis of the non-isothermal decomposition kinetics of the present carbonates.

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Zusammenfassung — Die Kinetik der thermischen Zersetzung von CaCO_3 , SrCO_3 und BaCO_3 zu den Oxiden wurden durch Thermogravimetrie bei konstanter und linear ansteigender Temperatur untersucht. Die Kinetik der isothermen Zersetzung von Calcium- und Strontium-carbonat folgt dem Gesetz $R_n = 1 - (1 - \alpha)^{1/n}$, wo $n = 1,8$ bzw. $1,2$. Die Kinetik der nichtisothermen nach den Methoden von Ozawa und Coats–Redfern analysierten Zersetzung der zwei Carbonate ist in Übereinstimmung mit der isothermen Zersetzung. „Wahre“ kinetische Kompensationsgesetze wurden für die Zersetzung der beiden Carbonate erhalten, einschließlich der sich sowohl auf isotherme als auch auf nichtisotherme Bedingungen beziehenden Daten. Was die Zersetzung von Bariumcarbonat betrifft, so wurden einige

Unterschiede im kinetischen Verhalten bei der Zersetzung unter isothermen und nichtisothermen Bedingungen festgestellt. Ein „wahres“ kinetisches Kompensationsgesetz konnte in diesem Falle nicht ermittelt werden.

Резюме — Кинетика термического разложения карбонатов кальция, стронция и бария до их оксидов была изучена с помощью термогравиметрии при постоянной и линейно увеличивающейся температуре. Кинетика изотермического разложения карбонатов кальция и стронция описывается законом $R_n = 1 - (1 - \alpha)^{1/n}$, где n равно, соответственно, 1,8 и 1,2. Кинетика неизотермического разложения этих двух карбонатов, анализ которой проводился методами Озавы и Коутса–Рэдферна, соответствовала таковой при изотермическом разложении. Для каждого разложения обоих карбонатов были установлены «истинные» кинетические компенсационные законы, включая данные изотермического и неизотермического разложения. Однако, относительно разложения карбоната бария, наблюдали некоторые различия между кинетикой изотермического и неизотермического разложения. Для этого соединения не был установлен какой-либо «истинный» компенсационный закон.