

KINETIC EQUATIONS FOR THERMAL DISSOCIATION PROCESSES

Part IV. Experimental evaluation of new selected kinetic equations

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Abstract

The kinetics of thermal dissociation was studied for polydisperse systems (naturally occurring calcite and precipitated calcium carbonate) with normal and Rosin–Rammler–Sperling distributions. Experimental rate constants at selected temperatures and activation energies were calculated. The experimental results (kinetic curves) were compared with the theoretically derived curves and the usability of the selected kinetic models for description of the kinetics in such systems was estimated.

Keywords: kinetics in polydisperse systems, thermal dissociation of solids

Aim and scope of the work

In our former works [1–3] we have presented a method for using and application of kinetic equations derived enabling the description of the process of thermal dissociation of such polydisperse systems that can be characterised with normal and Rosin–Rammler–Sperling grain size distributions. The aim of this work has been to determine the possibility of using the equations for the description of experimental data obtained for some model reactions.

The model materials used in the experimental work were: manually ground natural calcite (from Raja cave, Świętokrzyskie Mountains, Poland) characterised by a normal grain size distribution and precipitated calcium carbonate (POCh Gliwice, Poland) characterised by the Rosin–Rammler–Sperling distribution.

Experimental

Thermal analyses were performed for natural calcite and precipitated calcium carbonate samples, previously subjected to sieve analysis, in order to determine the grain size distributions.

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The results of the sieve analysis have shown that the sample of natural calcite has the normal grain size distribution, and the precipitated calcium carbonate is characterised by the Rosin–Rammler–Sperling distribution (Figs 1a and b). The results of the sieve analysis have enabled also the value of the n factor which is specific for the Rosin–Rammler–Sperling distribution basing the following relationship: $\lg R$ vs. $\lg d_z$. (where d_z – grain diameter of the sample under test) (Fig. 1c).

The samples of the starting materials were subjected to X-ray phase analysis in a HZG-4C diffractometer. The results of the analyses have shown that the sole component in both of these materials is CaCO_3 (Fig. 2).

A thermoanalyser SDT 2960 produced by TA Instruments was used for the thermal and thermogravimetric analyses of both preparations (Figs 3a and b), then the rate of decomposition at isothermal conditions was determined at 700, 750, 800 and 850°C for natural calcite, and at 720, 750, 770 and 820°C for precipitated calcium carbonate samples.

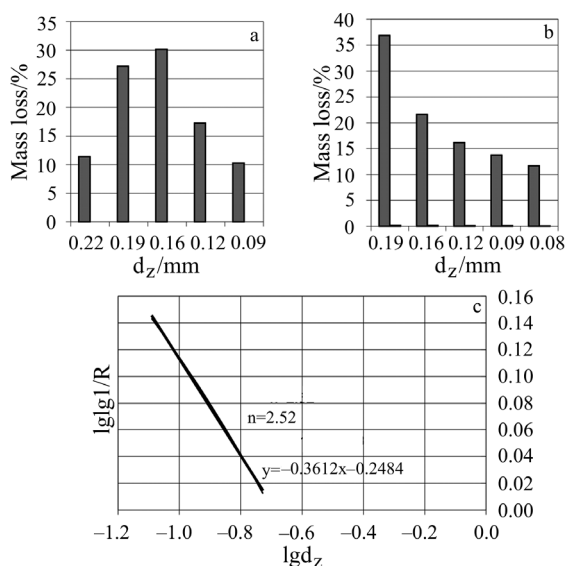


Fig. 1 The results of sieve analysis: a – normal distribution of natural calcite, b – Rosin–Rammler–Sperling distribution of precipitated calcium carbonate, c – n values (d_z – equivalent grain diameter/mm n – coefficient characterizing the Rosin–Rammler–Sperling distribution)

The values of mass loss at individual temperatures were used for calculating the degree of conversion at the given temperature and kinetic curves of thermal dissociation of the preparations were drawn (Figs 4a and b).

The obtained values of conversion degree and time of decomposition were used for calculating the values of rate constant k by means of previously selected kinetic models [1–4]. The lack of directionality in the changes of the k values (maximum constancy and minimum deviations from the mean value) was the necessary condi-

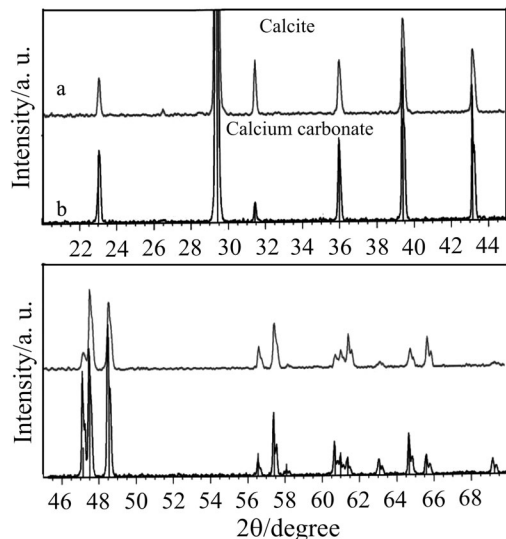


Fig. 2 X-ray phase analysis: a – for natural calcite and b – for calcium carbonate

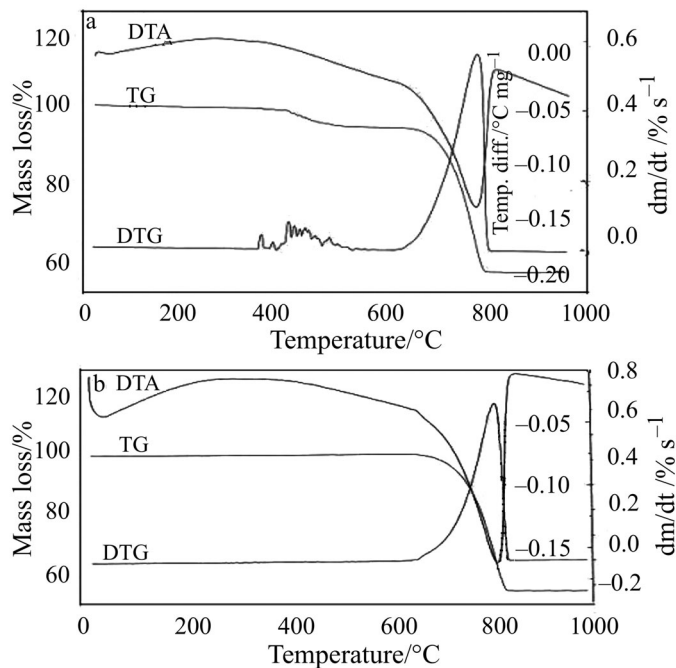


Fig. 3 Thermal analysis: a – for natural calcite and b – for calcium carbonate

tion for the selection of a kinetic equation for further studies; the condition was fulfilled by equations F0, R2 for the decomposition of natural calcite, and by equations F0, D1 for the decomposition of precipitated calcium carbonate.

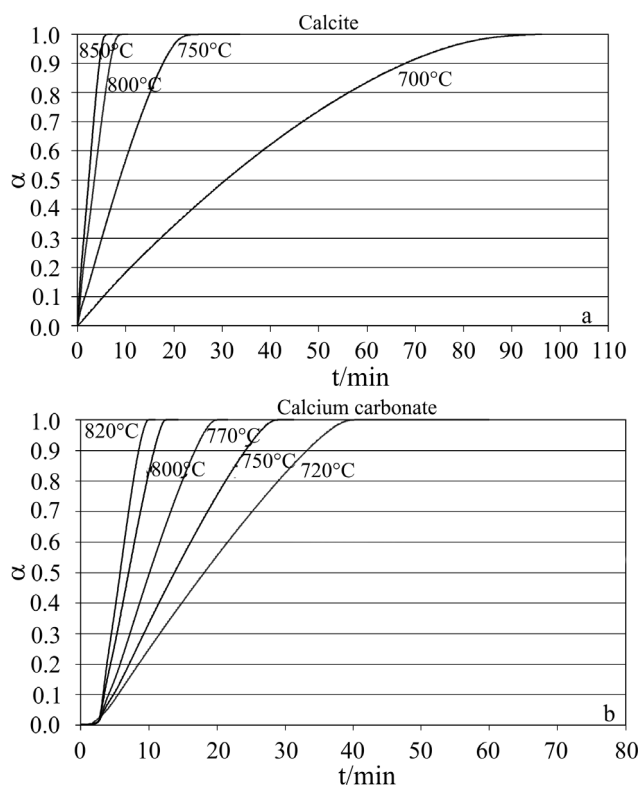


Fig. 4 Experimental kinetic curves; a – for the distribution of natural calcite, b – for the distribution of calcium carbonate

The mean values of k (k_{avr}) were then used for calculation of the activation energy. The confidence intervals were estimated for the accepted reliability 0.95 using the Student's method and using the Analysis Tool Pak in the module Analysis of Data of MS Excel [5]. The values of k_{avr} and $\ln k_{avr}$ have been collected in Table 1. Assuming that the values of k_{avr} conform to Arrhenius equation:

$$k = k_0 \exp(-E_a/RT) \quad (1)$$

the values of $\ln k_{avr}$ and $1/T$ taken from Table 1 were used, by means of the MS Excel program [5], for determining the parameters of linear regression for the following equation:

$$\ln k = -E_a/RT + \ln k_0 \quad (2)$$

The parameters $a = E_a/RT$ and $b = \ln k_0$ are components of the trend line equation; the parameter a determines the value of activation energy $E_a = -Ra$ (where R – universal constant).

The values of E_a determined from the relation $\ln k_{avr}$ vs. $1/T$ are given in Table 1 and in Figs 5a–d.

Table 1 Kinetic parameters of thermal decomposition of natural calcite and calcium carbonate

Distribution	T/K	$1/T \cdot 10^{-4}$	$K_{avr} \cdot 10^{-2}$	$\ln k_{avr}$	$E_a/kJ \text{ mol}^{-1}$
Equation F0					
Natural calcite	973	10.28	1.623	-4.13374	158.25
	1023	9.78	5.361	-2.92617	
	1073	9.32	12.96	-2.05602	
	1093	8.90	21.47	-1.53851	
Calcium carbonate	993	10.070	1.8086	-4.0128	158.28
	1023	9.780	3.2077	-3.4396	
	1043	4.992	4.9915	-2.9974	
	1073	7.377	7.3765	-2.6069	
Equation R2					
Natural calcite		10.28	1.0809	-4.52730	165.56
		9.78	3.6594	-3.30788	
		9.32	8.9236	-2.41647	
		8.90	16.5239	-1.80036	
Equation D1					
Calcium carbonate		10.07	0.9636	-4.64226	179.13
		9.78	2.0111	-3.90648	
		4.992	2.5808	-3.65707	
		7.377	5.0478	-2.98622	
Equation $\theta_i = k_{1,i} t_{m,i} / \bar{R} = R_{z,i}$					
Natural calcite			0.824	-7.10134	164.52
			2.816	-5.87229	
			7.755	-4.85942	
			11.767	-4.44242	
Calcium carbonate			1.105	-6.8569	164.03
			2.114	-6.1594	
			4.017	-5.9357	
			7.431	-5.5172	
				-4.9021	

The concordance of the experimentally derived kinetic curves with the calculated ones [1–3] was evaluated after calculation of $\theta_i = k t_{m,i} / \bar{R}$ (where $t_{m,i}$ – maximum duration of the reaction, \bar{R} – mean grain radius). Next, the values of θ_i were introduced (along with the calculated values of B for normal distribution and n for Rosin–Rammler–Sperling distribution) to the final equation which determines the mean values of the conversion degree $\bar{\alpha}$ [3], by obtaining the kinetic curves and determining the experimental points for each fraction (Figs 6 and 7).

Assuming that the maximum time of reaction relates to the coarsest fraction, all the values of θ_i were calculated and the kinetic curves $\bar{\alpha}$ vs. t were drawn. A good concordance was found on comparing the obtained curves with the experimentally derived ones for normal distribution and Rosin–Rammler–Sperling distribution – only for some equations. The relations of $\bar{\alpha}$ vs. t and the values found for each temperature were the same as those showed for both types of distribution on Figs 4a and b [6, 7].

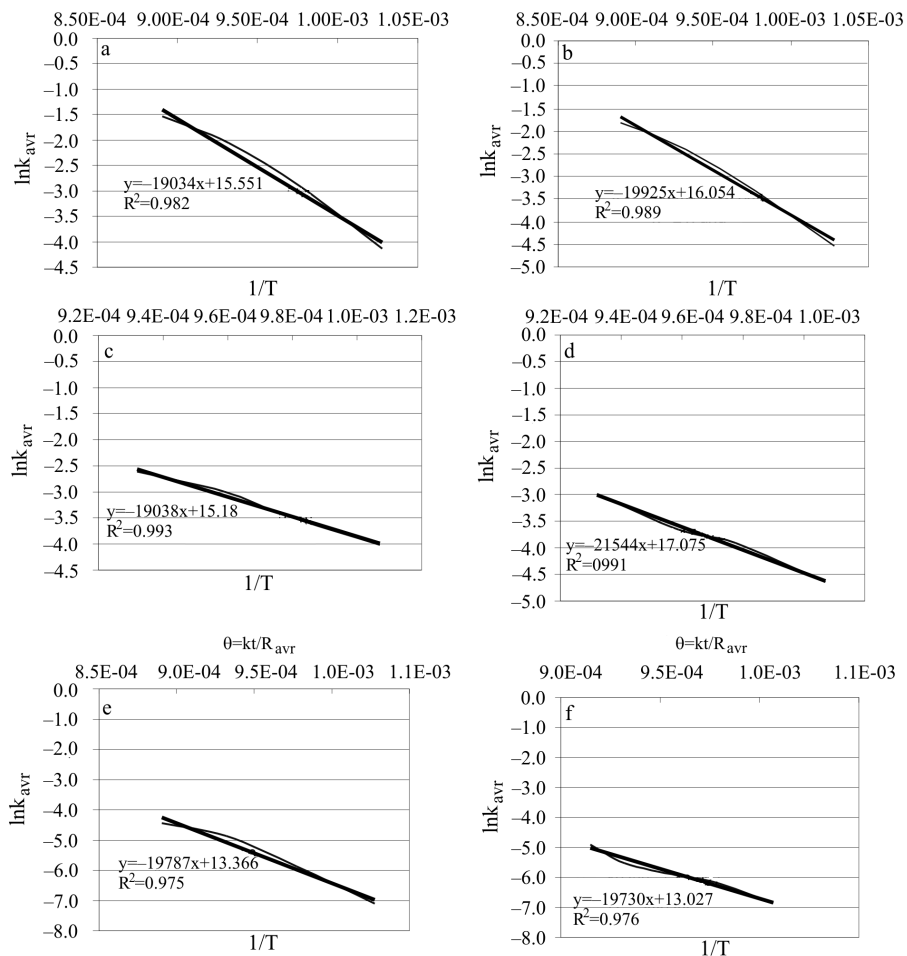


Fig. 5 Relation $\ln k-1/T$ and activation energy values: a, b – for the equation F0 and R2 for decomposition of natural calcite, c, d – for the equation F0 and D1 for decomposition of calcium carbonate, e – for $\theta_i=kt/\bar{R}$ (calcite), f – $\theta_i=kt/\bar{R}$ (precipitated calcium carbonate)

The relation $\theta_i=k_{1,i}t_{m,i}/\bar{R}=R_{z,i}$ – enables to determine the maximum time of reaction for each individual fraction, hence it becomes possible to calculate directly the values of rate constants of the process of dissociation. On rearranging the above relationship to obtain the form $k_i = \theta_i \bar{R} / t_{m,i}$ we can calculate the values of k_{avr} , draw the curves $\ln k$ vs. $1/T$ and find the values of activation energy (Figs 5e, f and Table 1) [8–12].

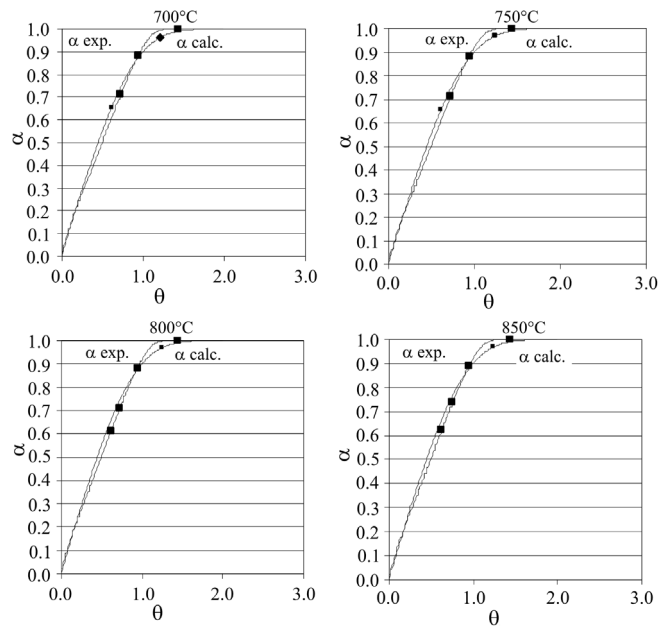


Fig. 6 Theoretical kinetic curves with experimentally determined points and experimental curves for F0 equation – calcite normal distribution for temperatures (700, 750, 800 and 850°C)

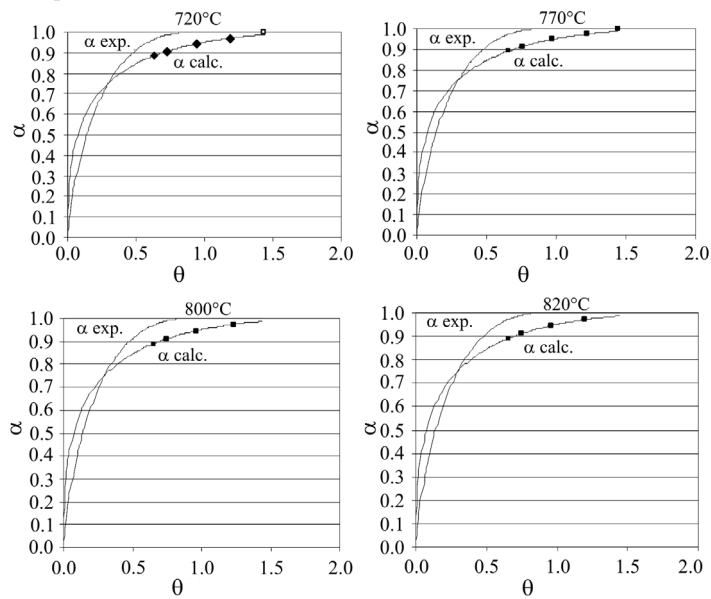


Fig. 7 Theoretical kinetic curves with experimentally determined points and experimental curves for D1 equation – calcium carbonate Rosin–Rammler–Sperling distribution – for temperatures (720, 770, 800 and 820°C)

Discussion of results and conclusions

The non-directional nature of the values of k is a necessary condition for selection of the kinetic equation. The condition was fulfilled only by the equations F0, R2 for the natural calcite and F0 and D1 for precipitated calcium carbonate.

The determined activation energy values are slightly smaller than the enthalpy of the reaction, which may be due to the occurrence of reverse reaction if the process is carried out under atmospheric pressure.

The conformity between the experimental curves and the calculated ones enables to state that the new kinetic equations may be used for description of the process of thermal dissociation in polydisperse systems after the grain size distribution has been determined.

The knowledge of the dimensionless values of B , n , $R_{z,i}$ and θ_i enables the determination of the maximum time of conversion for individual fractions, a direct description of the kinetics of decomposition, and calculation of the kinetic parameters of the process of thermal dissociation in polydisperse systems both in the case of normal distribution and in the Rosin–Rammler–Sperling distributions.

Determination of the nature and the type of the grain size distribution enables a proper selection of the kinetic equation and a description of the process of thermal dissociation of solids in polydisperse systems.

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